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SPME-Adsorption versus Absorption: Which Fiber is Best for Your Application?

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The continuing development of SPME fiber coatings has presented some difficulties for analyst to select the appropriate fiber for their application. The goal of this presentation is to provide you with a guideline on how to select the appropriate SPME fiber. A critical part of the selection process is determining whether to use an adsorbent type fiber or an absorbent type fiber. This presentation will attempt to provide you the information needed to determine when each type is appropriate.

Overview of Presentation

- **Difference between an Adsorbent and Absorbent**
- **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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To help you select the appropriate fiber, this presentation will first briefly describe the difference between an adsorbent and absorbent type fiber and the various types of SPME fibers. The differences in the fibers will be shown in a study involving low-molecular-weight analytes and a study comparing the efficiency of the fibers on the extraction of semi-volatile analytes. The effects of the size of analytes on the extraction efficiency of the fibers will be discussed. And lastly a discussion on fiber capacity and detection limits between adsorbent and adsorbent fibers will be given.

Adsorbent vs. Absorbent Fibers

Adsorbent type fibers

- **Physically traps or chemically reacts bonds with analytes**
 - porous material
 - high surface area
 - chemical derivatizing agent
- **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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Absorbent type fibers extract by the partitioning of analytes into a “liquid-like” phase. It is somewhat like a sponge. The analytes migrate in and out of the coating. The ability of the coating to retain and release the analyte is dependent primarily on the thickness of the coating and the size of the analyte. The polarity of the fiber coating may enhance the attraction of an analyte to that particular coating, but it's the thickness of the fiber that retains the analytes. There is virtually no competition between analytes. It is basically how fast the analytes migrate in and out of the phase. The thicker film coatings have high sample capacity.

Adsorbent type fibers extract analytes by physically interacting with the analytes. Adsorbents are generally solids that contain pores or high surface areas. The extraction can be accomplished by trapping the analytes in internal pores. These micro- and meso- pores are ideal for trapping small and mid-sized analytes and usually retain the analytes until either energy is applied or they are displaced by a solvent. Macropores, primarily on the surface of the material, can also trap larger analytes, but generally retain the analytes through hydrogen bonding or Van der Waals interactions. Because there are a limited number of sites, the analytes can compete. This can result in reduced capacity and/or displacement of analytes with low distribution constants by those with higher distribution constants.

Suspension of the adsorbents in a liquid phase can enhance selectivity based upon polarity of the phase. This phase helps to bond the adsorbent to the fiber.

By placing a derivatizing agent into the fiber coating, an absorbent fiber acts more like an adsorbent fiber. The reagent chemically reacts with the analytes and binds them to the fibers. Adsorbent type fibers also may be altered with derivatizing reagents.

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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There are four absorbent type fibers. These are the polydimethylsiloxane (PDMS) and the polyacrylate (PA). The nonpolar PDMS come in 3 different coating thicknesses and the PA, a polar fiber, comes in only one thickness.

The adsorbent type fibers contain either divinylbenzene (DVB) and/or Carboxen™ 1006. Depending upon the desired polarity, the DVB fibers are available suspended either PDMS or Carbowax® (CW), a moderately polar phase. Carboxen is only available suspended in PDMS. Attempts to suspend it in CW resulted in poor analyte recovery. There is one fiber available that contains a combination of DVB-PDMS layered over Carboxen PDMS. This fiber will be discussed in later detail in the presentation.

Bare fused silica is listed as an adsorbent type fiber because the surface of the fused silica interacts with the analytes. This fiber is only available as a custom due to the fragility of bare fused silica.

All of the adsorbent fibers are available on a StableFlex™ core in addition to the standard fused silica. The thin coating of plastic on the fused silica makes the StableFlex fiber more flexible. The phase coating also bonds to the plastic better than fused silica. This results in a less breakable more stable fiber. We highly recommend the StableFlex version when developing applications.

Physical Properties of Divinylbenzene and Carboxen-1006

Material	Surface Area (m ² /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

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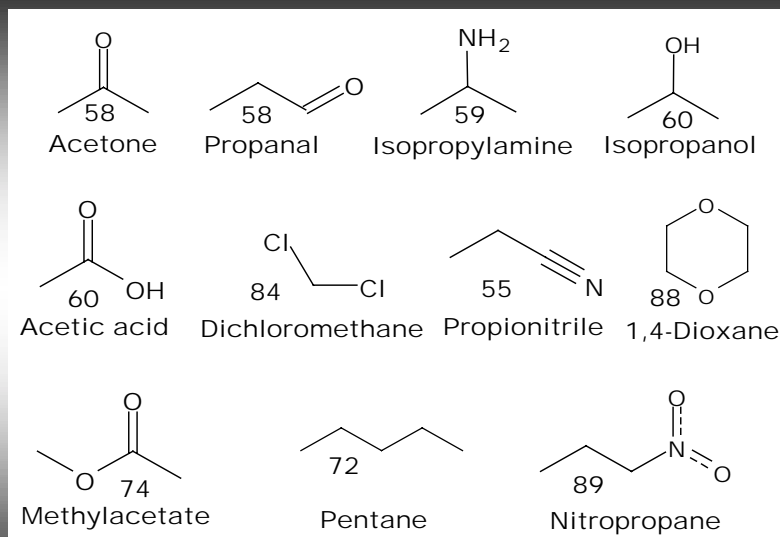
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The surface area of DVB is fairly high at 750m²/g. The material is primarily mesoporous with a moderate amount of macropores. There are very little micropores present in this DVB material.

Carboxen-PDMS has a similar surface area as DVB. The major difference is the much higher percentage of micropores. This material has a fairly even distribution of macro, meso and micro pores. It is also a more rigid carbon based material. Carboxens differ from other porous carbons because the pores are not sealed but pass entirely through the particle. The pores taper as they approach the center of the particle than expand as they approach the perimeter. This pore structure allows analytes to desorb more efficiently than with sealed pores common with charcoals and many carbon molecular sieves.

To take advantage of both adsorbents, a fiber was developed that layers DVB suspended in PDMS over a layer of Carboxen suspended in PDMS. Because the coatings are layered, the larger analytes will be retained in the meso and macro pores of the outer DVB layer, while the smaller analytes migrate through this layer and are retained by the micropores in the inner layer of Carboxen. This fiber expands the analyte molecular weight range and still enable extraction of analytes at trace levels. There is a reduction in the amount of analyte retained compared to the thicker single adsorbent, but it is suitable for many analyses.

Analytes in Volatile Study



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In the first study, the goal was to evaluate the various types of fibers for the extraction of low-molecular weight analytes. All of the above analytes are similar in size and vary only by functionality. The basis for selecting these analytes was to keep the size similar so to determine the effect of functionality on the extraction efficiency of the fibers. These are the smallest, stable, nongaseous analytes at ambient temperature for each of these groups. Only 1,4-dioxane had a structure that was not similar to the others, but diethylether, the first choice for an ether, co-eluted with pentane which was used as an internal standard.

The fibers selected to extract these analytes were those designed to retain volatile analytes. There were two absorbent type fiber 100 μ m PDMS and the 85 μ m PA fiber. The remaining fibers used in the study were adsorbent style fibers on a StableFlex core. These fibers were the CW-DVB and PDMS-DVB fibers along with the Carboxen-PDMS and DVB-Carboxen-PDMS fibers.

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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Response factors were calculated with respect to pentane using direct injections of the mixtures. If you multiple the area counts of each of the above analytes by the response factors, the area response would be similar to the pentane response. This eliminates FID discrimination and gives a better representation of the amount of each analyte extracted by the fibers.

