

Choosing the Right Adsorbent for your Thermal Desorption Gas Chromatography Applications

Separation Science Webinar
October 22, 2013
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sigma-aldrich.com/analytical

Topics Discussed:

Adsorbents

- Single-Bed & Multi-Bed Tubes
- Characteristics
 - Mesh Size
 - Surface Area
 - Temperature Limits

Sampling Conditions

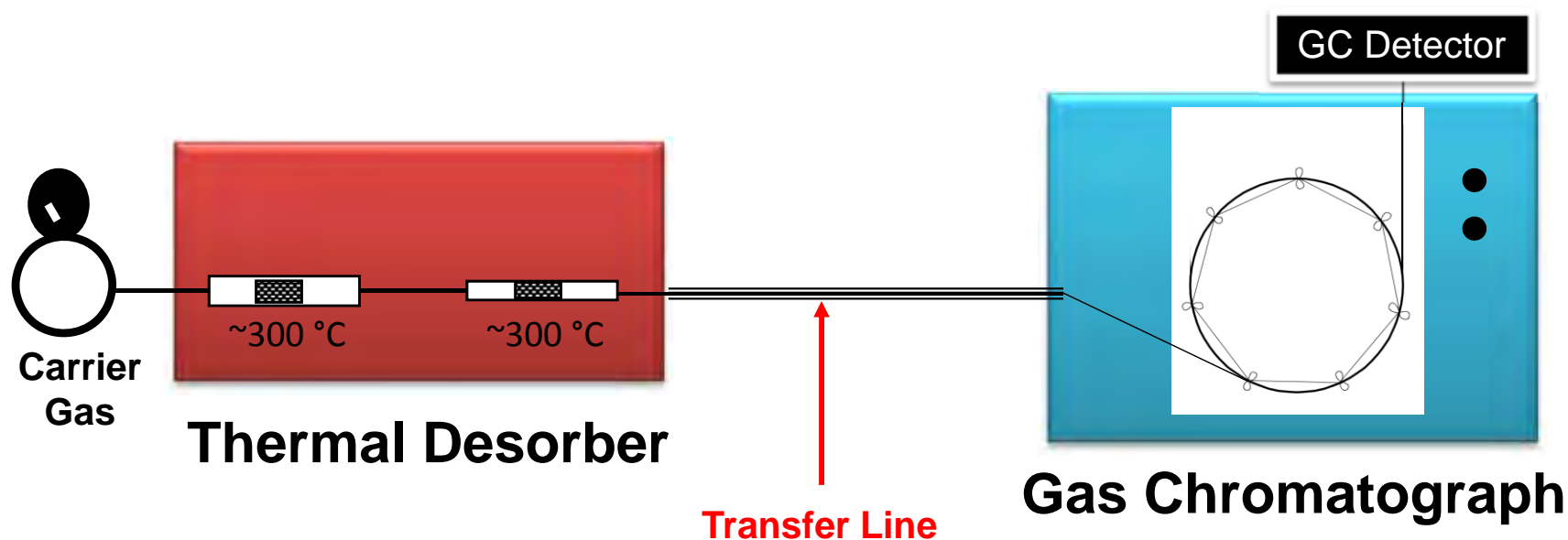
- Flow Rate & Linear Velocity
- Sample Volume
- Back Pressure
- Humidity



What is Thermal Desorption?

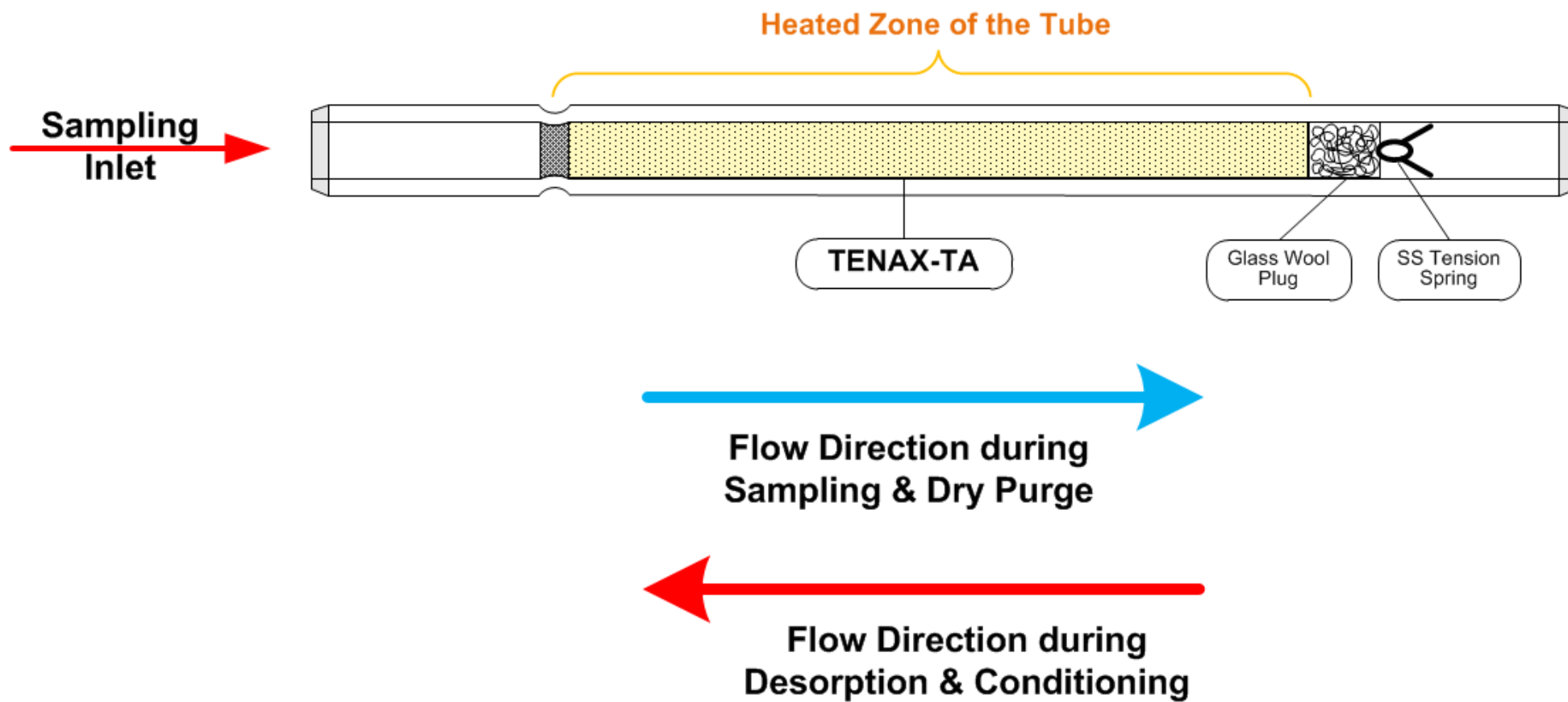
A sample preparation technique for gas chromatography.

- The sample is collected onto an adsorbent packed glass or stainless steel tube. *The sample is concentrated on the adsorbents.*
- The packed tube is heated (**Thermal**) and the compounds are released into the carrier gas (**Desorption**) where they are swept onto the GC column and analyzed by the gas chromatograph.



