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A Systematic Approach for Selecting the Appropriate SPME Fiber

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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

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Factors Affecting Fiber Selection

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

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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

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Types of SPME Fibers

Bare Fused Silica	Adsorbent	Unknown
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

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Physical Properties of Divinylbenzene and Carboxen-1006

Material	Surface Area (m^2/g)	Porosity (mL/g)* macro	meso	micro	Total
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

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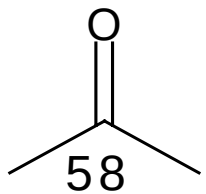
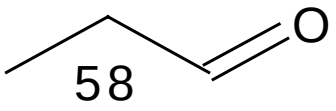
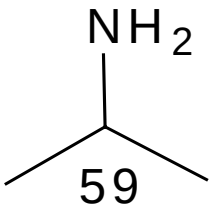
Analytes in Volatile Study



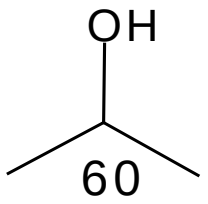
Acetone



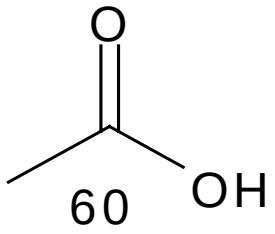
Propanal



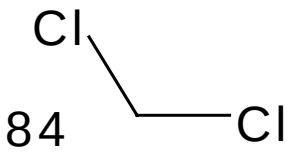
Isopropylamine



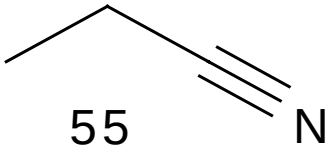
Isopropanol



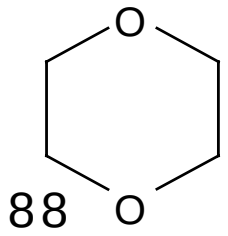
Acetic acid



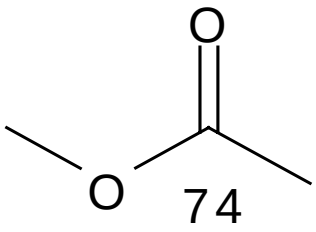
Dichloromethane



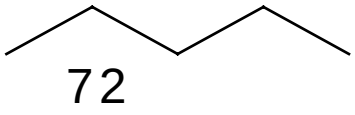
Propionitrile



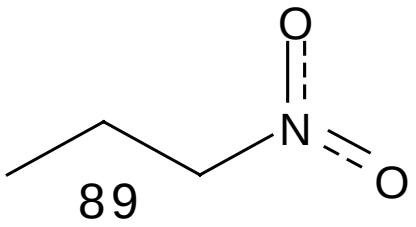
1,4-Dioxane



Methylacetate



Pentane



Nitropropane

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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

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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 4.0µm SPB™-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

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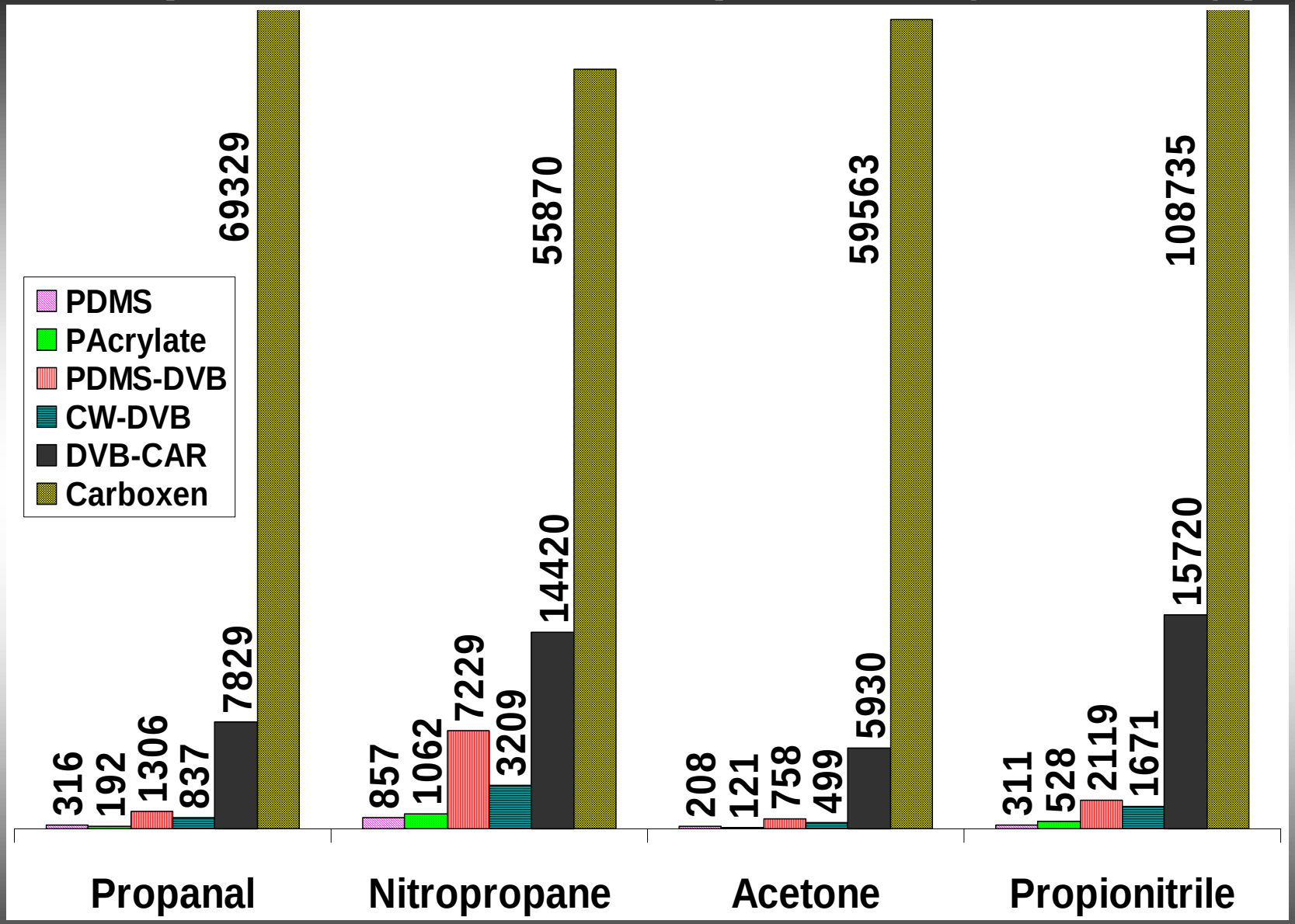
Comparison of Area Responses by Fiber Type



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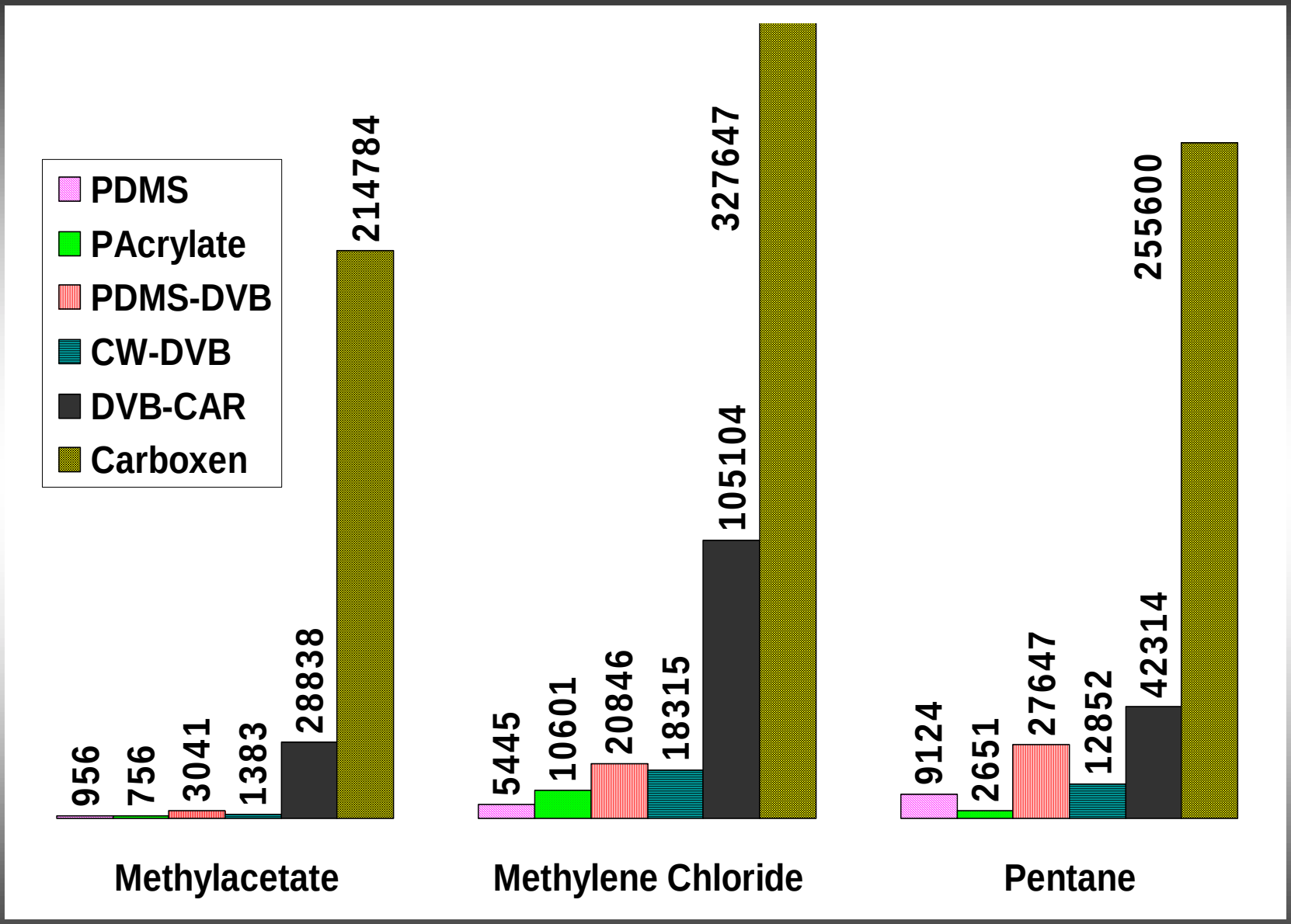
Comparison of Area Responses by Fiber Type