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 2 ppm

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

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

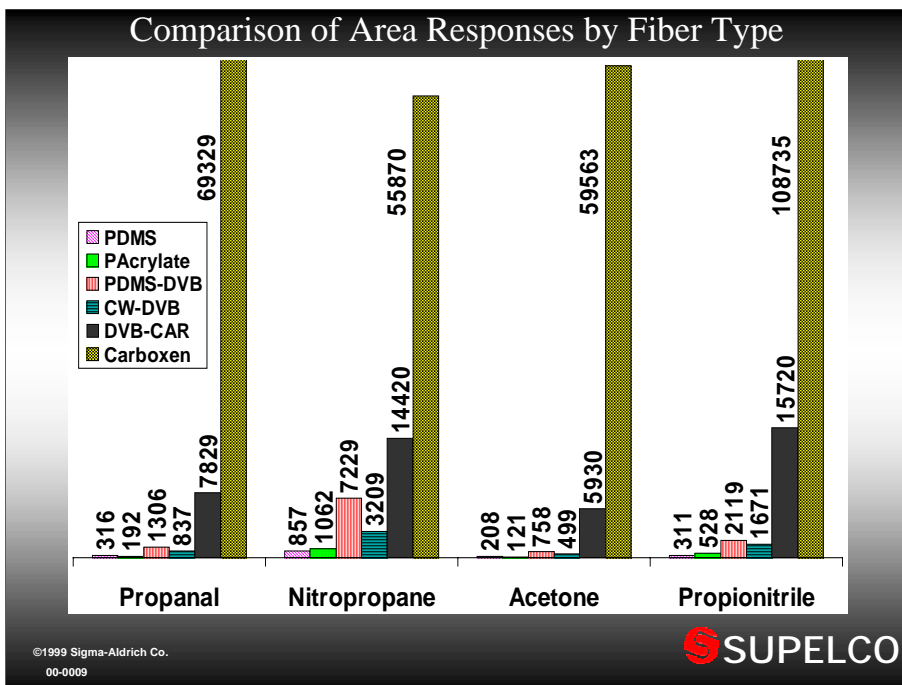
Detector: FID

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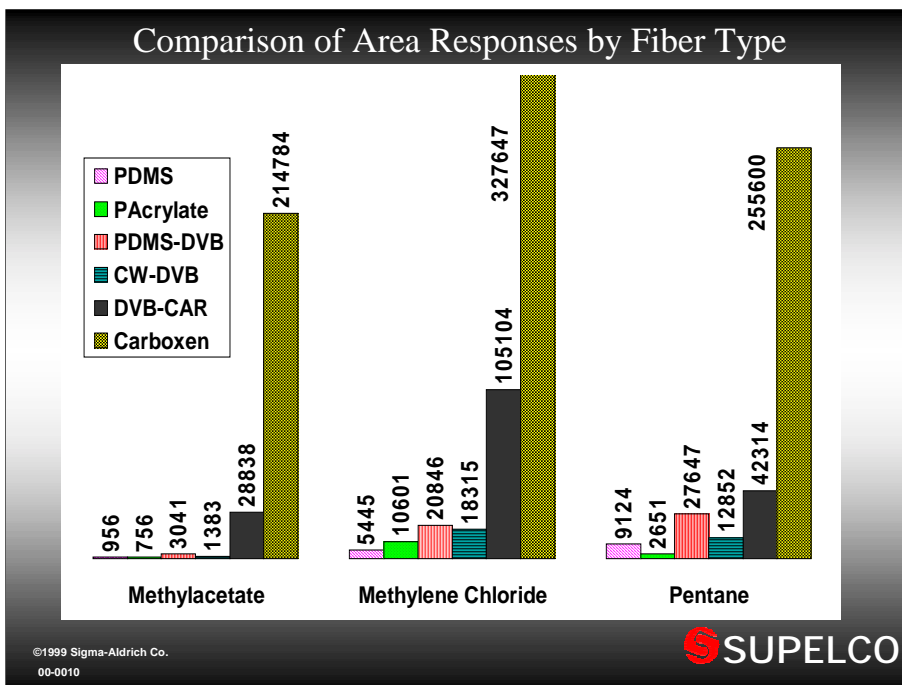
The analytes, contained in methanol at 2mg/ml, were spiked into the water solutions containing 25% NaCl and the appropriate 0.05M phosphate buffer that was either at a pH of 2,7 or 11. The final concentration of each analyte was 2ppm in water. The analytes were divided into 3 mixes to prevent co-elutions, and interactions. All of the solutions were extracted for 15 min by immersing the fiber into the water. The fiber was agitated to enhance recovery using the Varian 8200 Autosampler adjusted for SPME use. Each of the fibers used in this evaluation, extracted each mix at each pH level in triplicate.

The fibers were desorbed at 260°C except for the Carboxen-PDMS which was at 310°C and the PA fiber at 280°C. The fiber was kept in the injection port for 2 min, but the splitter was opened after 0.5 min. The analytes were desorbed onto a SPB™-1 Sulfur 30m x 0.32mmID x 4µm column. The analytes were eluted by programming the column from 40°C (2min) to 150°C at 8°C/min under a flow rate of 35cm/sec at 40°C. The analytes were detected with an FID.

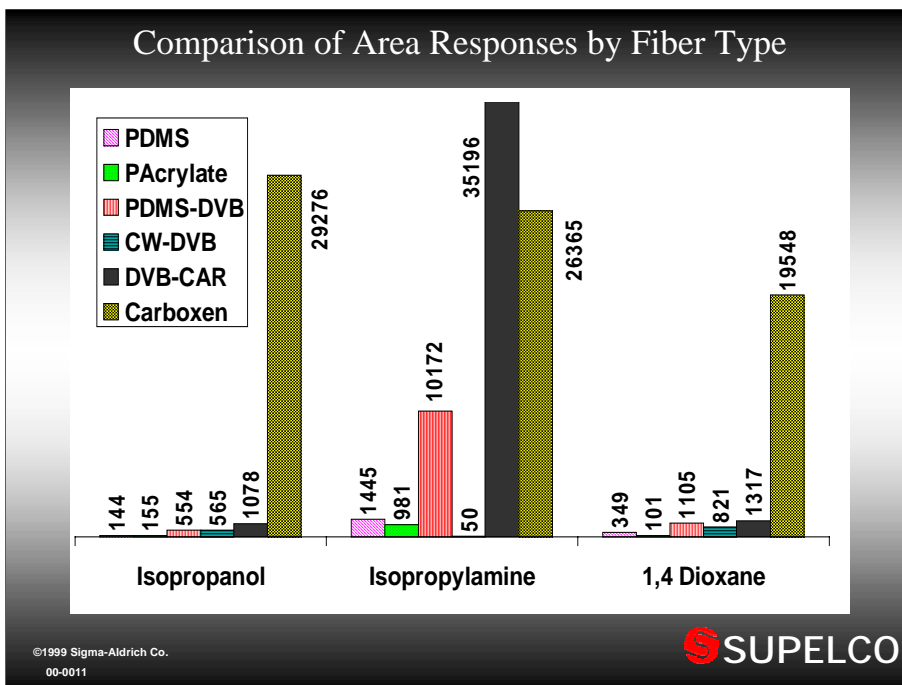


This slide shows a comparison of the adjusted responses for the various fibers for four of the relatively polar analytes. The area responses were obtained from the average of three extractions at the optimum pH level for each analyte.

The adjusted area responses show that the Carboxen-PDMS fiber was the best choice for extracting these analytes. The Carboxen coated fiber extracted up to 300 times as much analyte compared to the absorbent type fibers. The dual coated fiber with DVB layered over Carboxen was the second best fiber and the DVB containing fibers extracted more of each of the analytes than the absorbent type fibers. The micropores of the Carboxen-PDMS coated fiber retain these smaller analytes better than the other fibers.