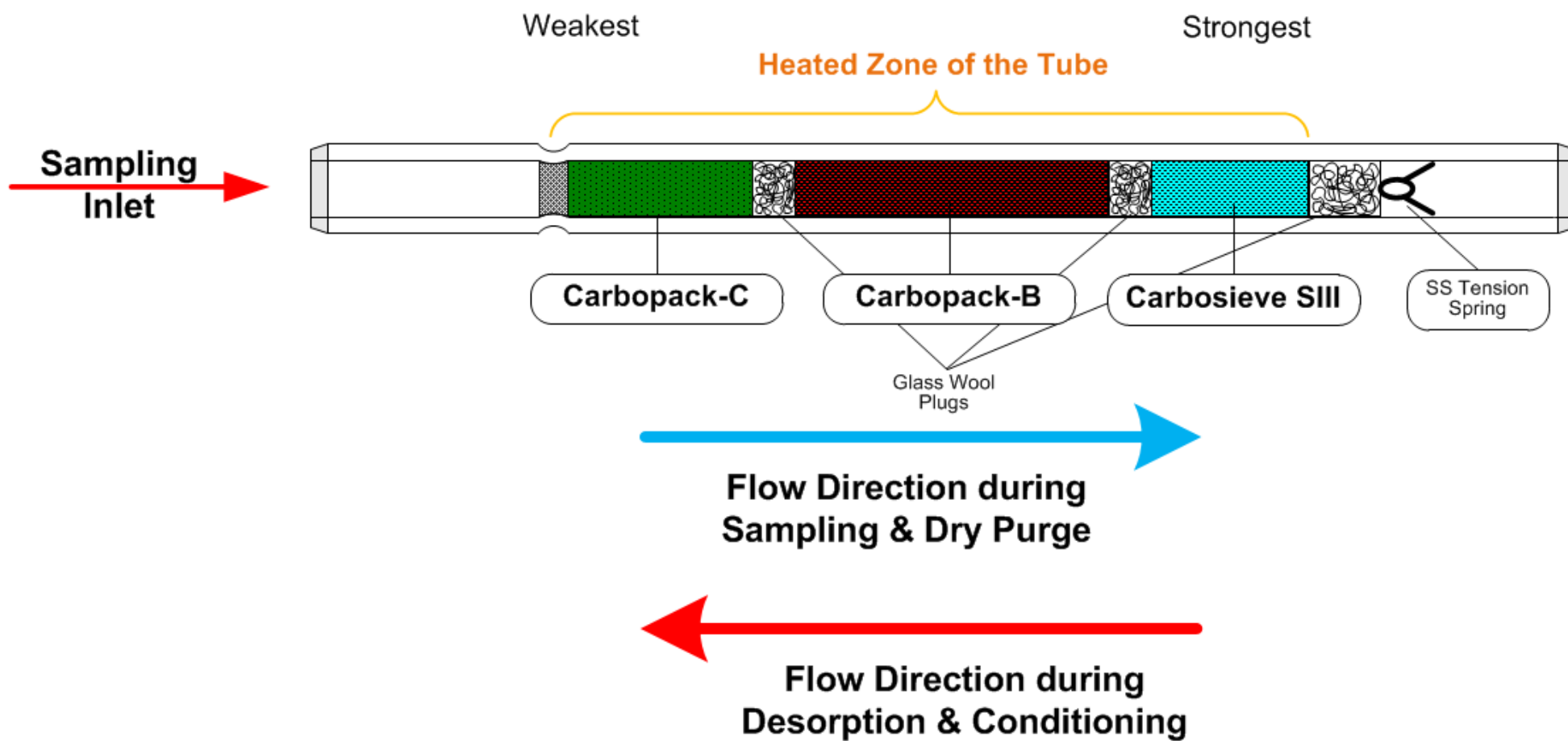
Single-Bed Thermal Desorption Tube

Single-Bed Tube (Tenax® TA)



Multi-Bed Thermal Desorption Tube

3-Bed Tube (Carbotrap® 300)



Glass vs. Stainless Steel Tubes

Glass

Advantages

- Glass can be more inert
- Can see the adsorbent(s)
- Glass frit in the inlet keeps the adsorbents in place

Disadvantages

- Tubes can break

Stainless Steel

Advantages

- Tubes will not break
- I.D. typically larger- allows higher flow rates

Disadvantages

- Cannot see the adsorbent(s)



Adsorbent Characteristics for Thermal Desorption

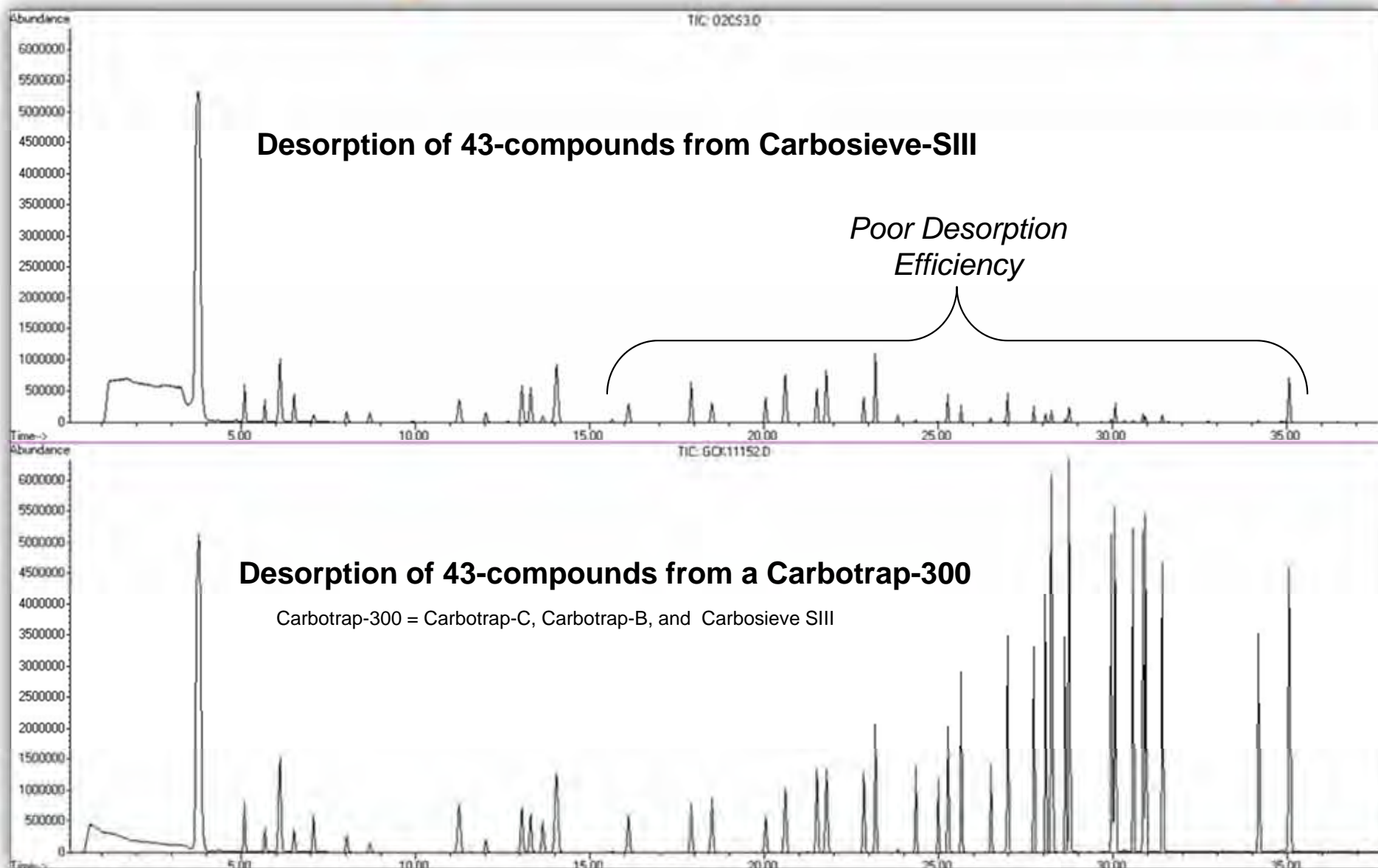
- Able to retain & release the compounds of interest
- Able to withstand high temperatures ~ 300°C
- Low background levels
- Low metal content
- Hydrophobic

Desirable

- Consistent mesh size
- Consistent density
- Low shrinkage
- Low amount of fines



Will the strongest adsorbent work for everything?