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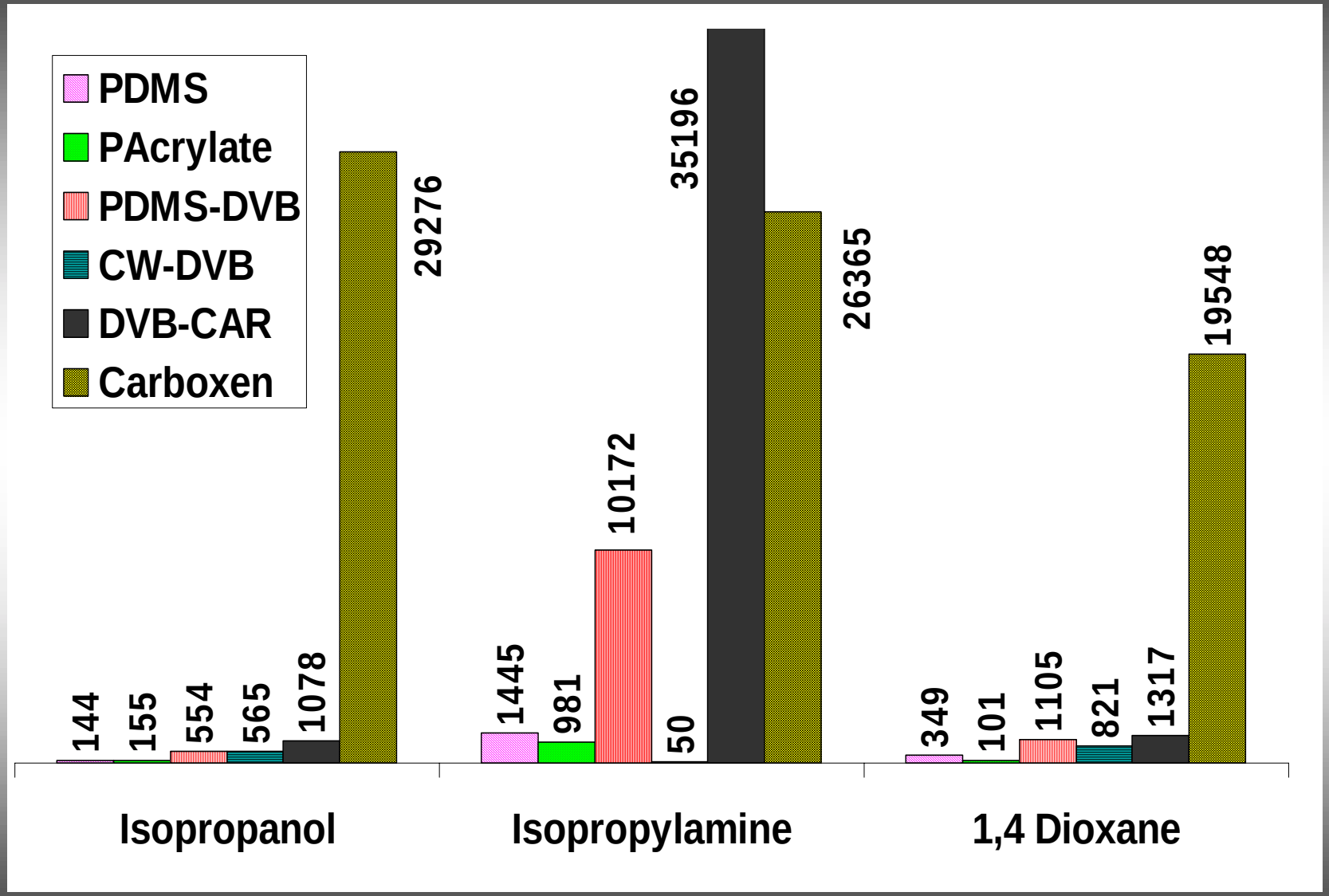
Comparison of Area Responses by Fiber Type



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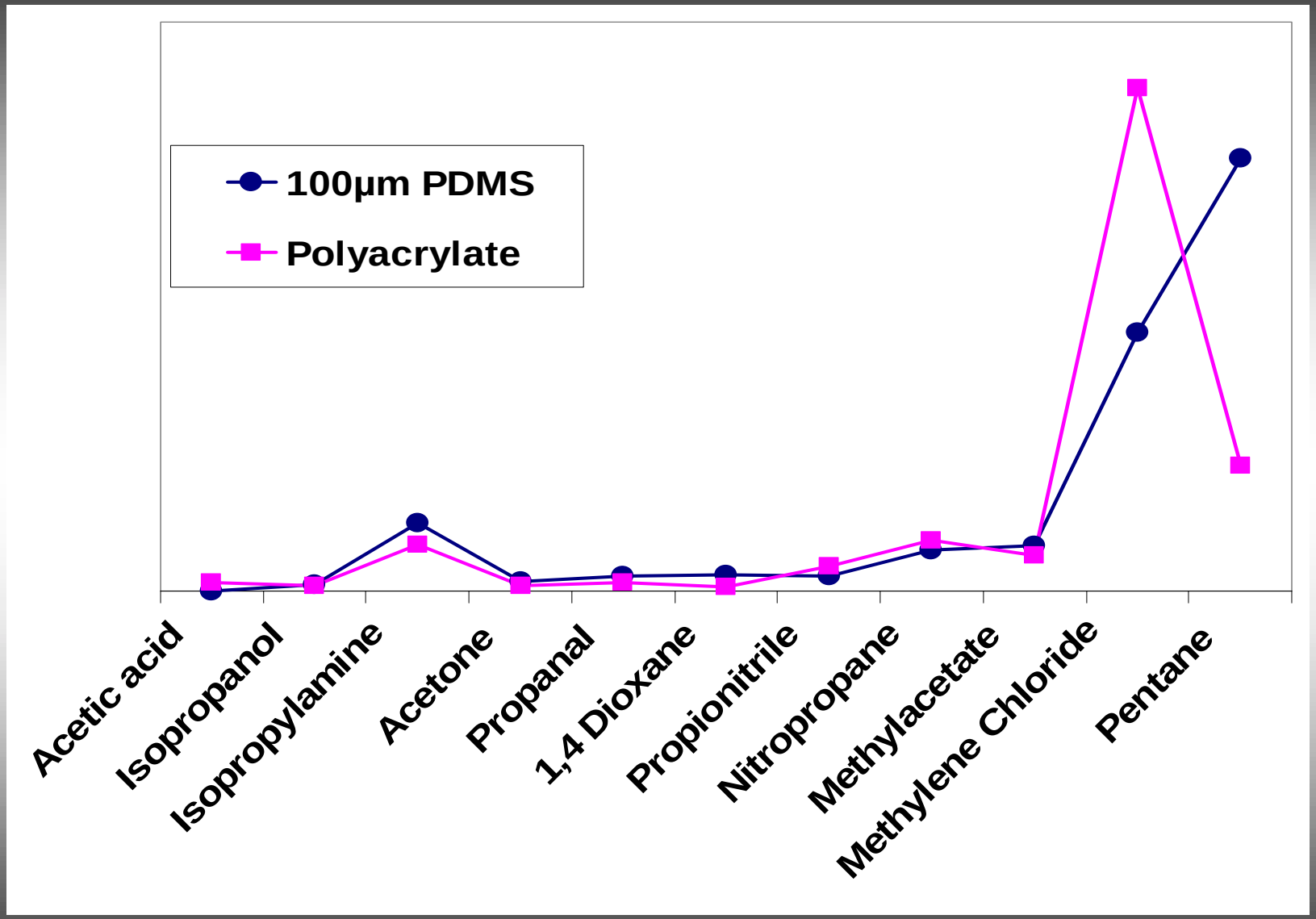
Analyte Polarity vs. Area Response