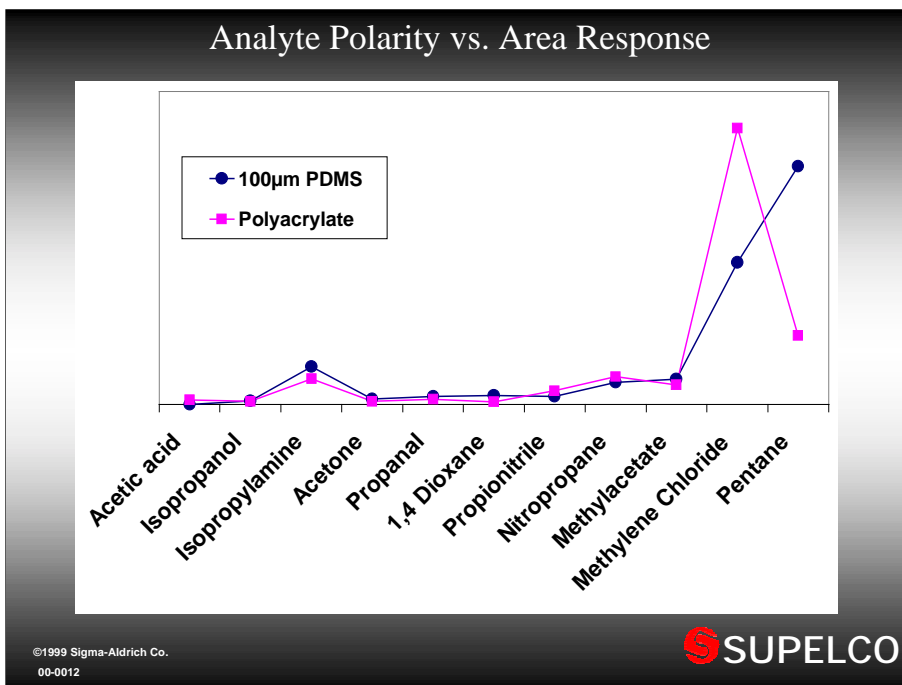


The same pattern is shown for the less polar analytes contained in this slide with the Carboxen-PDMS fiber extracting significantly more of the analytes than the other fibers. Again as with the previous slide, the dual coated fiber was the second best choice if optimum extraction efficiency is the desired goal. It was followed by the DVB containing fibers and then the absorbent type fibers. The differences between fibers is not as dramatic with nonpolar analytes, such as pentane, compared to the differences in response between fibers when extracting the more polar analytes.



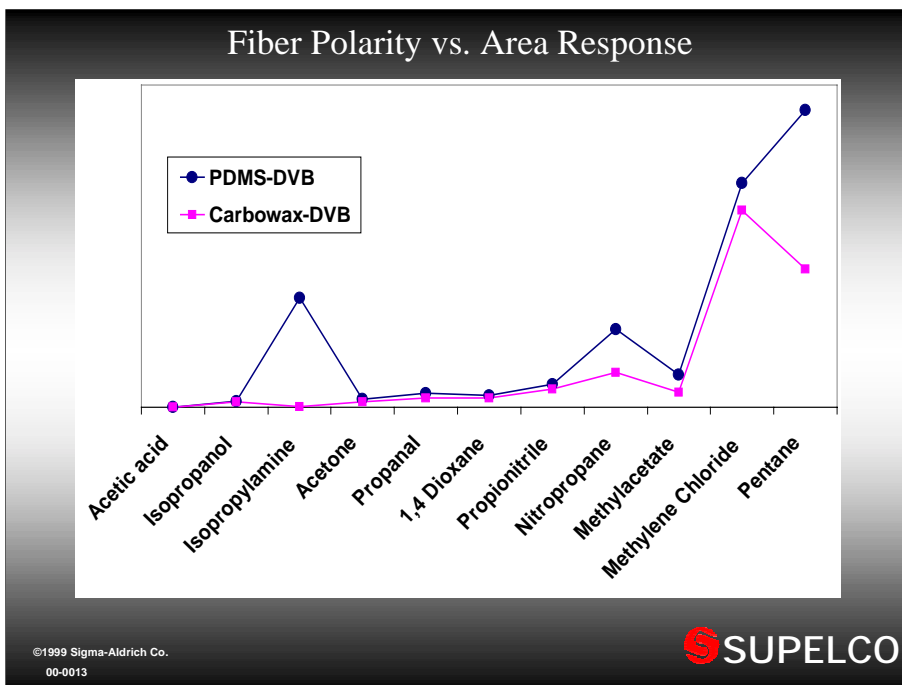
For the most polar analytes shown in this slide, the area responses are greatly reduced for all of the fibers compared to the area responses obtained with the less polar analytes. However, the Carboxen-PDMS coated fiber is still the best choice for extracting these small analytes except for isopropylamine. Previous studies have indicated that the PDMS-DVB coating has a high affinity for small aliphatic amines. This is apparent by the high area counts for isopropylamine with this fiber compared to the other small analytes extracted with this fiber. When you combine the affinity of the PDMS-DVB coating for small amines coupled with the ability of Carboxen to retain small analytes, the dual layered PDMS-DVB over Carboxen-PDMS makes this fiber the best choice for small amines.

In summarizing these three slides, the micropores of the Carboxen-PDMS fiber make it an overwhelming choice for the extraction of small analytes at trace levels. Carboxen containing fiber coatings retain more small analytes better than the DVB containing coatings which retain more than the liquid absorbent fiber coatings .



The effect of fiber polarity is shown in the next two slides. The analytes are arranged by decreasing polarity from left to right. In this slide, the two absorbent type fibers used for the extraction of volatile analytes are compared. There appears to be no advantage for using the more polar PA fiber for the extraction of the polar analytes over the nonpolar 100µm PDMS fiber.

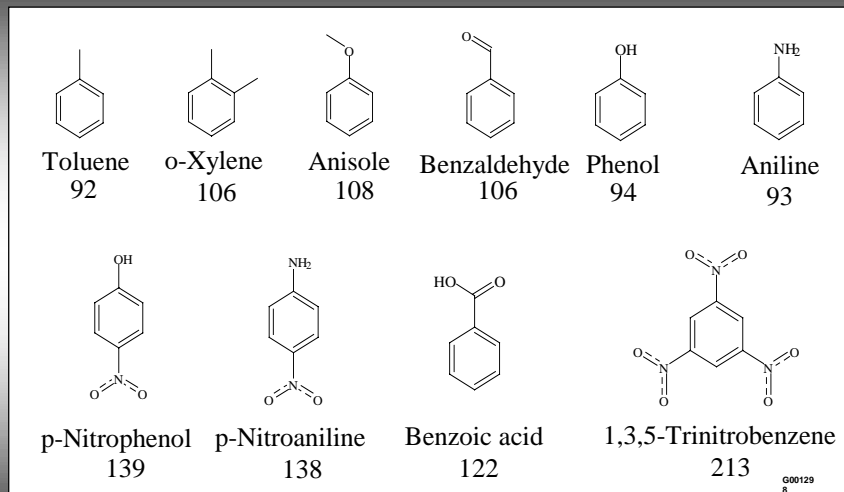
Some selectivity is observed by the fact that the polar fiber extracts much less of the least polar analyte, pentane. This could be advantageous if one wanted to extract polar analytes in a mixture containing an equal or larger concentration of a nonpolar analyte. By extracting less of the nonpolar analyte, the polar analytes would be more easily detected and extracted.



The same pattern was observed in this slide when comparing the polar and relatively nonpolar adsorbent style fibers. Again the more polar Carbowax-DVB fiber does not show any advantage for the extraction of these polar analytes over the less polar PDMS-DVB. But like the polyacrylate coated fiber, the Carbowax-DVB fiber extracts less of the nonpolar analytes relative to the PDMS-DVB fiber. This could be more critical for adsorbent fibers because of the limited capacity of the fibers. The reduction in the extraction of the nonpolar analytes is important when analytes are competing for sites on the fiber.

The affinity that the PDMS-DVB fiber for amines was demonstrated previously in the chart showing the extraction of isopropylamine. This graph shows that this same fiber also has an affinity for nitro groups as demonstrated by the increased response for nitropropane compared to the CW-DVB fiber. This fiber is suitable for extracting many nitrogen containing analytes.

Semi-volatile Analytes Used in Study



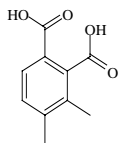
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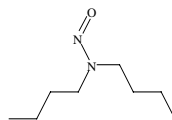
In the second study 15 different analytes (shown in this slide and the next slide) ranging in molecular weights from 92-500, representing a variety of organic classes were extracted with 9 different types of SPME fibers. The analytes in this slide are aromatic ring compounds with mono-, di- and tri- functional groups. The analytes range in polarity from nonpolar to highly polar.