Terms Defined

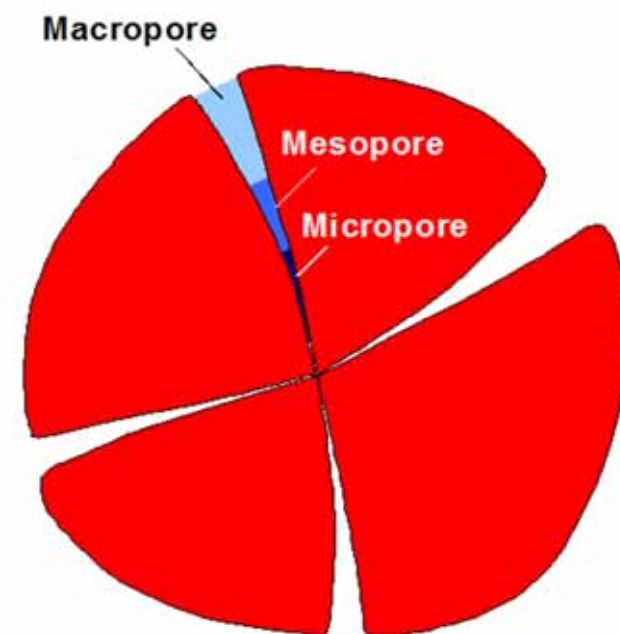
Surface Area:

- Surface Area provides a general idea of the adsorbent strength, but it doesn't provide the whole picture. Other characteristics such as: pore size, pore shape, and porosity can also play a role in the adsorbent's ability to retain and release different compounds.
- *General Rule: The higher the surface area value, the stronger the adsorbent. However when the surface area is $>800 \text{ m}^2/\text{g}$, the size and shape of the pore becomes more important.*

Terms Defined (cont.)

Pore Size:

- Macropores: > 50 nm diameter
- Mesopores: between 2 and 50 nm diameter
- Micropores: < 2 nm diameter



- **Molecules cannot access pores smaller than their size**

Adsorbent Types used in Thermal Desorption

Porous Polymers

Tenax®-TA

- The most popular adsorbent used in thermal desorption
- Maximum temperature: 350 °C
- Recommended desorption temp: 300 °C
- Recommended conditioning temp: 320 °C
- Methanol not retained (Good for spiking tubes with liquid calibration standards)

Typical Characteristics

- Granular - Tan in color
- Surface area: 35 m²/g
- Hydrophobic



Porous Polymers (cont.)

PoraPak™-N, Chromosorb®-106, HayeSep®-D

- Relatively low maximum temperatures: 225-290 °C
- Recommended desorption temp: 200 °C
- Recommended conditioning temp: 210 °C
- Typically has higher background levels than other adsorbents

Typical Characteristics

- Spherical - Light Yellow in color
- Surface area: 500 to 800 m²/g
- Hydrophobic



Graphitized Carbon Blacks

Carbotrap® and Carbopack™

- Maximum temperature: 400 °C
- Recommended desorption temp: 330 °C
- Recommended conditioning temp: 350 °C
- Methanol not retained by most of them

Typical Characteristics

- Granular - Flat Grey/Black in color
- Surface area: 5 to 240 m²/g
- Designed to retain and release mid to large molecular weight compounds
- Hydrophobic
- High Purity - Low Background



Adsorptive Strength of Graphitized Carbon Blacks



Carbopack F	5 m ² /g
Carbopack C	10 m ² /g
Carbopack Y	24 m ² /g
Carbopack B	100 m ² /g
Carbopack Z	220 m ² /g
Carbopack X	240 m ² /g