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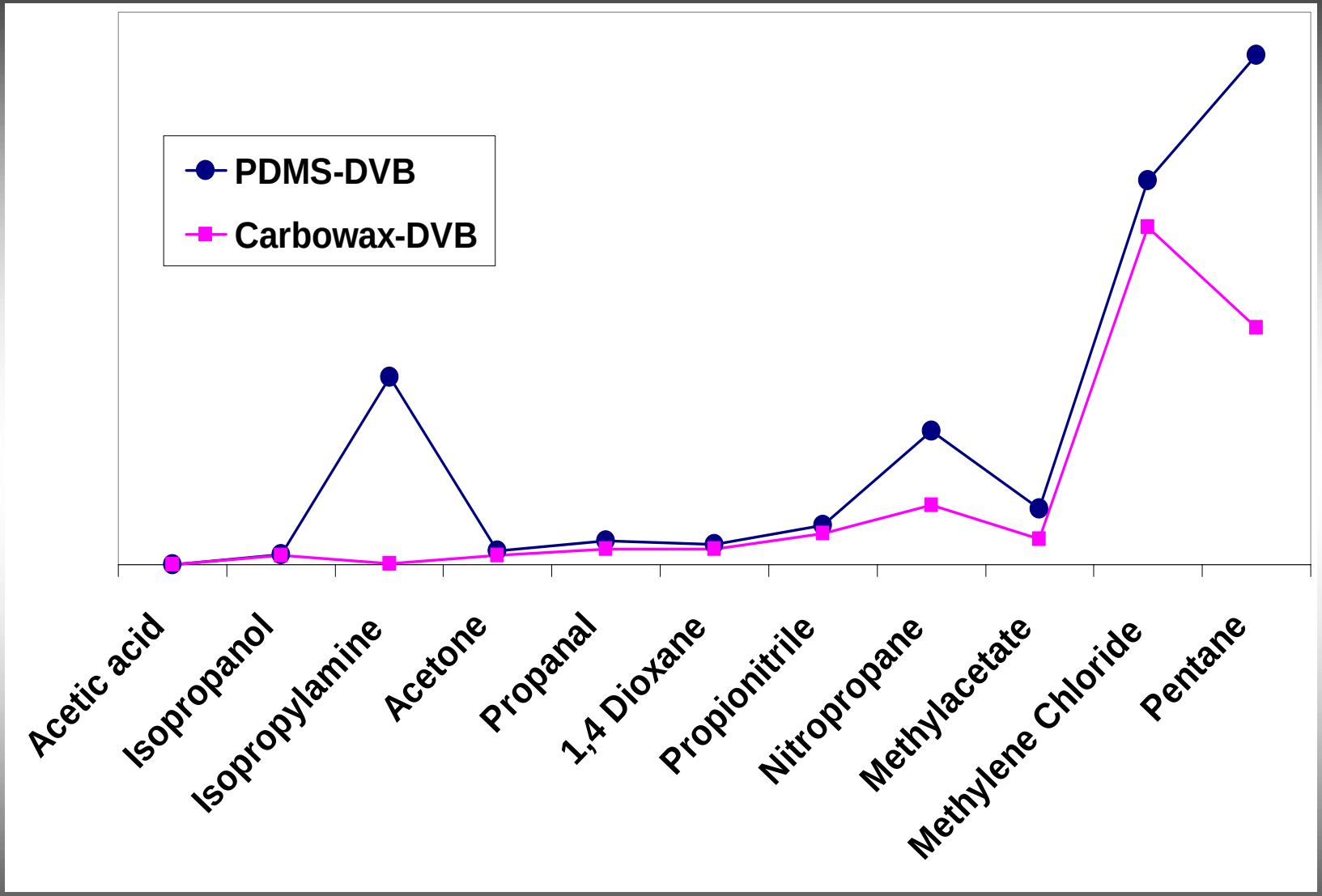
Fiber Polarity vs. Area Response



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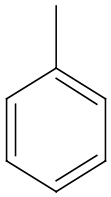
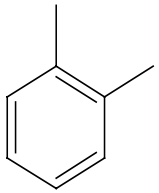
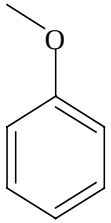
Semi-Volatile Analytes Used in Study



Toluene
92



o-Xylene
106



Anisole
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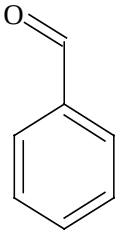

Benzaldehyde
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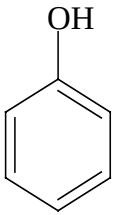
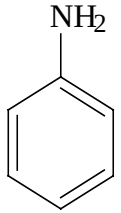
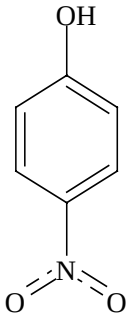


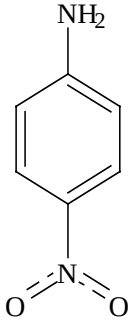
Phenol
94



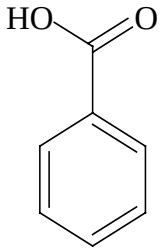
Aniline
93



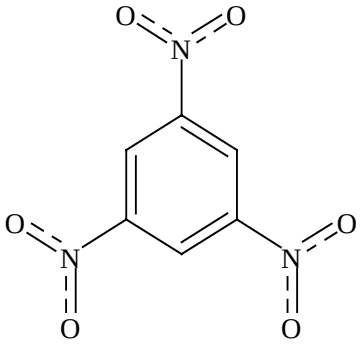
p-Nitrophenol
139



p-Nitroaniline
138



Benzoic acid
122



1,3,5-Trinitrobenzene
213

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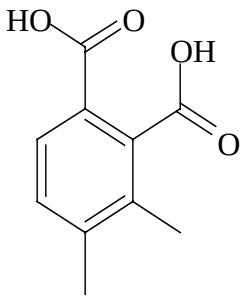
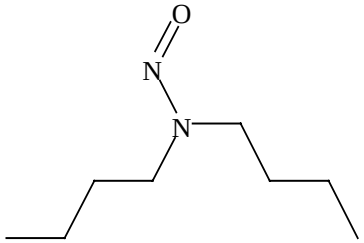
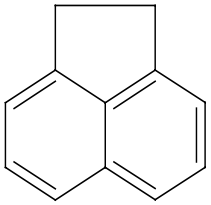
Semi-Volatile Analytes Used in Study (contd.)



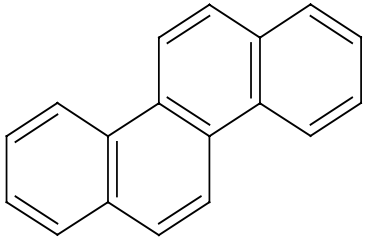
Dimethylphthalate
194



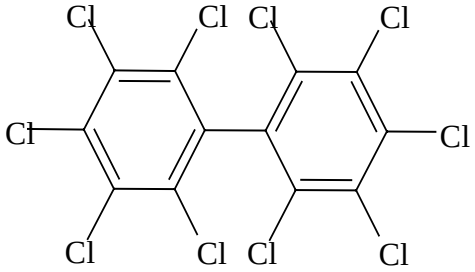
N,N-Nitrosodibutylamine
158



Acenaphthene
154



Chrysene
228



Decachlorobiphenyl
499

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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