There were two purposes of this study. One purpose was to demonstrate the effects of analyte polarity on the extraction efficiency of all commercially available SPME fiber coatings. The other purpose was to determine the effects of fiber coating thickness relative the size of the analyte.

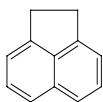
Semi-volatile Analytes Used in Study (cont..)



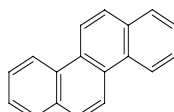
Dimethylphthalate
194



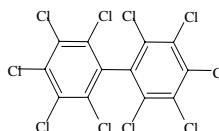
N,N-Nitrosodibutylamine
158



Acenaphthene
154



Chrysene
228



Decachlorobiphenyl
499

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In this slide the larger analytes are shown. Most of these analytes are nonpolar with the exception of the moderately polar N,N-nitrosodibutylamine. These analytes were selected primarily to show the effects of fiber coating thickness on their extraction efficiency.

The analytes in this and the previous slide were made into one mix at a final concentration of 100ng/ μ l in methylene chloride. This mixture was spiked into the appropriate solution to obtain a final concentration 75 ppb for each analyte.

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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Because the degree of fragmentation varies greatly when they are ionized and because only selected ions are used for quantitation, response factors are also needed for MS discrimination. Using acenaphthene as an internal standard, the responses were calculated based on multiple direct injections.

Even though compounds such as decachlorobiphenyl respond well in the total ion chromatogram, the compound is highly fragmented with respect to acenaphthene. As a result, it has a high response factor of 3.16. Some of the highly polar analytes are reactive with inlets, columns, and the ion source and also require higher response factors. Using the response factors better represents what the fiber is capable of extracting, not an evaluation of the analytical system.

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 μ 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

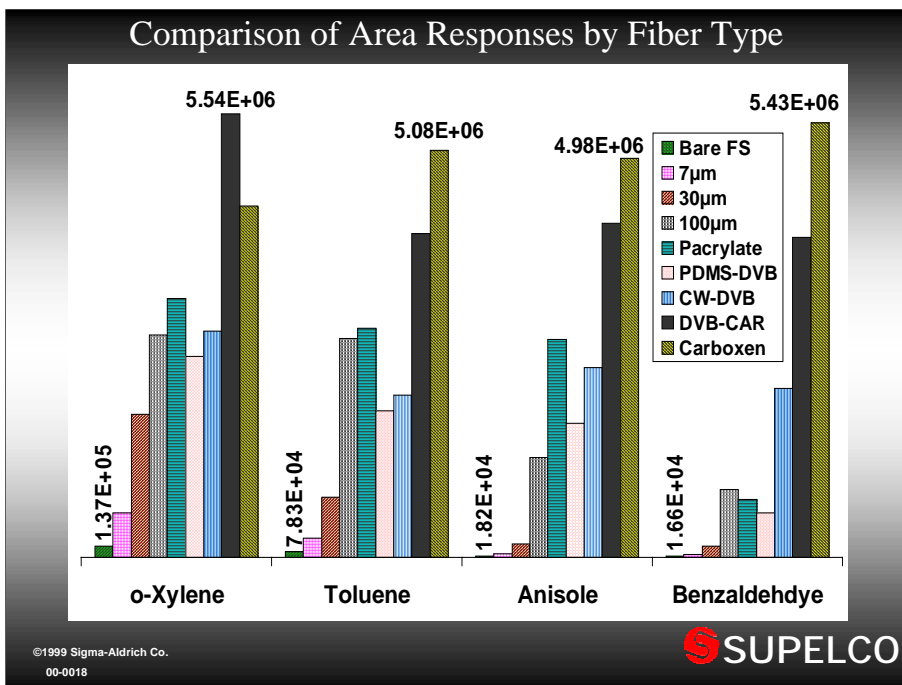
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The samples were prepared by spiking 3 μ l of the standard mix at 100ng/ml into a 4ml vial (nominal, actual 4.2) containing 4ml of the appropriate 0.05M phosphate buffer and 25% NaCl in water. The final concentration was 75 ppb. The analytes were extracted in duplicate at 3 different pH levels (2,7, and 11) using each SPME fiber. The summary of fiber efficiency, shown in the next several slides, was based on the pH level that provided optimum extraction efficiency of each analyte.

The fibers were directly immersed in the solution and the analytes were extracted for 30min at ambient temperature with stirring. After extraction the analytes were desorbed in the injection port containing a 0.75mm ID straight liner. The desorption temperature was set at 270°C for all of the fibers except Carboxen-PDMS at 310°C, PA at 290°C and CW-DVB set at 260°C.

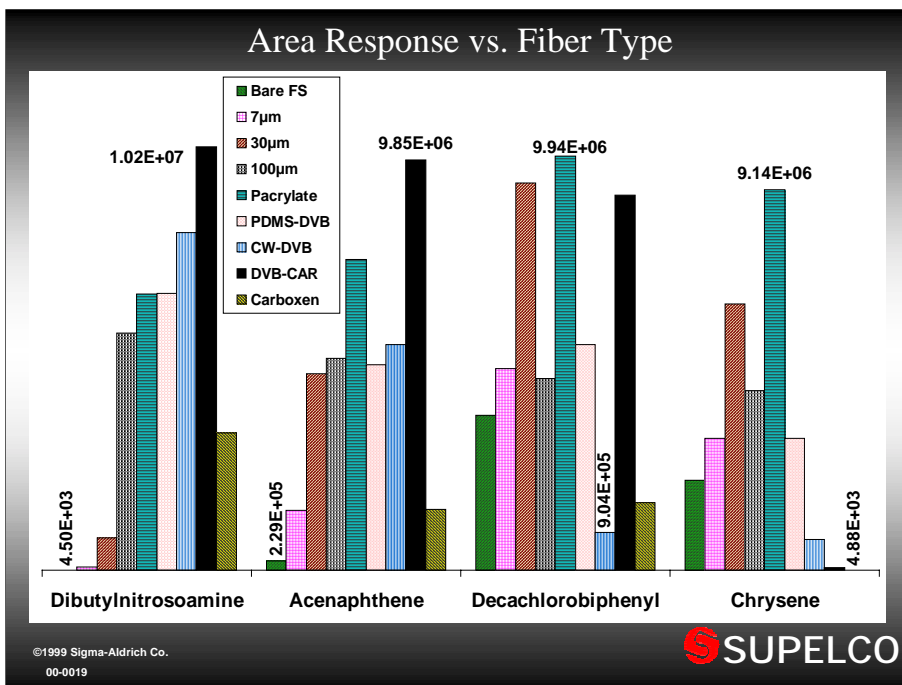
The analytes were desorbed into a 30m x 0.25mm ID x 0.25 μ m PTE™-5 column that was programmed as described above. The data were collected in the full scan mode with an ion trap; however, selected ions were used to quantify the peaks.



This and the next three slides compares the adjusted responses of the analytes extracted by the various fibers. Each analyte was extracted from solutions at pH levels that provided the optimum response for that analyte. The smaller less polar analytes in this series are shown in this slide. As expected for these smaller analytes, the Carboxen-PDMS fiber is the best choice. However, compared to the volatile analytes in the previous study, the advantage of the Carboxen fiber is not that much better than some of the other fibers. The DVB-Carboxen PDMS fiber extracts these analytes similarly and for xylene slightly better than the Carboxen PDMS fiber. The area counts for the fibers that extracted the most and the least of each analyte are listed so that a relative comparison can be made.

These analytes are also extracted well by the DVB containing fibers and by the thicker absorbent fibers the 100µm PDMS and the 85µm PA. The area counts obtained with most of these fibers are within the same order of magnitude as those for the Carboxen-PDMS; however, the Carboxen containing fiber coatings are the better choices for these analytes.