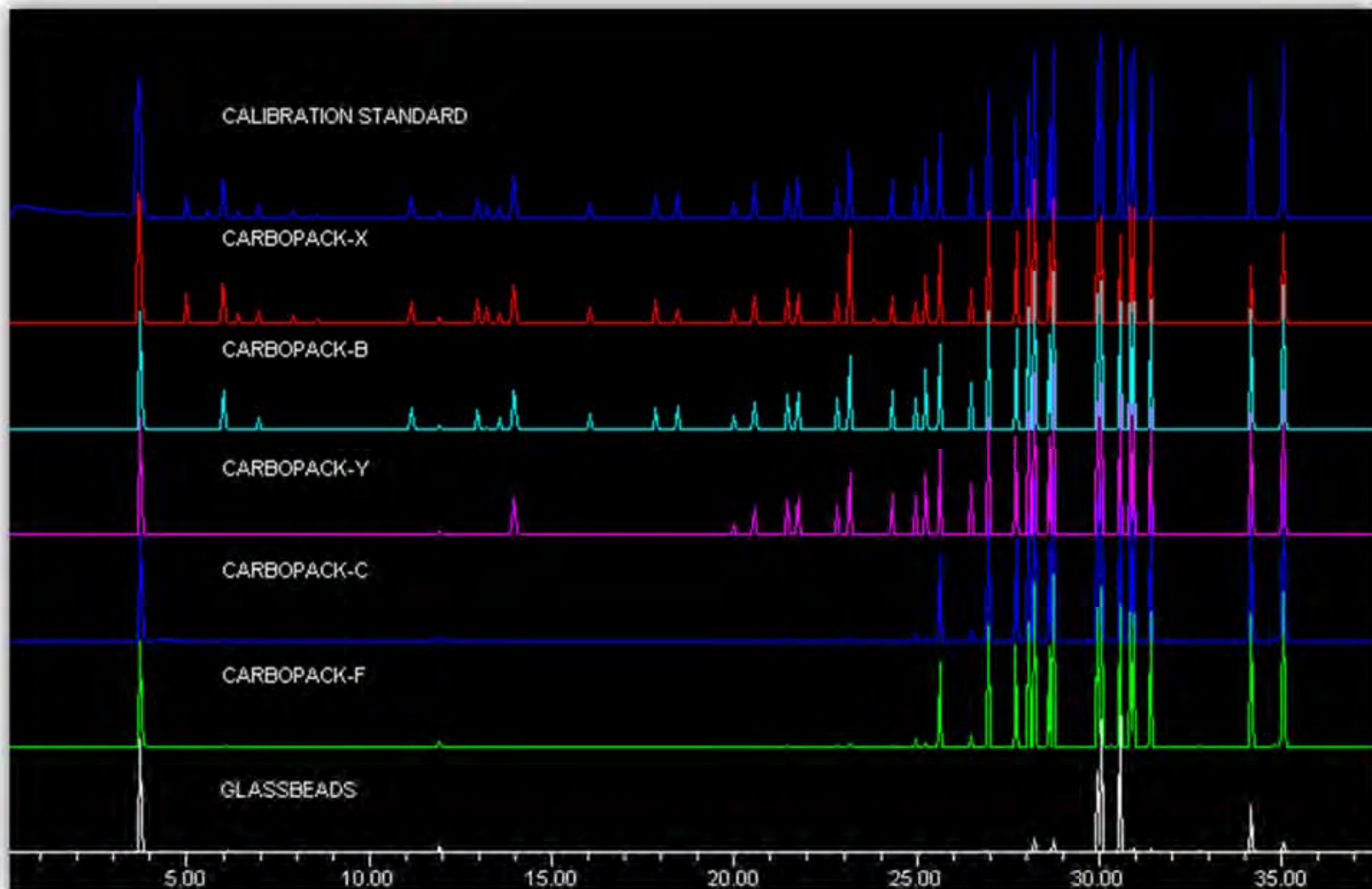
Relative Adsorption
Strength

Weakest



Strongest

Graphitized Carbon Blacks



Carbotrap vs. Carbopack – What is the Difference?

It's only the size of the adsorbent particles.

- Carbotrap = 20/40 mesh
- Carbopack = 40/60, 60/80, 80/100, and 100/120 mesh



Mesh Size	(mm)	Example	
20	0.850	●	Large
40	0.425	●	↓
60	0.250	●	
80	0.180	●	
100	0.150	●	
120	0.125	·	Small

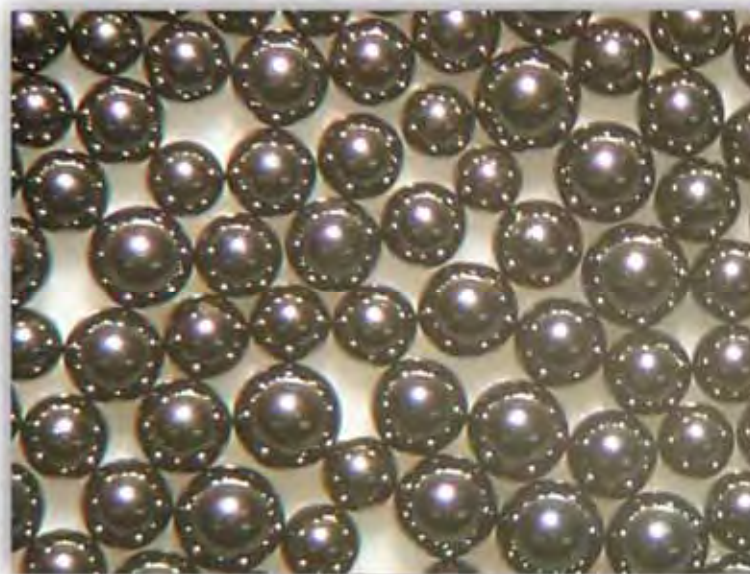
Carbon Molecular Sieves

Carbosieve® and Carboxen®

- Maximum temperature: 400 °C
- Recommended desorption temp: 330 °C
- Recommended conditioning temp: 350 °C
- Methanol is retained

Typical Characteristics

- Spherical (*Carbosieve-G is granular)
- Shiny/Dull Black in color
- High surface area 400 to 1500 m²/g
- Designed to retain and release small molecular weight compounds



Adsorptive Strength of Carbon Molecular Sieves



- Carboxen-1016 (75 m²/g)
- Carbosieve-G (1160 m²/g)
- Carboxen-1012 (1500 m²/g)
- Carboxen-564 (400 m²/g)
- Carboxen-1000 (1200 m²/g)
- Carboxen-1001 (500 m²/g)
- Carboxen-569 (485 m²/g)
- Carboxen-1003 (1000 m²/g)
- Carboxen-1018 (675 m²/g)
- Carbosieve-SIII (975 m²/g)
- Carboxen-1021 (1160 m²/g)

Relative Adsorption
Strength

Weakest



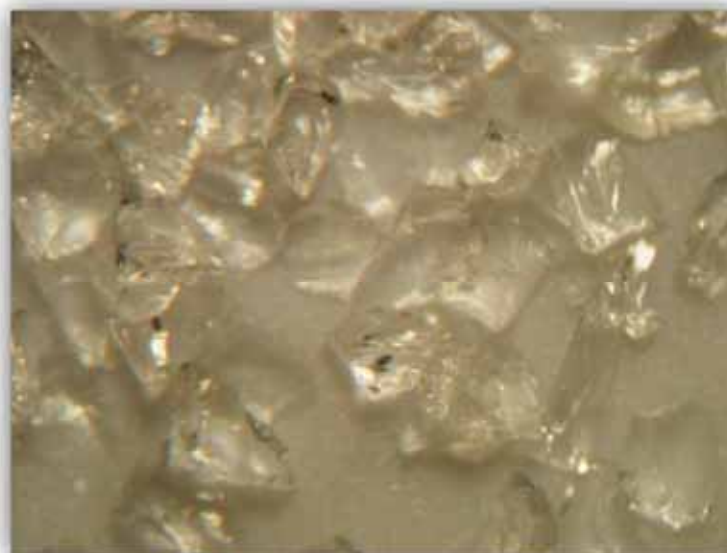
Strongest

Other Adsorbents

Glass Beads 5 m²/g ("good pre-filter")

Rarely used for Thermal Desorption

- Petroleum Charcoal
- Coconut Charcoal
- Silica Gel
- Molecular Sieves (Zeolites)



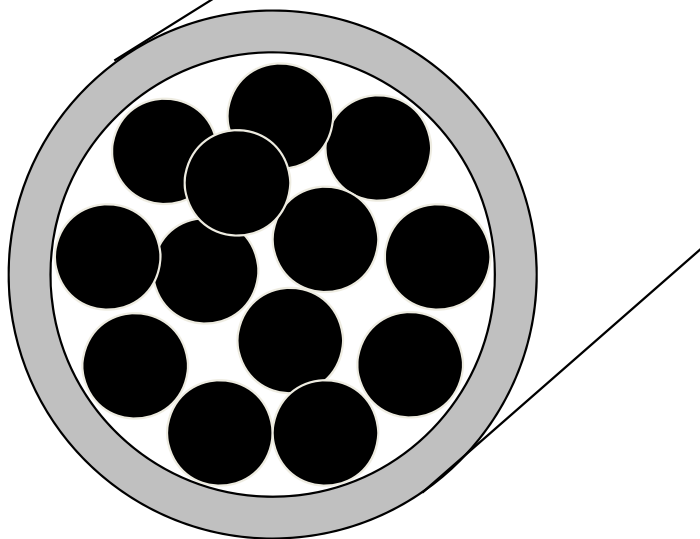
Adsorbent Mesh Size

Does Adsorbent Mesh Size Matter ?