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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 0.25µm 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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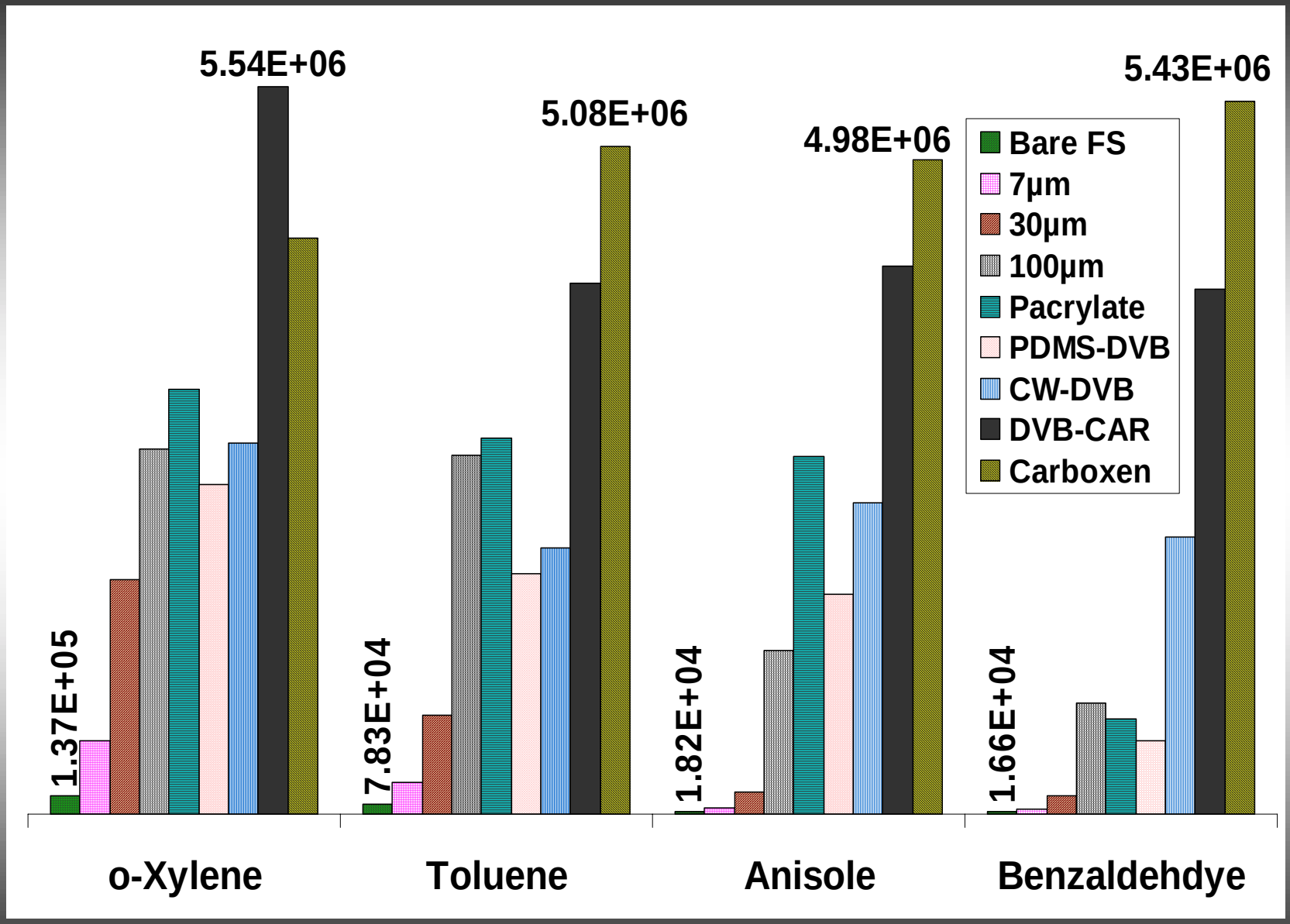
Comparison of Area Responses by Fiber Type



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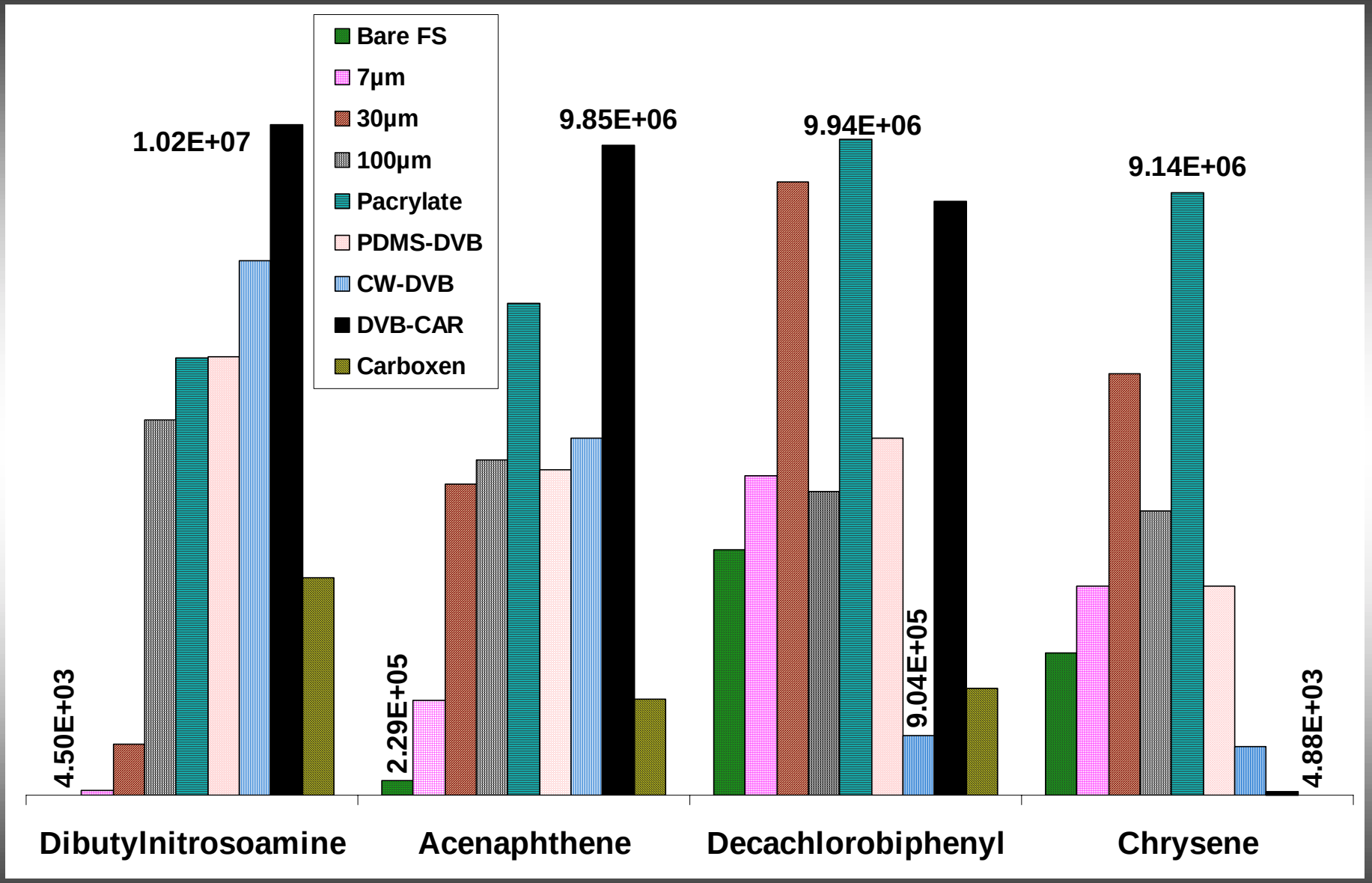
Area Response vs. Fiber Type



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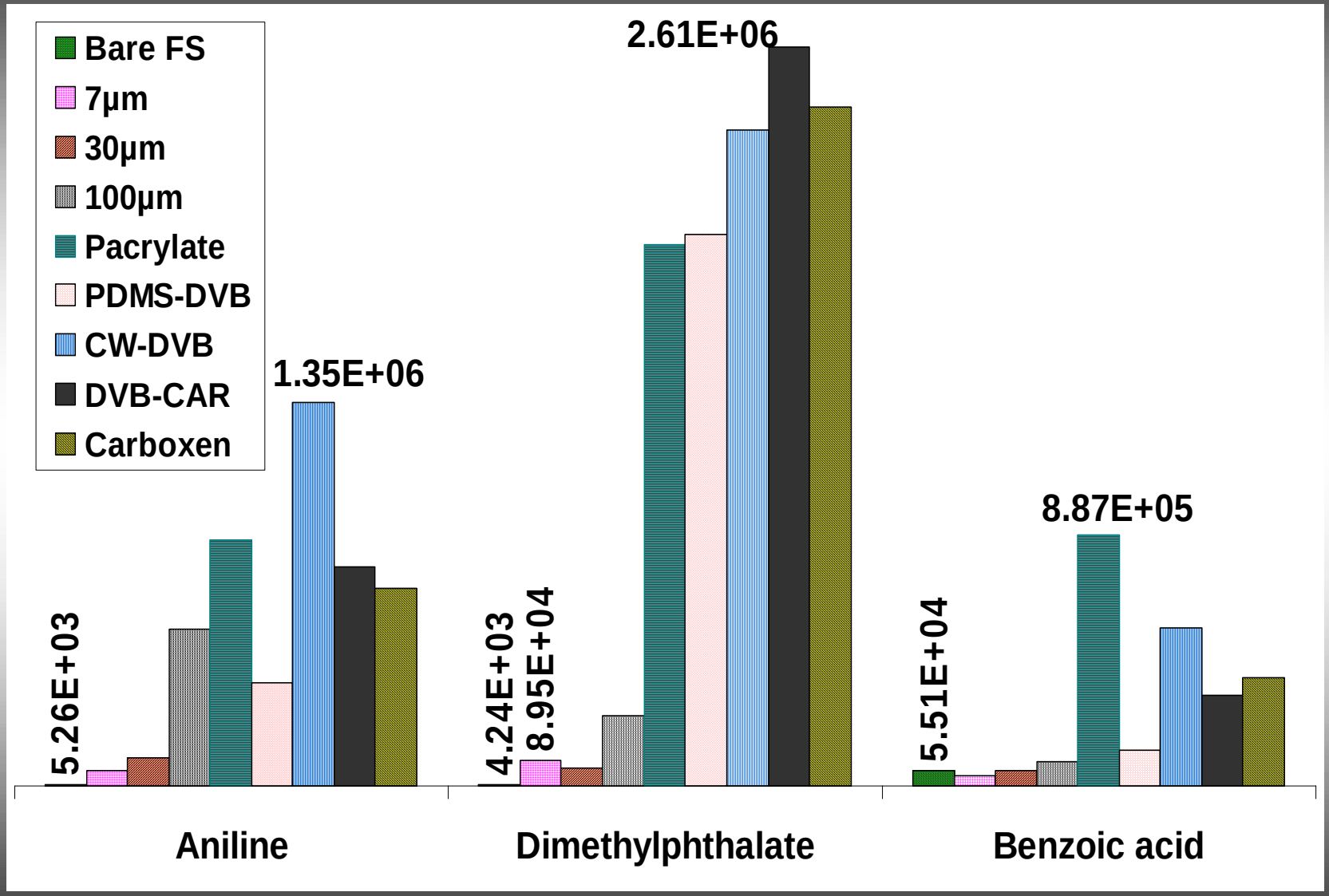
Area Response vs. Fiber Type