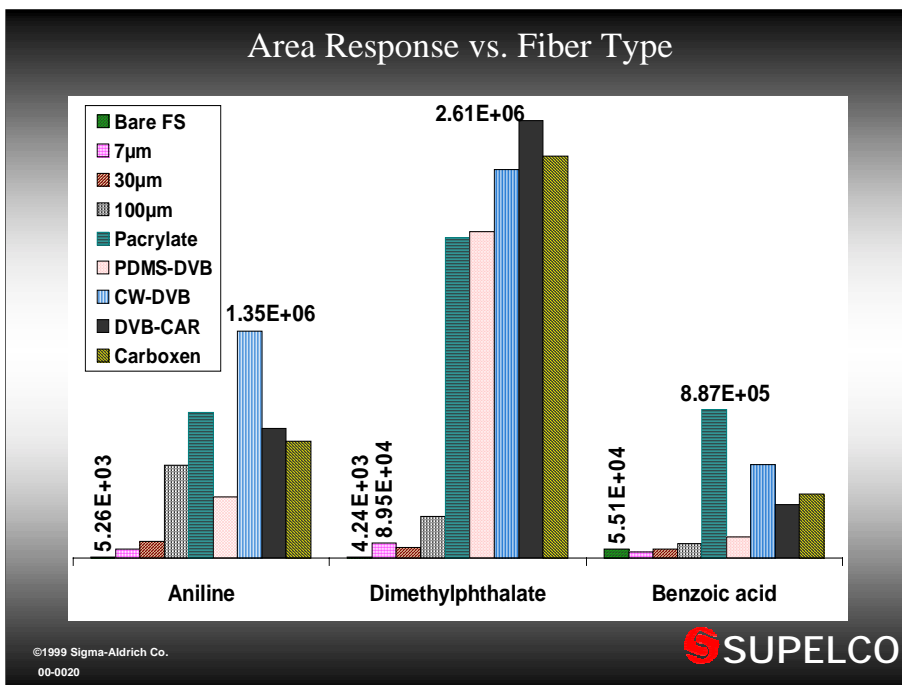
The uncoated fused silica and the 7µm PDMS fibers extract these analytes poorly compared to the other fibers (up to 2 orders of magnitude less). This would be expected due to their small size. It was surprising that the bare fused silica fiber could retain any amount of these smaller analytes. This demonstrates that there is an interaction between the analytes and the bare fiber.



This slide shows a comparison of the larger nonpolar analytes and dibutylnitrosamine that is moderately polar. The effect of size and shape is greatly noted in this slide. The large planer chrysene molecule is easily extracted by the thinner coated fibers and also bare fused silica. Because of its planar configuration, the response for chrysene is poor when using Carboxen-coated fibers. This is probably due to the poor release of this molecule from the Carboxen surface when thermally desorbing.

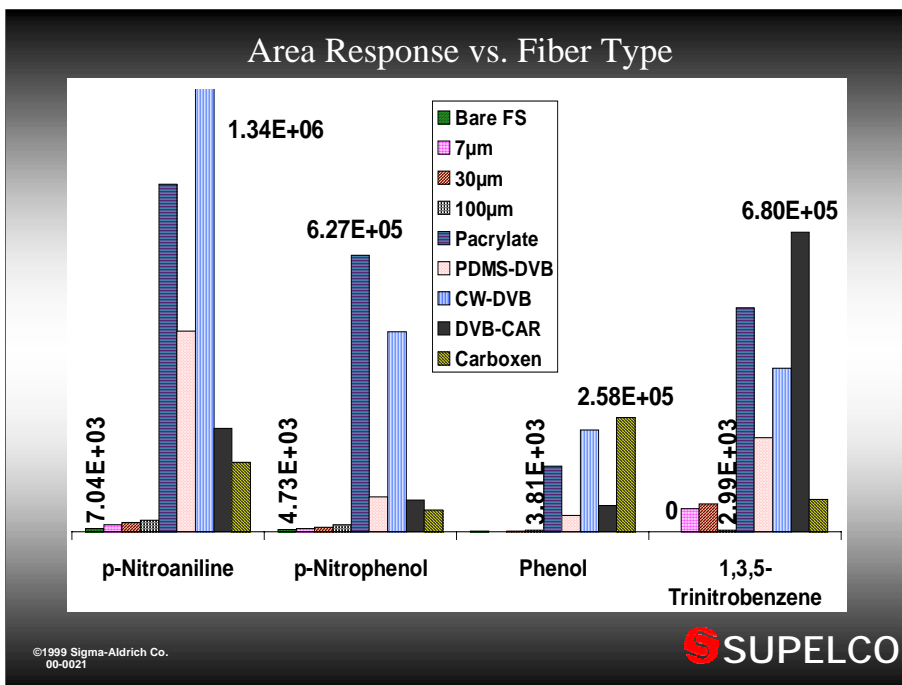
The polyacrylate coating even though moderately polar and thick has a high affinity for aromatic compounds, so it extracts the PAHs and decachlorobiphenyl well. Although decachlorobiphenyl is larger than chrysene, it is extracted better by the Carboxen containing fibers. This indicates that the shape as well as the size of the molecule is important. Apparently the chlorine groups prevent the biphenyl rings from laying tightly on the surface of the Carboxen molecule which would allow them to be released more efficiently during desorption.

All of the DVB containing fibers extract dibutylnitrosamine well with the dual layered fiber performing best. Carbowax-DVB extracts this analyte slightly better than PDMS-DVB due to the increased polarity of this analyte compared to the others in this slide. The advantage of the PA fiber for polar analytes is less with this analyte because it is not aromatic. PA still extracts this analyte well, but it does not show a large advantage as it did for some of the polar aromatic analytes. Bare fused silica, which extracted all of the large nonpolar analytes, had difficulty extracting the more polar dibutylnitrosamine.

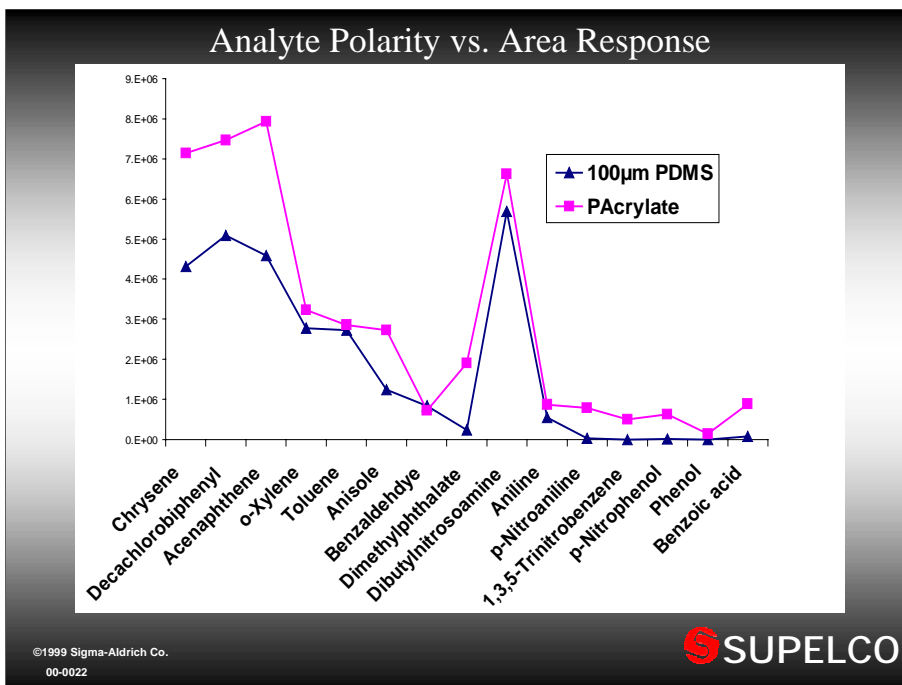


This slide shows some of the more polar analytes in the mix. The advantage of a polar fiber is obvious. For the more polar benzoic acid and aniline, the two polar fibers, polyacrylate and CW-DVB extract these analytes best.