Mesh Size vs. the Tube Inside Diameter

Poor

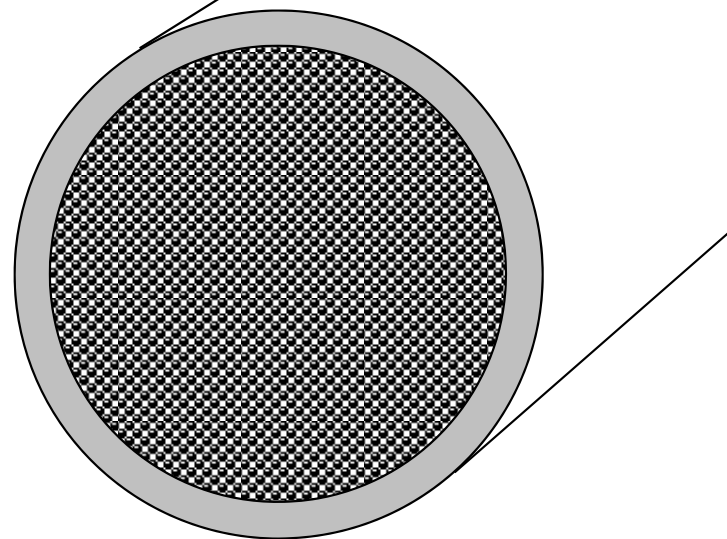
Compounds can travel around the adsorbent



Adsorbent particles are **too large** for this diameter of tube.

Good

Compounds interact with adsorbent



Adsorbent particles are packed in the tube **uniformly**.

What Mesh Size to Use?

Ratio of the Adsorbent Particle Diameter to the Tube Internal Diameter

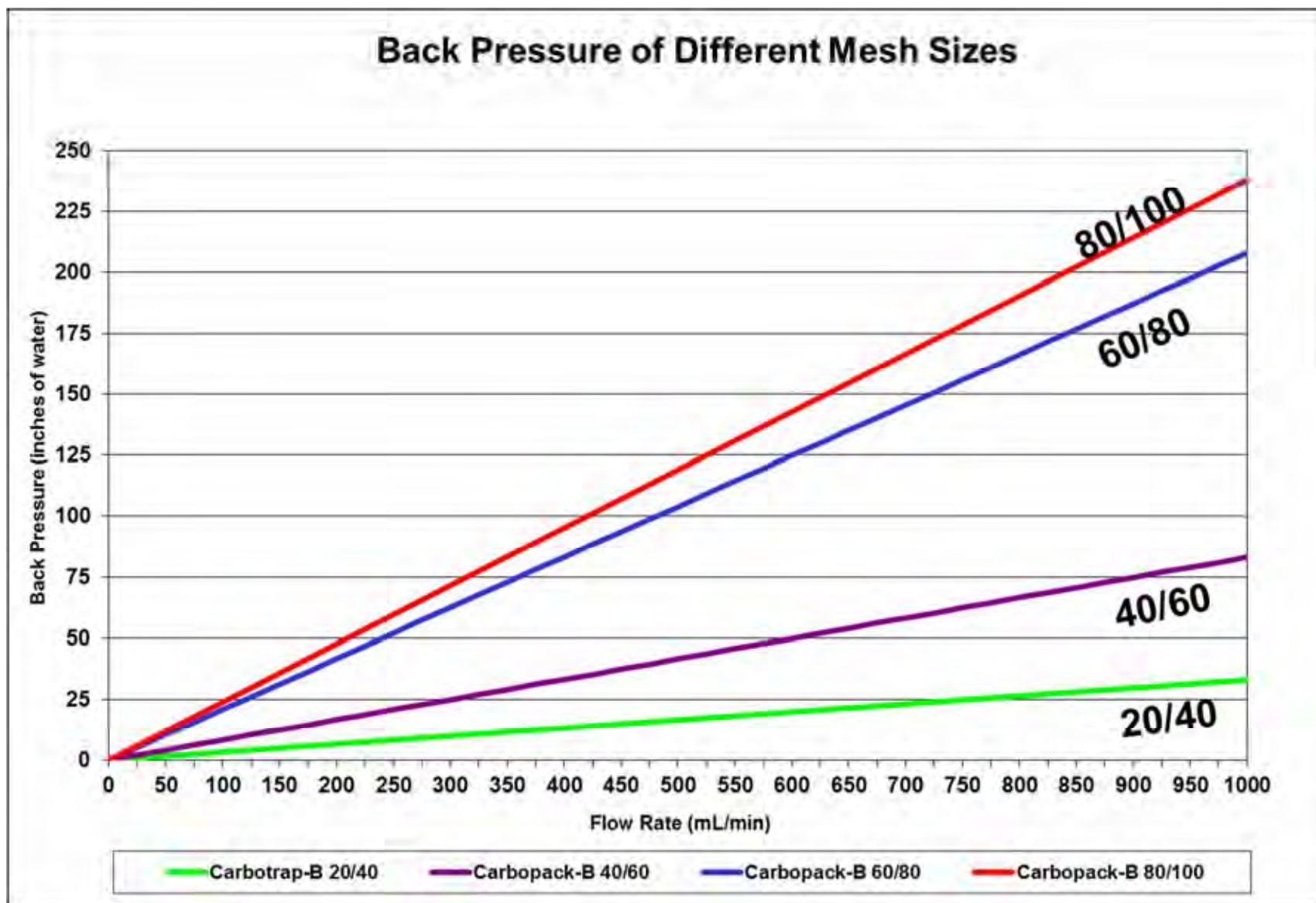
- Best ratio is between 0.10 to 0.25

	Tube ID			
Mesh Size	1 mm	2 mm	4 mm	5 mm
10	2.00	1.00	0.50	0.40
20	0.85	0.43	0.21	0.17
40	0.43	0.21	0.11	0.09
60	0.25	0.13	0.06	0.05
80	0.18	0.09	0.05	0.04
100	0.15	0.08	0.04	0.03