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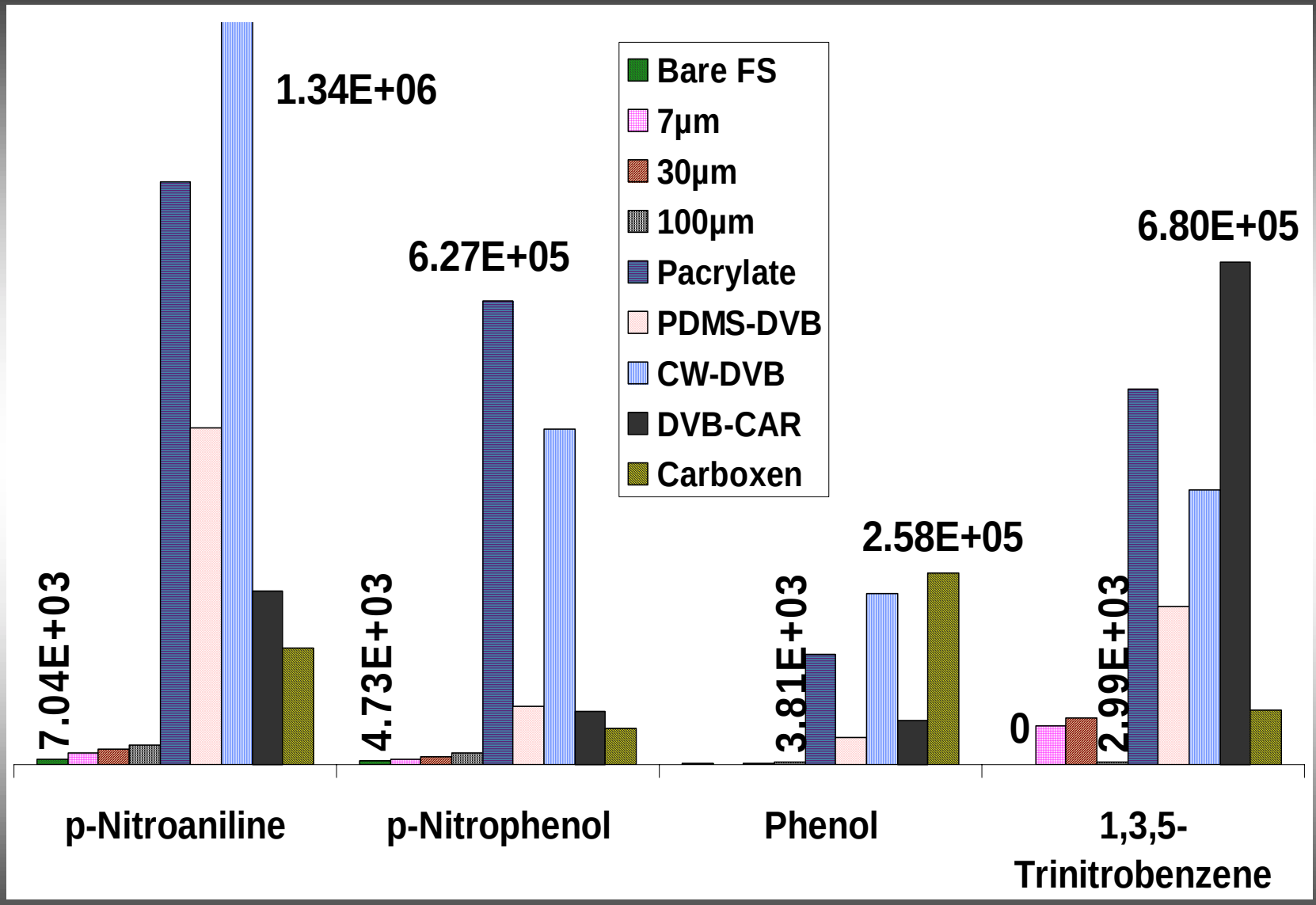
Area Response vs. Fiber Type



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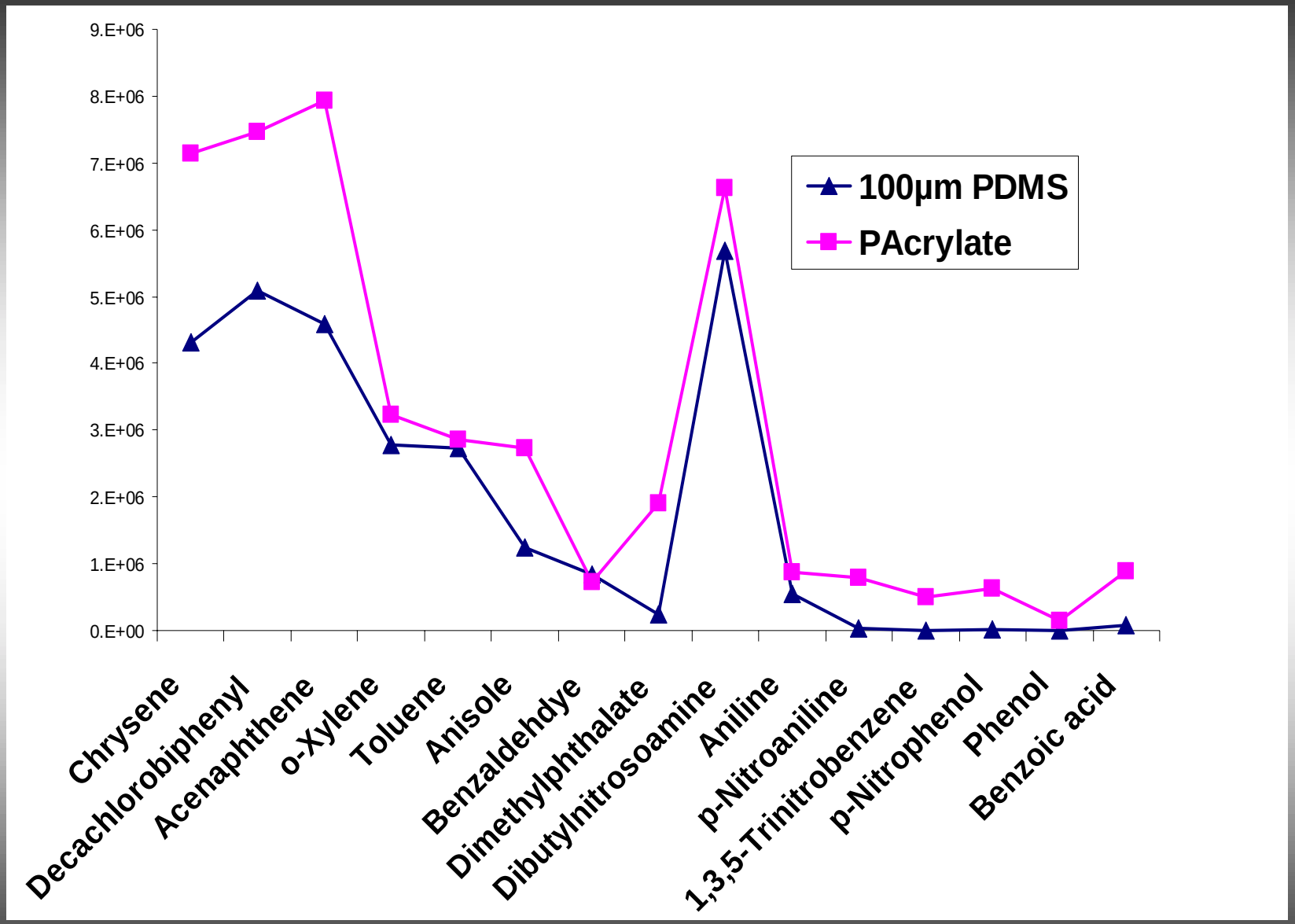
Analyte Polarity vs. Area Response