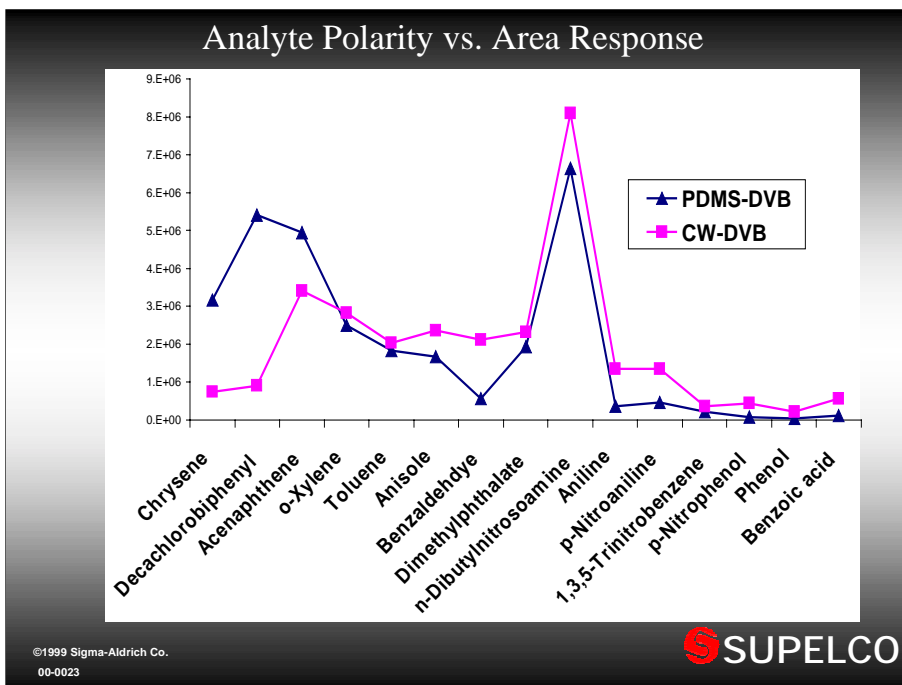
For the less polar dimethylphthalate, adsorbent type fibers extract much better than absorbent type fibers. Again the PA fiber, though an absorbent type fiber, extracts dimethylphthalate well because of its aromatic nature.



The most polar analytes in the group are best extracted with the polar fibers. Carbowax-DVB and PA coated fibers are best for the nitroaniline and nitrophenol. They are also well suited for the extraction of phenol and trinitrobenzene. Carboxen-PDMS is capable of retaining phenol while the DVB-Carboxen was good for extracting trinitrobenzene. As demonstrated with the smaller analytes PDMS-DVB has a fairly high affinity for nitrogen based analytes.



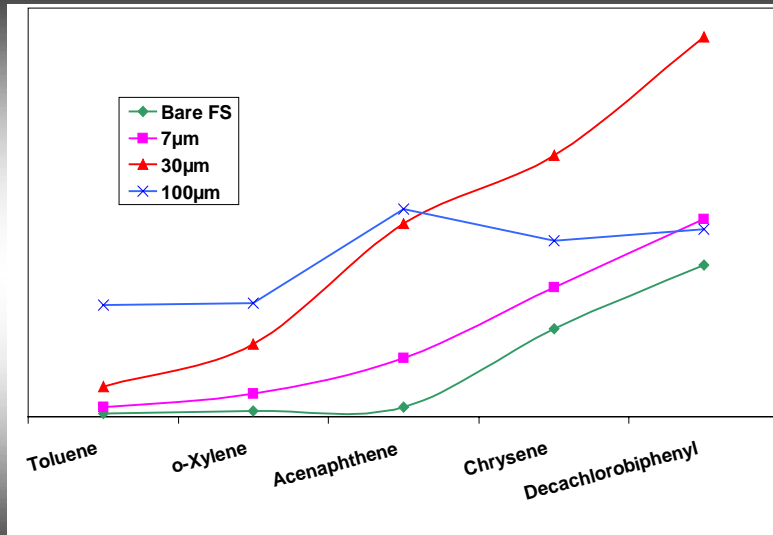
The next two slides show the effect of fiber polarity on the recovery of the analytes with this slide focusing of the absorbent type fibers. In this case, polarity increases from left to right. The more polar PA fiber extracts the more polar analytes from 1-2 orders of magnitude greater than the 100µm PDMS fiber. The advantage for using a polar fiber to extract polar analytes is significant for analytes with molecular weights greater than 90. Surprisingly the polyacrylate fiber even extracted the more nonpolar analytes better than the PDMS fiber. As stated previously, we have observed that the PA fiber appears to have some pi-pi interactions with aromatic rings.



This slide compares the analyte response and polarity obtained by extraction with 2 adsorbent type fibers. The less polar PDMS-DVB extracted the less polar analytes, shown on the left side, more efficiently than the polar CW-DVB fiber. But as the polarity of the analytes increased, the response of the analytes with the PDMS-DVB decreased with respect to the CW-DVB. The advantage the more polar CW-DVB coated fiber is significant. The improvement in response ranges from 2-10 times greater.

Unlike the 100µm PDMS, shown in the previous slide, the PDMS-DVB was capable of extracting the polar analytes at levels that were easily detected. This made the advantage of the CW fiber over the PDMS-DVB fiber less than the PA fiber over the PDMS fiber. If you compare the CW-DVB fiber to the PA fiber for the extraction of polar analytes, the responses were nearly the same.

Effects of Coating Thickness on Analyte Recovery



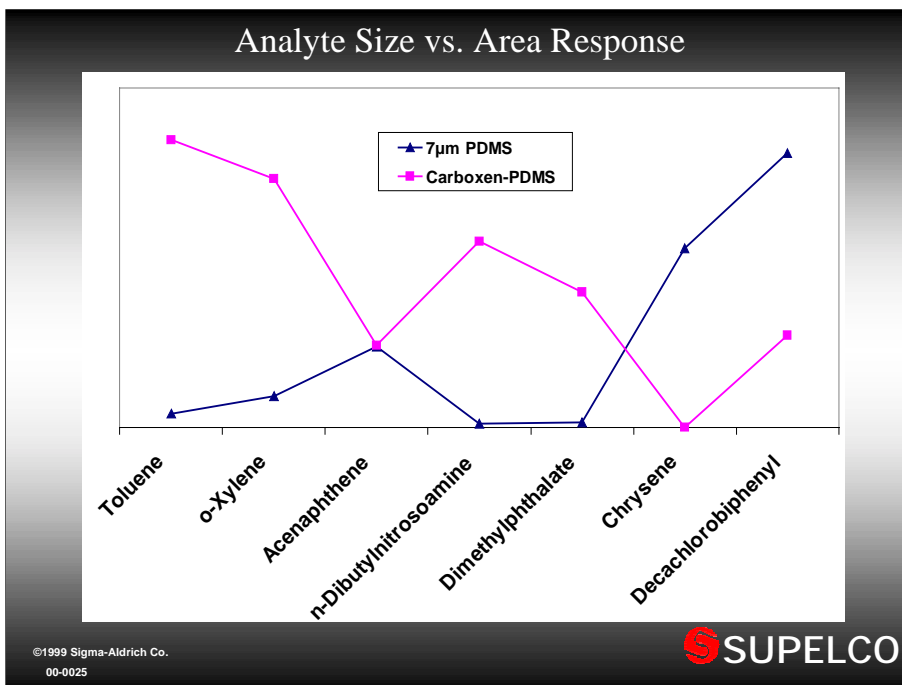
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This slide shows the effects of analyte size and fiber coating thickness using 3 PDMS fibers and bare fused silica. The molecular weights increase from left to right. The smaller analytes as expected are extracted best with the thicker coating. The results show that the response is directly proportional to the thickness of the fiber coating. The 100µm PDMS fiber extracts these analytes very well with respect to the others. However, the advantage of the thick film diminishes as the size of the analytes increase. The larger analytes such as chrysene and decachlorobiphenyl do not migrate quickly into this phase. For the response to increase, the extraction time would need to be increased.