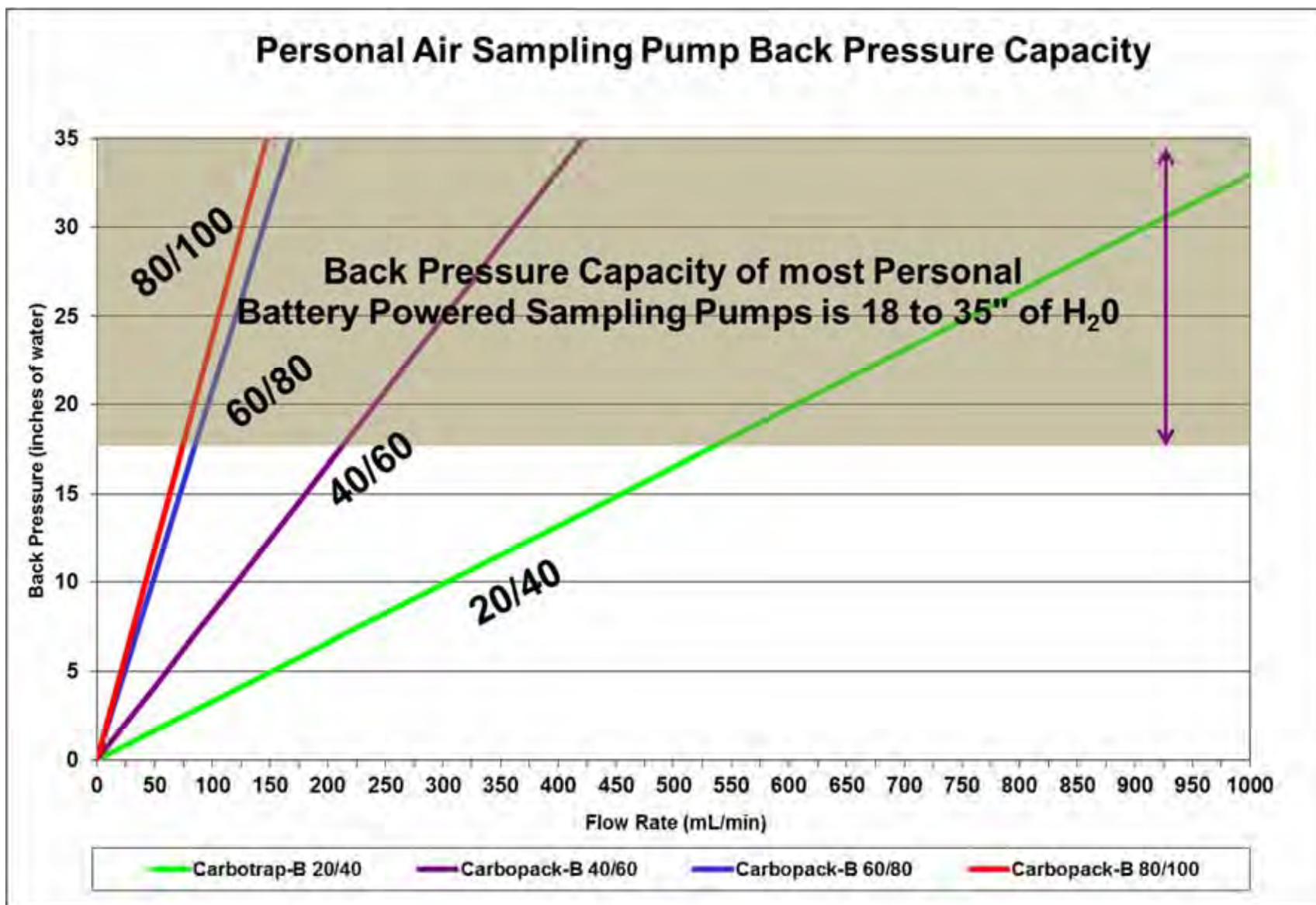
$$\text{Ratio} = \frac{\text{Particle Size (mm)}}{\text{Tube I.D. (mm)}}$$

Mesh Size is too large >0.26 - Channeling may occur
Mesh Size is within range >0.10 <0.25 - Optimum Ratio
Mesh Size is smaller than required <0.10 - Excessive back pressure

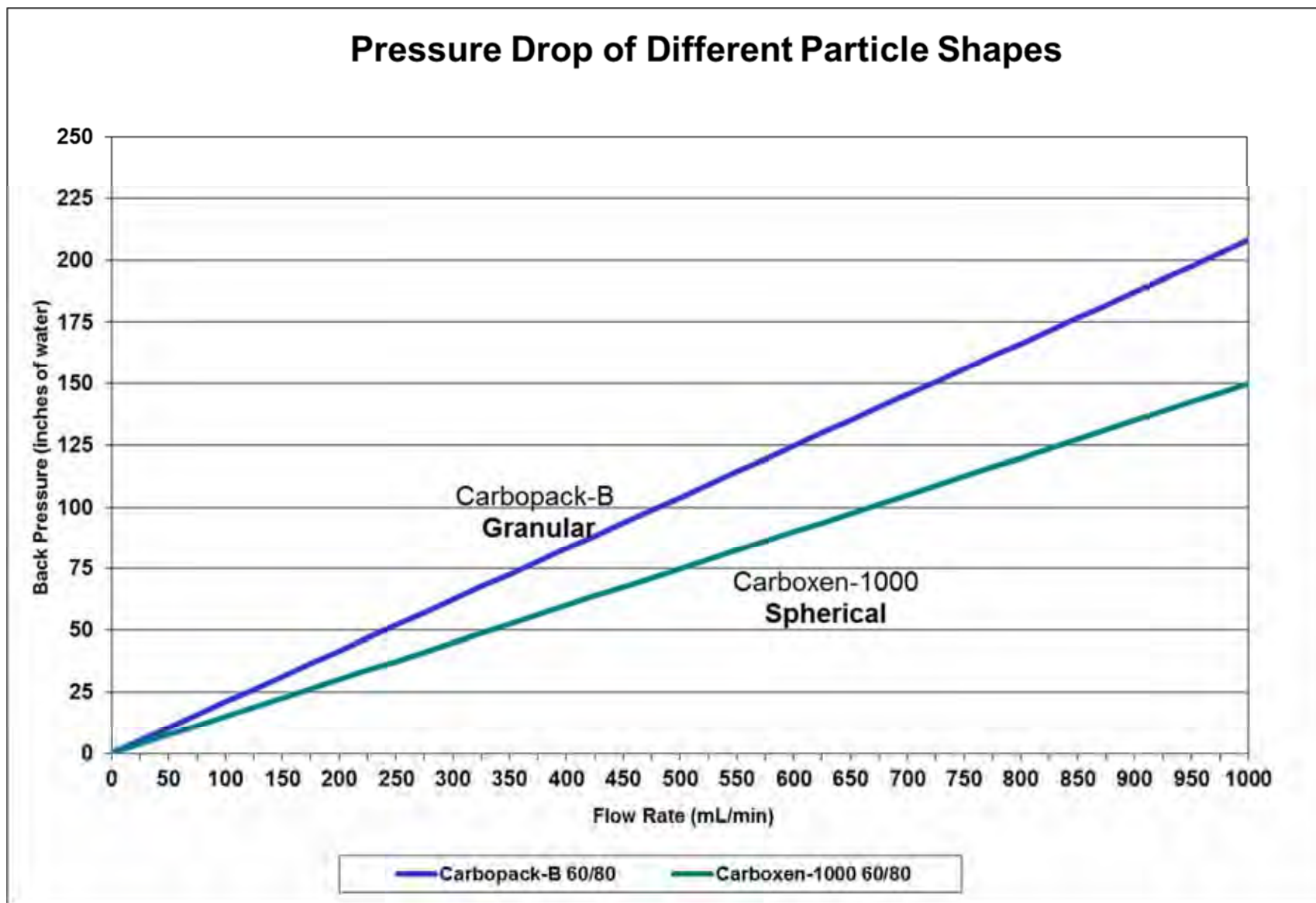
Mesh Size - How it affects Back Pressure



Mesh Size - Air Sampling Pump Capacity



Shape of the Adsorbent Particle



Flow Rate and Sample Volume

Linear Velocity

The speed at which the molecules pass through the adsorbent:

Velocity	TUBE ID				
	1 mm	2 mm	3 mm	4 mm	5 mm
@ 10 cm/sec	2 mL/min	8 mL/min	17 mL/min	30 mL/min	47 mL/min
@ 20 cm/sec	4 mL/min	15 mL/min	34 mL/min	60 mL/min	94 mL/min

Too Fast - Molecules don't have enough time to interact

Too Slow - Risk of Back-Diffusion

$$F_c = \pi(r^2)(u)(\epsilon)(60)$$

F_c = tube flow rate (mL/min)