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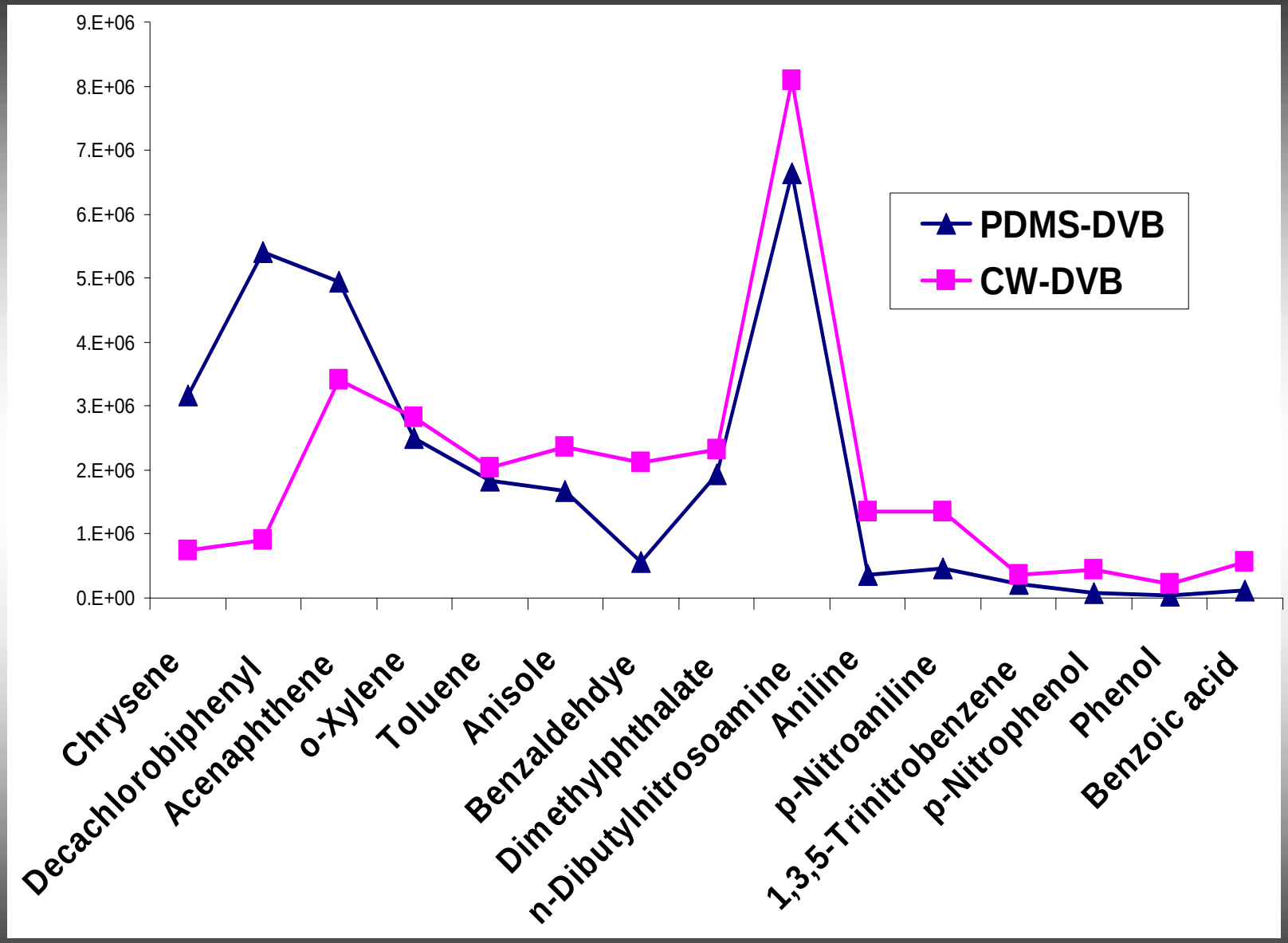
Analyte Polarity vs. Area Response



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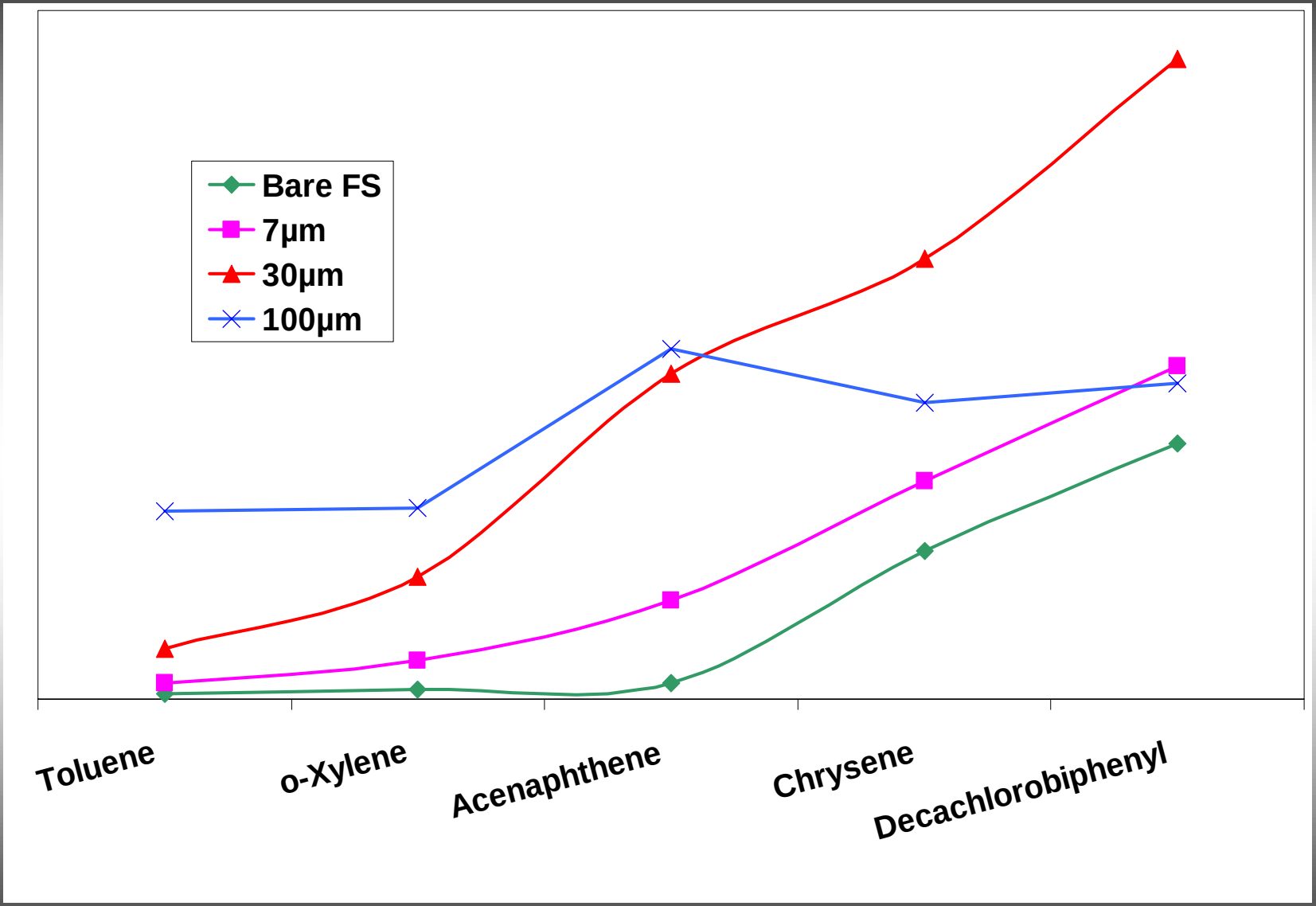
Effects of Coating Thickness on Analyte Recovery