Bare fused silica and the 7µm PDMS do not extract the smaller analytes well as expected. The interesting fact is that the bare fused silica lines and the 7µm PDMS lines run parallel with each other. This indicates that the same mechanism for retaining the analytes on the bare fused silica are also apparent with the 7µm PDMS. The coating did not impede the interaction with the silica.

The 30µm PDMS fiber is an excellent choice for extracting a wide molecular weight range if the analytes are nonpolar. It appears that the amount of analyte extracted is directly proportional to the size of the molecule. Even at a molecular weight 500, the response is linear. The smaller analytes are sufficiently extracted to provide a good response.



This slide shows the analyte response relative to their molecular weight with the Carboxen-PDMS fiber and the 7µm PDMS fiber. The Carboxen-PDMS fiber is the strongest fiber whereas the 7µm PDMS is the weakest coated fiber in terms of retention of analytes.

For the Carboxen coated fiber the amount of analyte extracted or detected decrease as the molecular weight increases. If one ignores the PAHs that are not desorbed well off the fiber, there is a fairly linear decrease in response as the size of the analyte increases.

Conversely, for the 7µm PDMS fiber the opposite is true. The amount of analyte detected increases as the size of the analyte increases. If one overlooks the more polar analytes dimethylphthalate and dibutylnitrosamine, that are not well extracted by this fiber, the increase in response is proportional to the molecular weight of the analyte.

Classical Adsorption Mechanism for a Uniform Surface

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

Langmuir's Isotherm

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

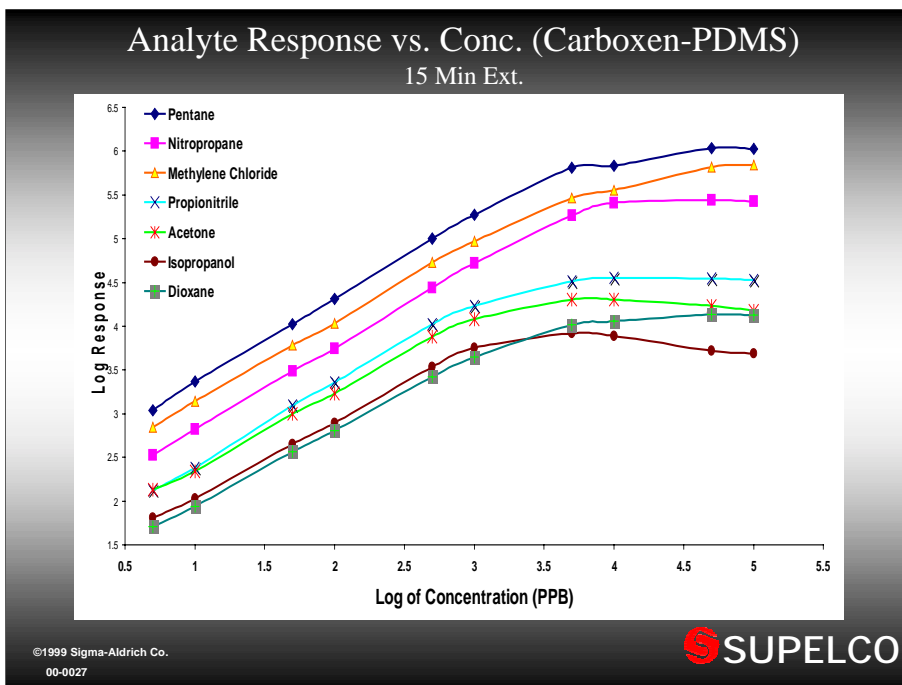
where $K = k_a/k_d$ k_a = rate of adsorption k_d = rate of desorption

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In the third study, our goal was to determine the capacity and linear range of the analytes. By monitoring the adsorption profiles of an analyte versus its concentration, the capacity of the fiber for that analyte can be determined. However, this becomes more complex when there is more than one analyte being extracted simultaneously.

For adsorbent type fibers, there are a limited number of sites or pores. Analytes may compete for the same site. This becomes a particular problem when the pores are uniform. According to Langmuir's Isotherm, when there is a uniform pore and under constant pressure conditions, the analyte with the highest distribution constant will displace the analyte with the lower constant. This theory only holds when you have a uniform pore. The Carboxen 1006 particles used in the fiber, are tapered and not uniform; whereas, the DVB contains primarily uniform pores. By increasing the concentration of a mixture of analytes, eventually the sites will become occupied. At this point no more sample will be adsorbed or displacement will occur. This study should be able to determine if Langmuir's Isotherm applies to the current SPME fiber coatings.



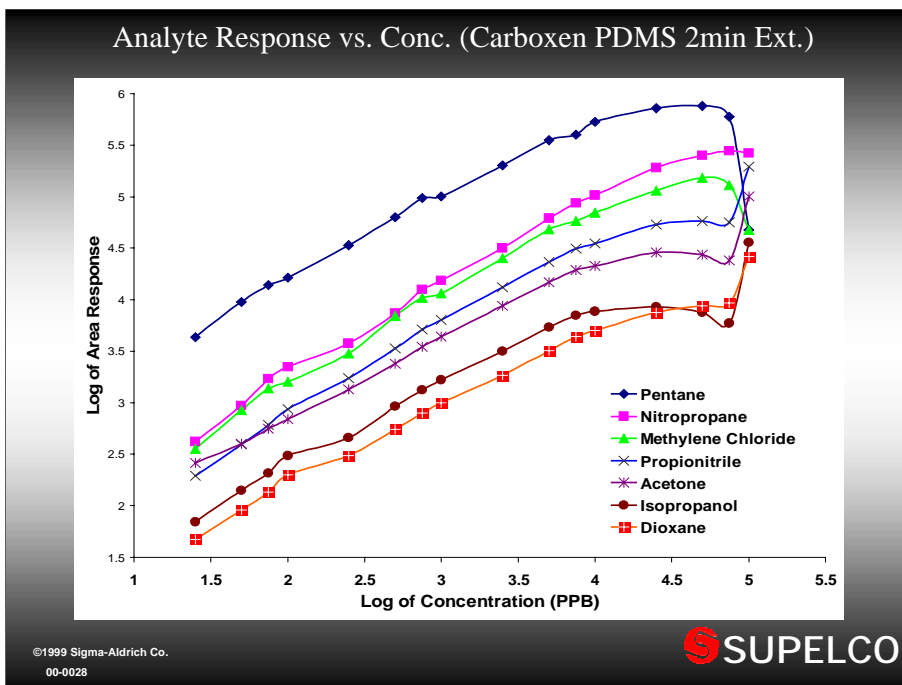
This slide shows the response of the 7 analytes versus concentration of the analytes from a 15 min. extraction using the Carboxen-PDMS coated fiber. The graph is plotted in log/log form, because it covers 6 orders of magnitude. The range in ppb is 5 ppb to 100,000 ppb or 100 ppm. On the log scale, the number 1 is equivalent to 10 ppb and the number 5 represents 100,000 ppb.

There are several interesting results from this study. All of the analytes in this mix could be extracted and quantified at 5 ppb with the Carboxen-PDMS fiber. This shows that this material maintains these analytes as previously shown.

The second point is that the plot was linear from 5ppb to 1000ppb. At higher concentrations the response began to level off.