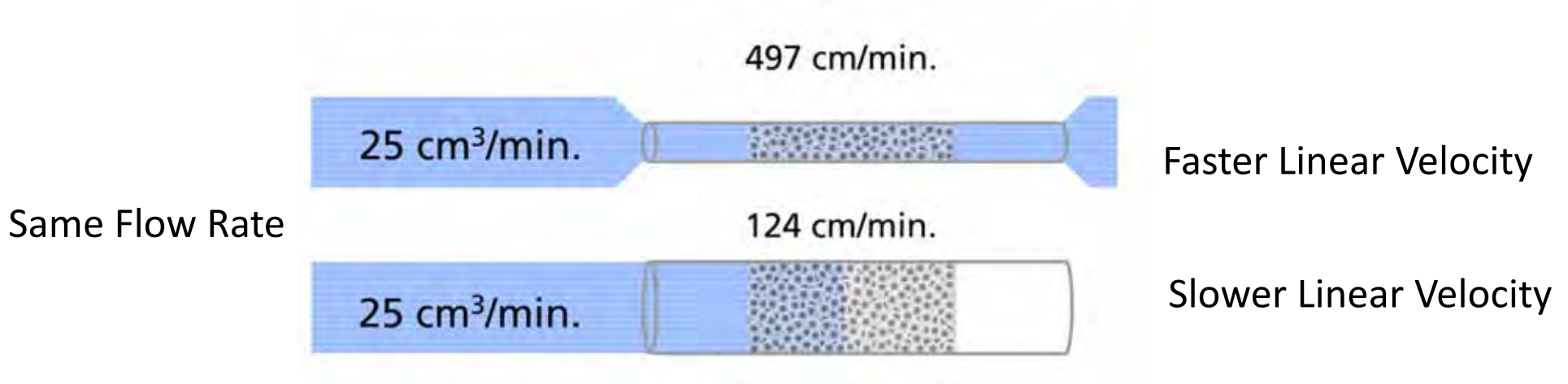
r = tube radius (cm)

u = linear velocity (cm/sec)

E = interparticle porosity of the adsorbent packed in the tube. For typical sampling tubes the value of *E* = 0.4

Linear Velocity (cont.)

Linear Velocity is different depending on Tube I.D.



When the tube I.D. gets smaller, the linear velocity (speed) will be faster at the same volumetric flow rate.

Sampling Flow Rates (Good Starting Point)

Typically range is between 10 and 250 mL/min.

- A good starting flow rate is 50 mL/min.



Collection (Sample) Volume

Recommended Sample Volumes:

Single Bed Tubes with Hydrophobic Adsorbents

- 1 - 10 Liters

Multi-Bed Tubes with Carbon Molecular Sieves

- 1 - 5 Liters

Multi-Bed Tubes with Hydrophilic Adsorbents

- 0.5 - 1 Liters



$$\text{Sample Flow Rate} \times \text{Sampling Time} = \text{Sampling Volume}$$

Humidity

Humidity Problems

Problems During Sampling:

- Water vapor can be retained by the adsorbent.
- Can mask the available sites of the adsorbent.
- Can in (some cases) displace the compounds.



Problems During Analysis:

- Water vapor can alter split flow ratios during desorption.
- Can create chromatographic separation issues.
- Can blow out the FID flame.
- Reduces the vacuum of an MS detector.

How much water is in the air ?



Absolute Humidity (mg/L)

Air Temp (°C)	% Relative Humidity										Air Temp (°F)
	10%	20%	30%	40%	50%	60%	70%	80%	90%	100%	
40°	5	10	15	20	26	31	36	41	46	51	104°
35°	4	8	12	16	20	24	28	31	36	40	95°
30°	3	6	9	12	15	18	21	24	27	30	86°
25°	2	5	7	9	12	14	16	18	21	23	77°
20°	2	3	5	7	9	10	12	14	16	17	68°
15°	1	3	4	5	6	8	9	10	12	13	59°
10°	1	2	3	4	5	6	7	8	8	9	50°
5°	1	1	2	3	3	4	5	5	6	7	41°
0°	0	1	1	2	2	3	3	4	4	5	32°

Figures are based an atmospheric pressure of 760mm Hg

Humidity



Silica gel is hydrophilic and will retain ~40% of its own weight in water. Why silica gel is not typically used for thermal desorption applications.

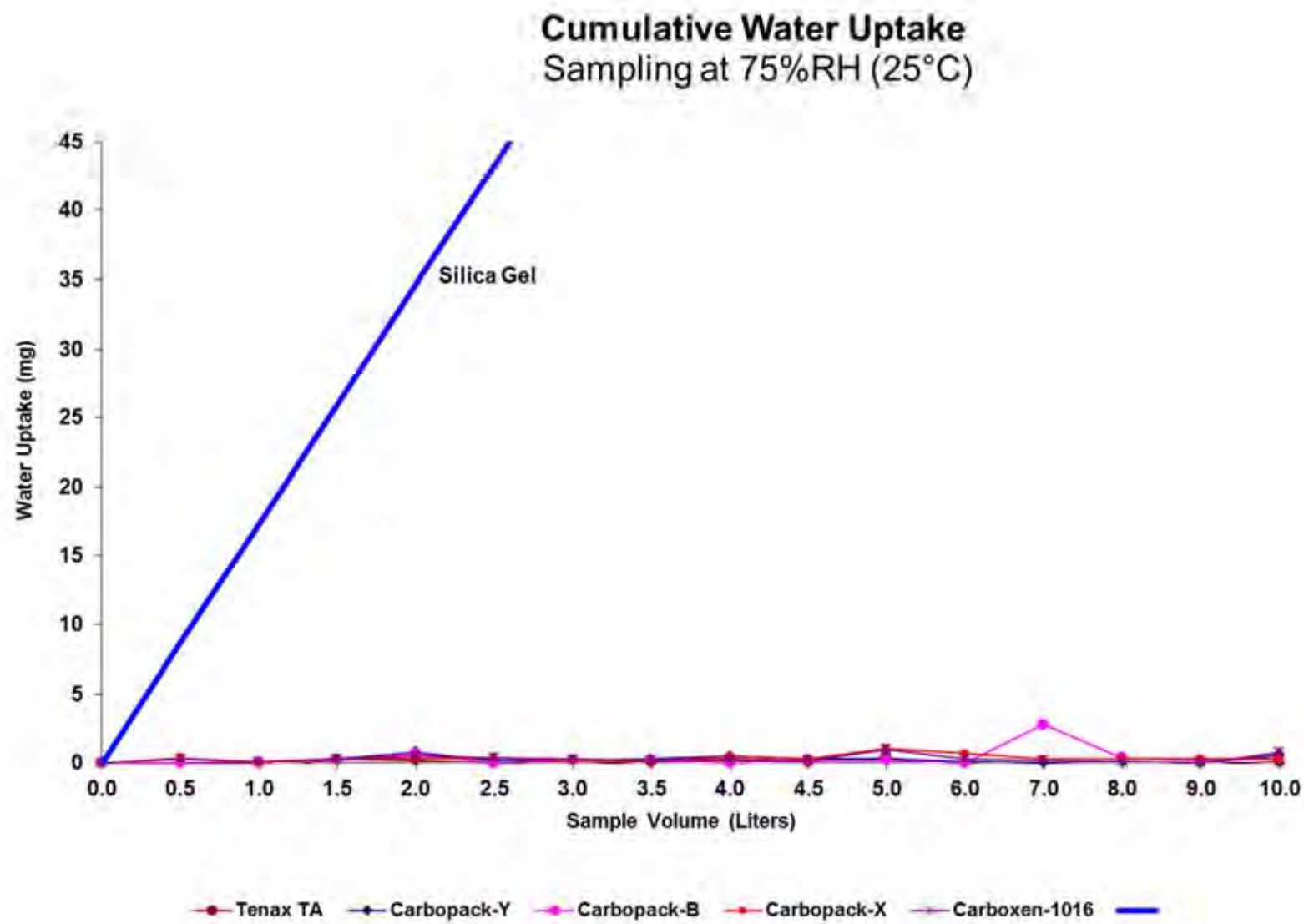
Some adsorbents are more hydrophobic than others.