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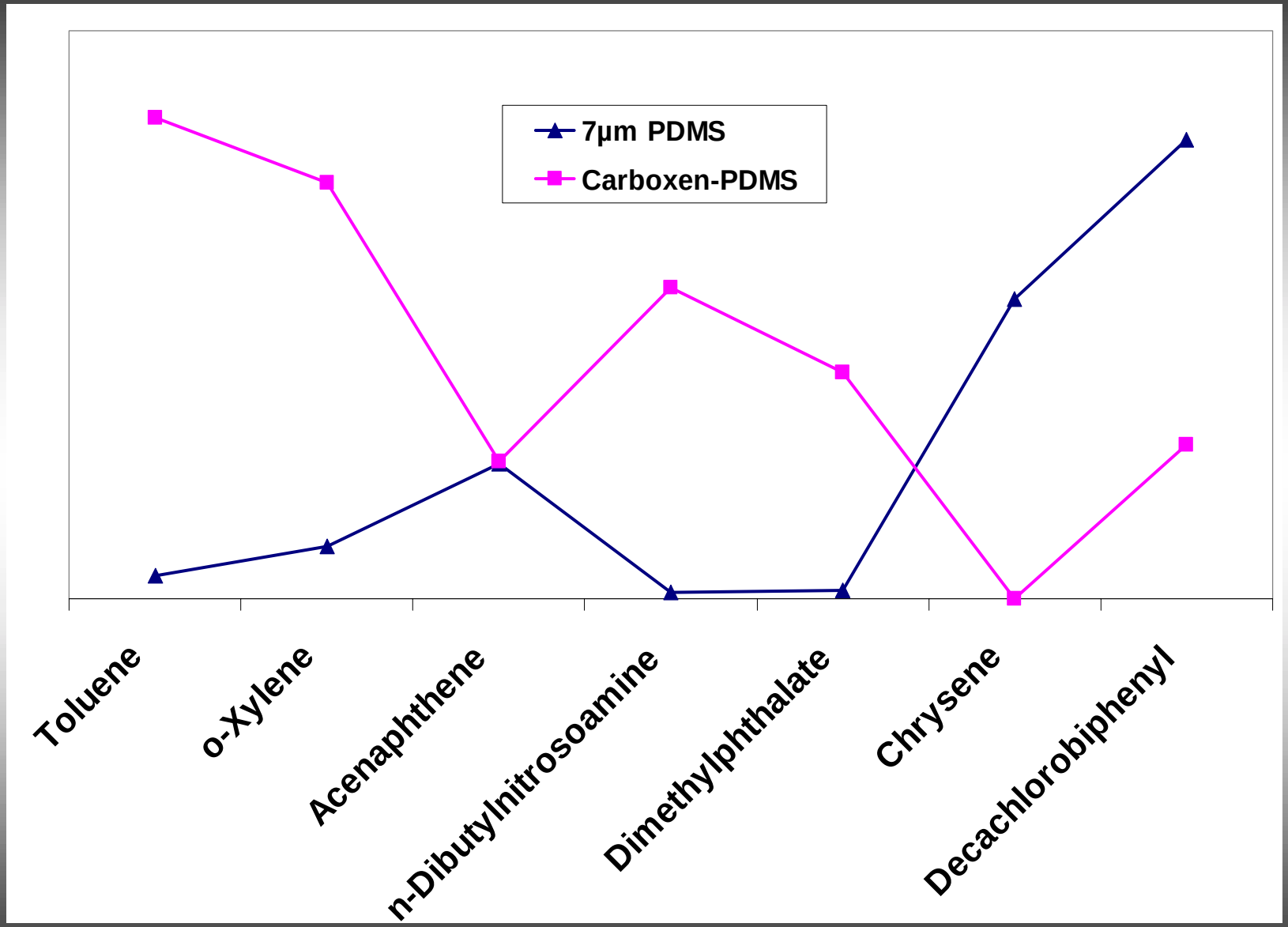
Analyte Size vs. Area Response



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Classical Adsorption Mechanism for a Uniform Surface

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

Langmuir's Isotherm

$$\text{Ø} = KP_A / (1 + KP_A)$$

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

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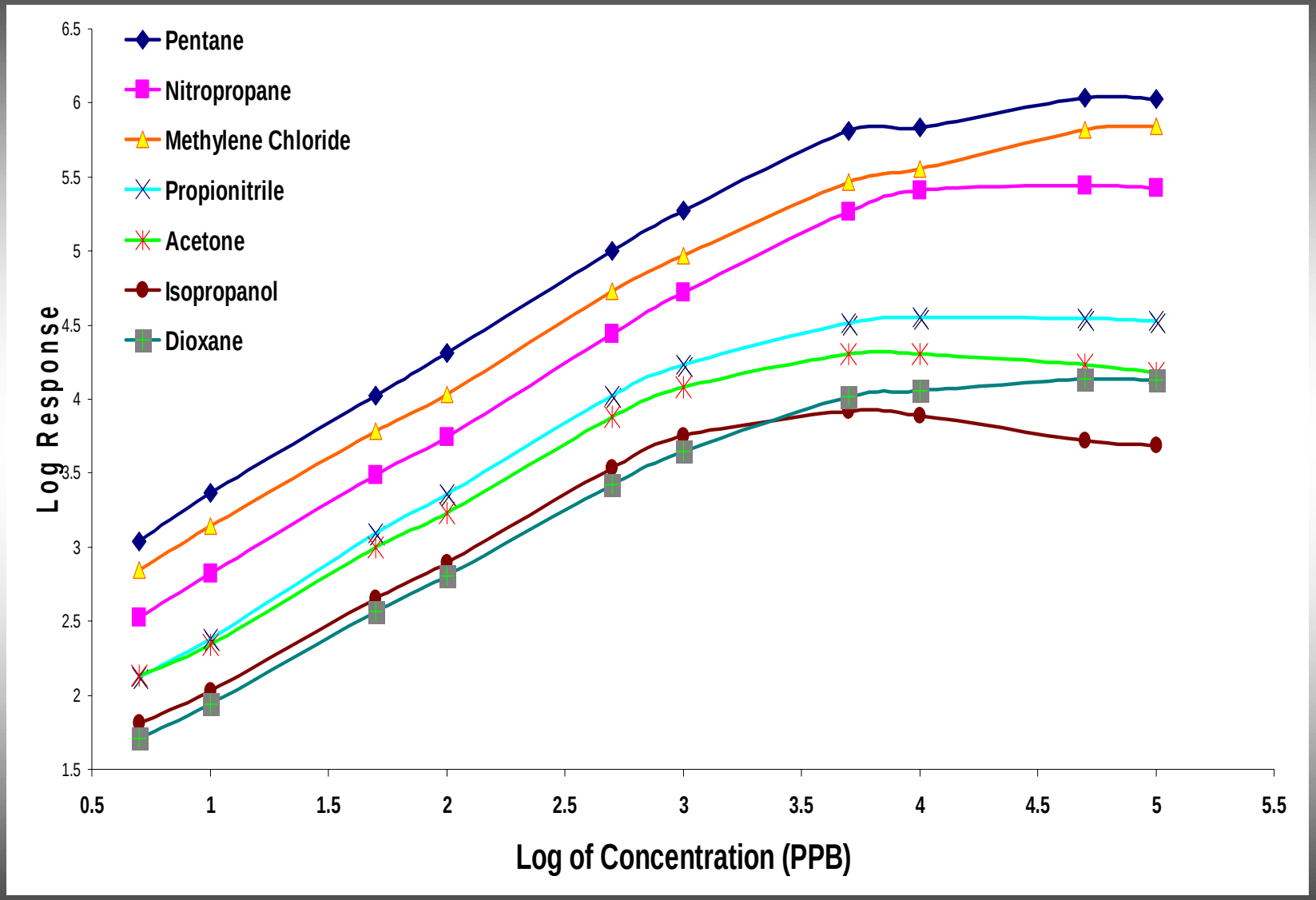
Analyte Response vs. Conc. (Carboxen-PDMS)

15 Min Ext.



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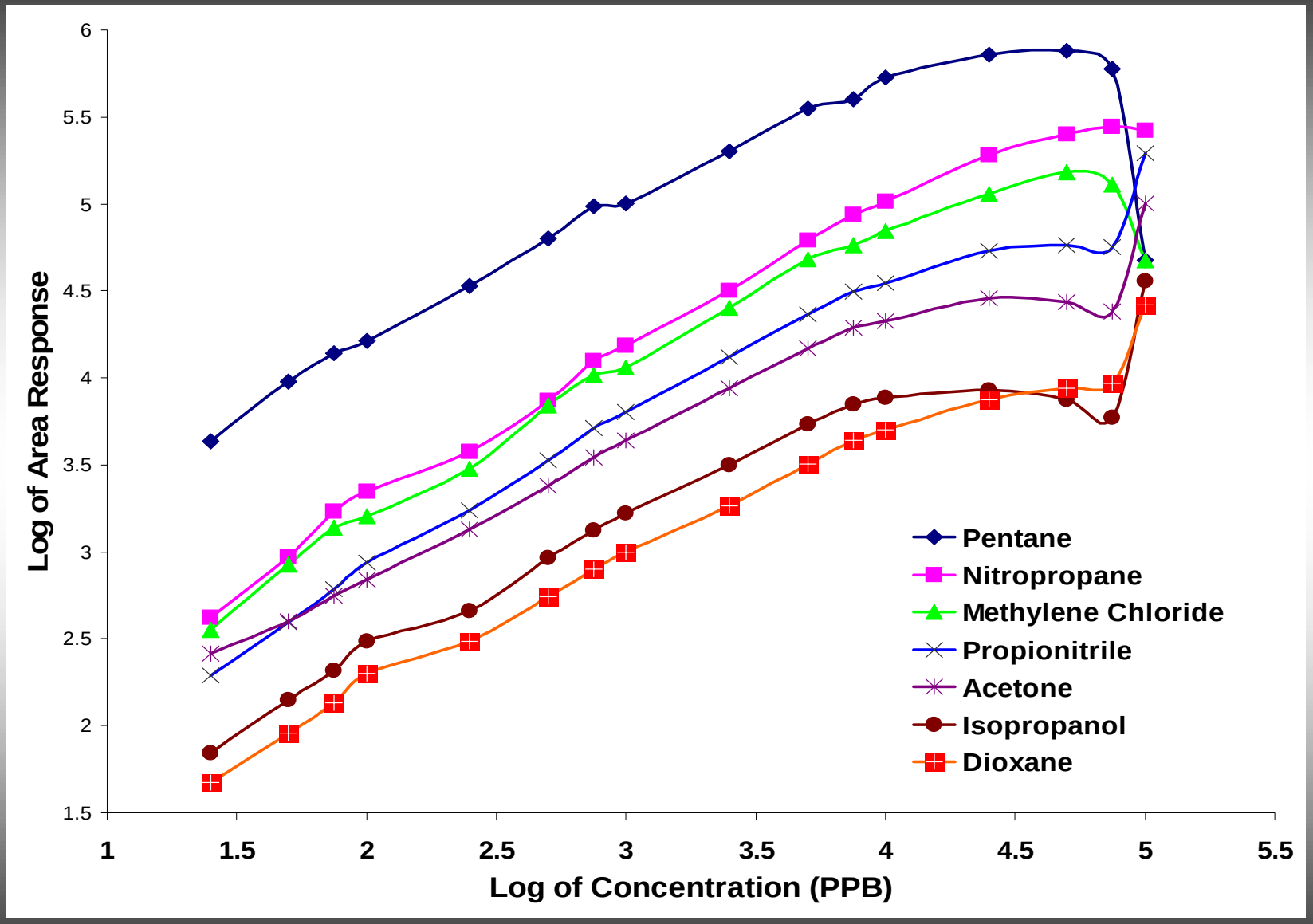
Analyte Response vs. Conc. (Carboxen PDMS 2min Ext.)