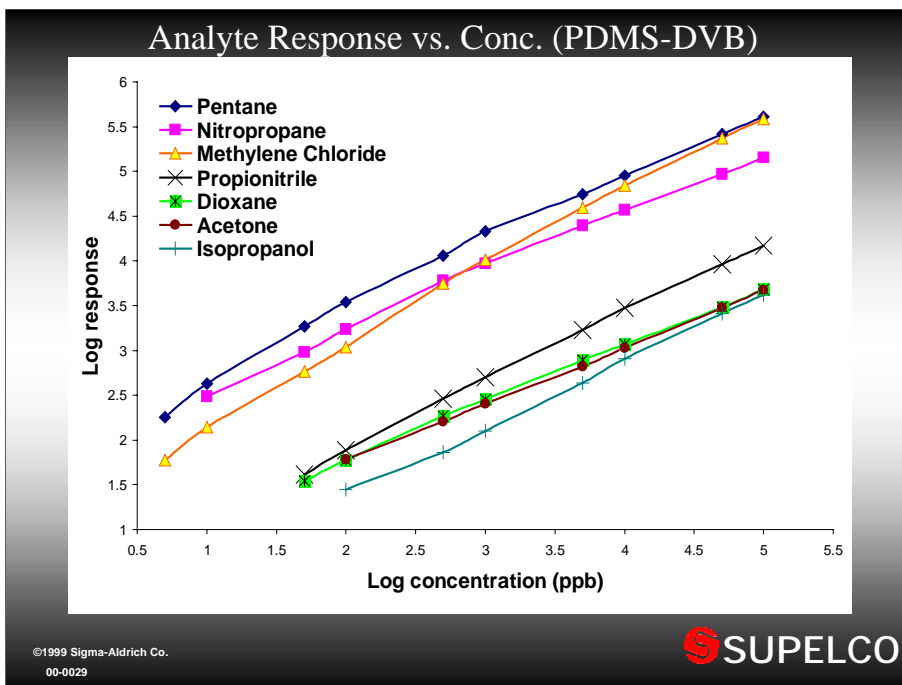
The third point is that there was only a slight displacement of isopropanol as indicated by its response decreasing as the concentration increased. When the lines on the curves crossover each other, this usually indicates displacement. The lack of displacement was expected since the pores in Carboxen 1006 are not uniform.

The lower response may be more of a solubility issue than displacement. The high concentration of seven solvents in the water made isopropanol more soluble. Because of its high solubility, in water, it could be greatly affected by other solvents. It could be a combination, because if one analyte is being displaced by another analyte, the response for the displacing analyte should continue to rise. For the most part this is not the case, but there may be a slight indication that methylene chloride might be displacing isopropanol.



By reducing the extraction time to 2 min, the linear range for the Carboxen-PDMS could be extended to 25,000 ppb. However, the minimum quantitation limit was increased from 5 ppb to 25 ppb. Simply by reducing the extraction time, you reduce the amount of the analytes extracted.

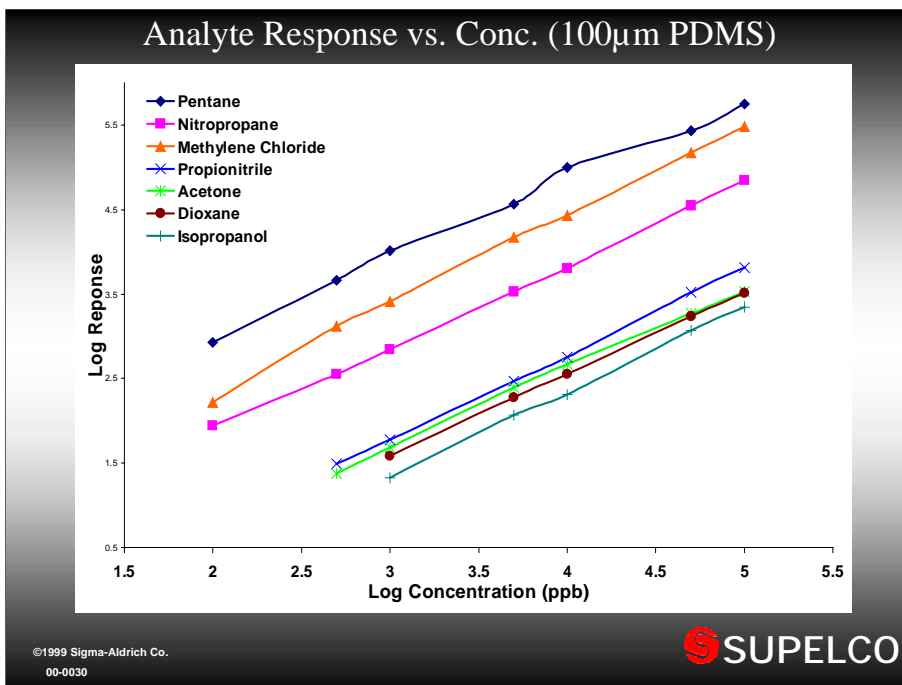
You will notice that the points for the analytes representing 100,000 ppb dramatically shifted. The response for the polar analyte sharply increased whereas the response for the nonpolar analytes dropped. This strange phenomenon was not expected and would only occur with improper sampling or handling. When the vial representing 100,000 ppb was checked, it was determined that the lid was not on as snugly as the others. Also it was the last vial in the tray to be analyzed. The nonpolar analytes, being less soluble in water evaporated. This reduced the co-solvating effects and thus the response for the polar analytes dramatically increased. One could also interpret the results by noting the nonpolar analytes were not occupying sites which enabled more of the polar analytes to be extracted. Either case could be correct.



When the analytes were extracted with the PDMS-DVB fiber for 15min, the curve appeared to be more linear than the Carboxen-PDMS fiber throughout the range. There was never a decreased response as the concentration increased, only the rate of increase was reduced for some analytes.

If you look at methylene chloride and propionitrile, these analytes were linear throughout the range, but if you look at acetone and isopropanol, you see the curves drop, relative to the curves for the other analytes encompassing them. This would mostly likely indicate that displacement is occurring, but it was not as obvious as expected. Because of the relatively uniform pore size in DVB, more displacement was expected; however, this result may indicate that there is a sufficient amount of non-uniform pores to reduce displacement.

The other factor observed with this fiber is that all of the lower detection limits were higher than the Carboxen coated fibers and that the limits were dependent upon the polarity of the analyte. For the less polar analytes the minimum quantitation limit was 5 ppb, but for the polar analytes the minimum quantitation limit was 50-100 ppb.



As expected the absorbent type 100 μ m PDMS fiber was linear at high analyte concentrations; however the minimum quantitation limits were quite high ranging from 100 ppb for the nonpolar analytes to 1000ppb for the most polar analytes. There is no displacement observed with this fiber. Most of the curves are quite parallel. Only acetone showed a slight decrease in the linear rate at the higher concentration levels. The correlation coefficients for all of the analytes had R values of three 9's or better. This demonstrated the ability of the absorbent type fibers to extract analytes at high concentrations and not be concerned about displacement.

The various slides show that selecting a fiber is based on the concentration range and the detection limits that the analyst needs. There is no need to use an adsorbent type fiber for extraction of analytes at high concentration levels. However, if trace detection limits are needed, the adsorbent type of fibers are better.

Conclusions

- **Carboxen-PDMS is best for extracting small analytes (MW<90)**
- **Adsorbent and absorbent fibers are suitable for larger analytes**
- **Fiber polarity has little effect on the extraction of small analytes**
- **Fiber polarity influences the extraction of larger analytes**
- **Carboxen-PDMS has good linearity at trace analyte concentration levels but saturates at high levels with little displacement**
- **PDMS-DVB has good linearity at low levels but exhibits displacement at higher levels**
- **Absorbent fibers yield higher MDLs,**
- **Absorbent fibers have greater capacity and wider linear range**

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Based on these three studies, the following conclusions can be made. The Carboxen-PDMS coated fibers are the best for extracting small analytes at trace levels. But with larger analytes the advantages of the other fibers exceed those for the Carboxen-PDMS fiber.

Fiber polarity has little effect on the extraction of small polar analytes, but fiber polarity has a great effect on the extraction of larger, polar analytes. The PA fiber and the CW-DVB were suitable for extraction of both polar and nonpolar larger sized analytes.

The Carboxen-PDMS fiber can be easily saturated, but displacement is not common. The DVB containing fibers can also be saturated, with some displacement. The absorbent type fibers show no displacement and are linear at high concentrations, but their minimum detection limits are much higher.

The overall summary is that analyte size, concentration levels, and detection limits must all be taken into consideration when selecting fibers. There is not going to be one fiber that will do all the analytes at trace levels to high concentrations, but this presentation should help you pick the best fiber for your particular application need.