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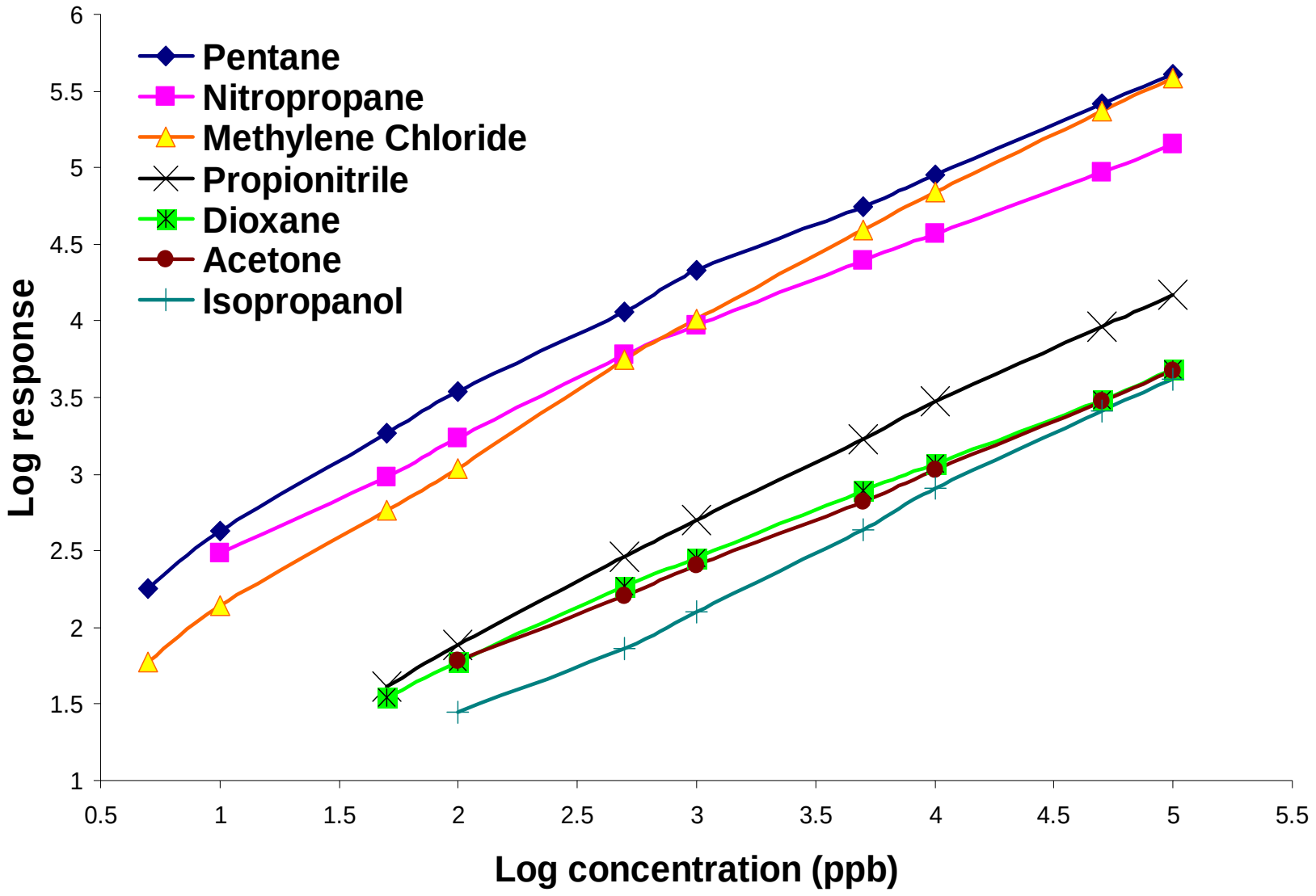
Analyte Response vs. Conc. (PDMS-DVB)



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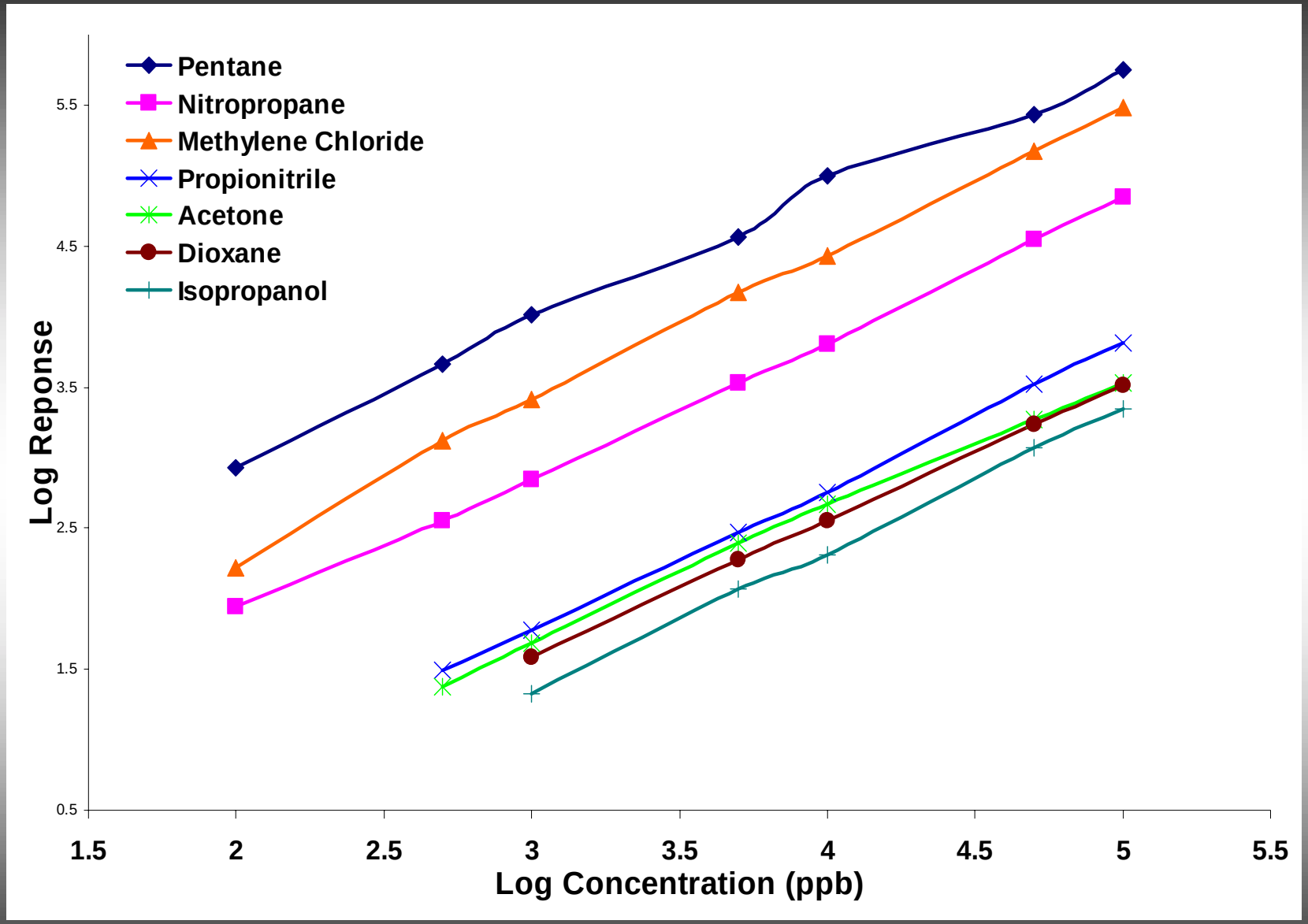
Analyte Response vs. Conc. (100µm PDMS)



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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.

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