Tenax, Carbopack, and Carbotrap are very hydrophobic and virtually no water will be retained on them while sampling in humid conditions.

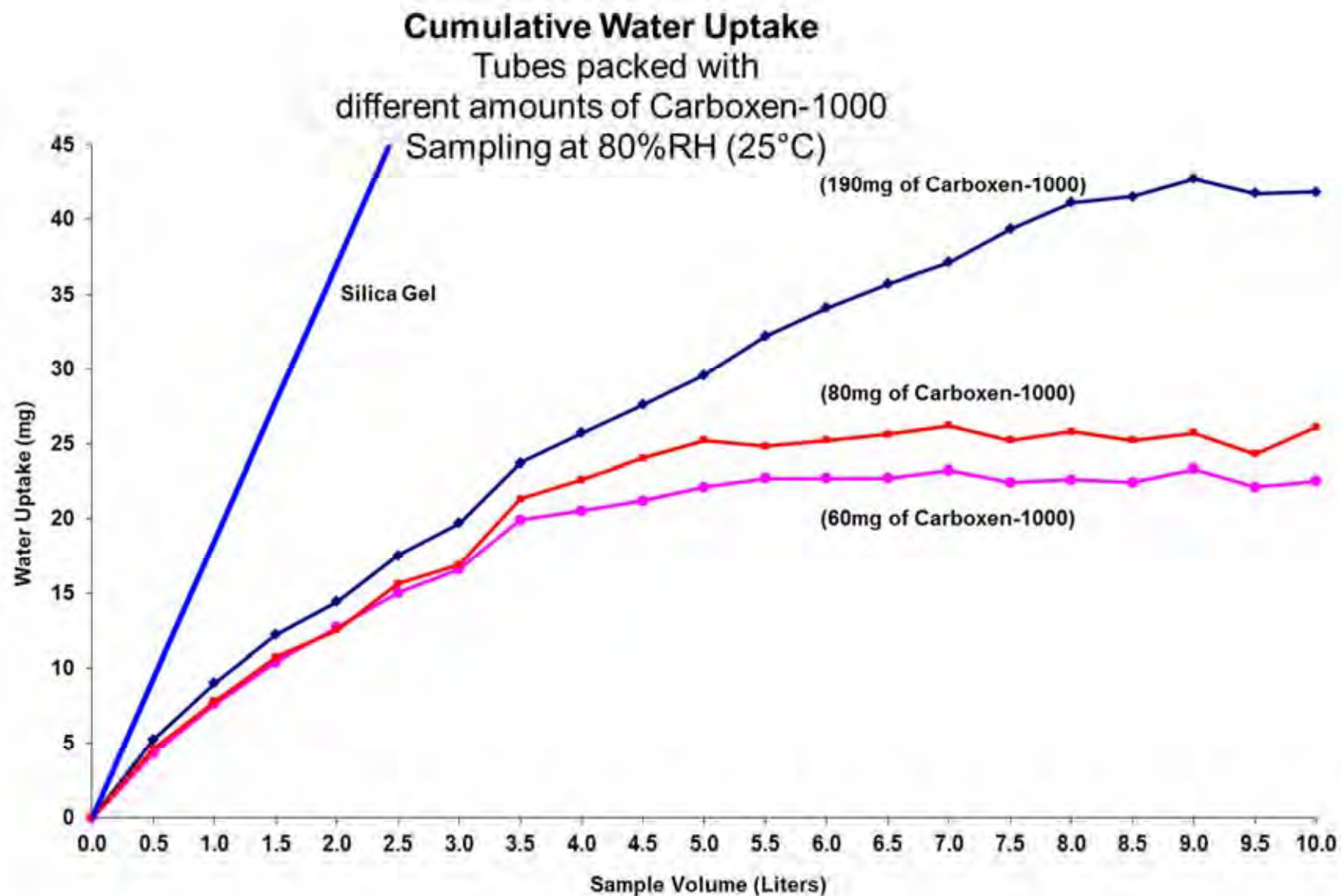
Carbon Molecular Sieves are still classified as hydrophobic.

At high humidity some water is retained, but the bond to the water is weak. It can be driven off at ambient temperatures using a dry purge prior to analysis.

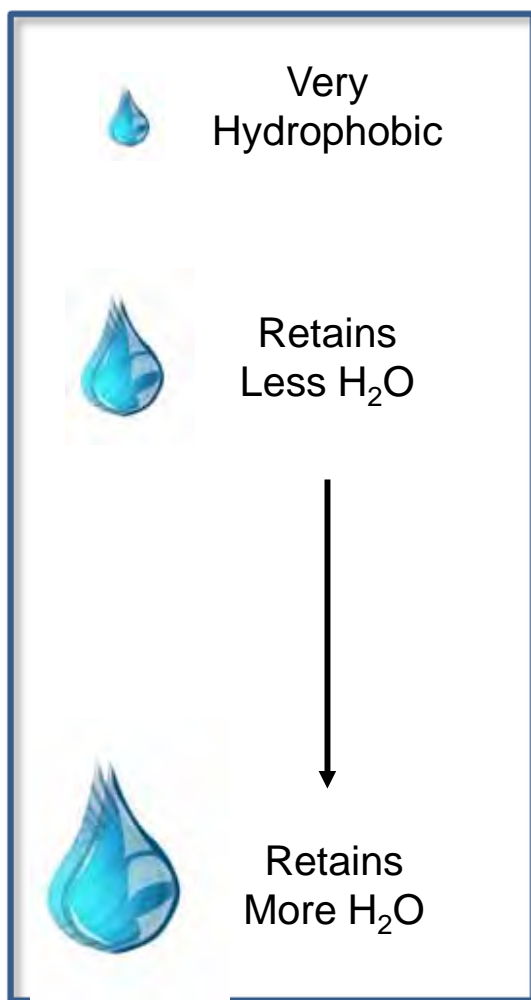
Water vapor retained by Carbo-pack(s) & Tenax-TA



Water vapor retained by Carboxen-1000



Relative Hydrophobicity



Glass Beads

Graphitized Carbon Blacks

Porous Polymers

Carboxen-1016

Carboxen-569,1001,1003

Carboxen-563

Carboxen-564

Carboxen-1000

Carboxen-1012

Carboxen-1018,1021, Carbosieve G & SIII

Silica Gel, Mole Sieve 5x, 13x

Dry Purging prior to Analysis

The key to dry purging is to allow enough (dry) gas to pass through the tube and carry the water away. But too much dry purge can actually start to push the compounds of interest through the adsorbent (i.e., breakthrough).

Recommended Dry Purge Volumes:

- Tenax and Carbotrap(s) typically only need 0.25 Liter, regardless of humidity level.
- Carbosieve and Carboxen(s) adsorbents may need 0.5 to 3 Liters, depending on absolute humidity level.

Practical way to determine the required dry purge volume

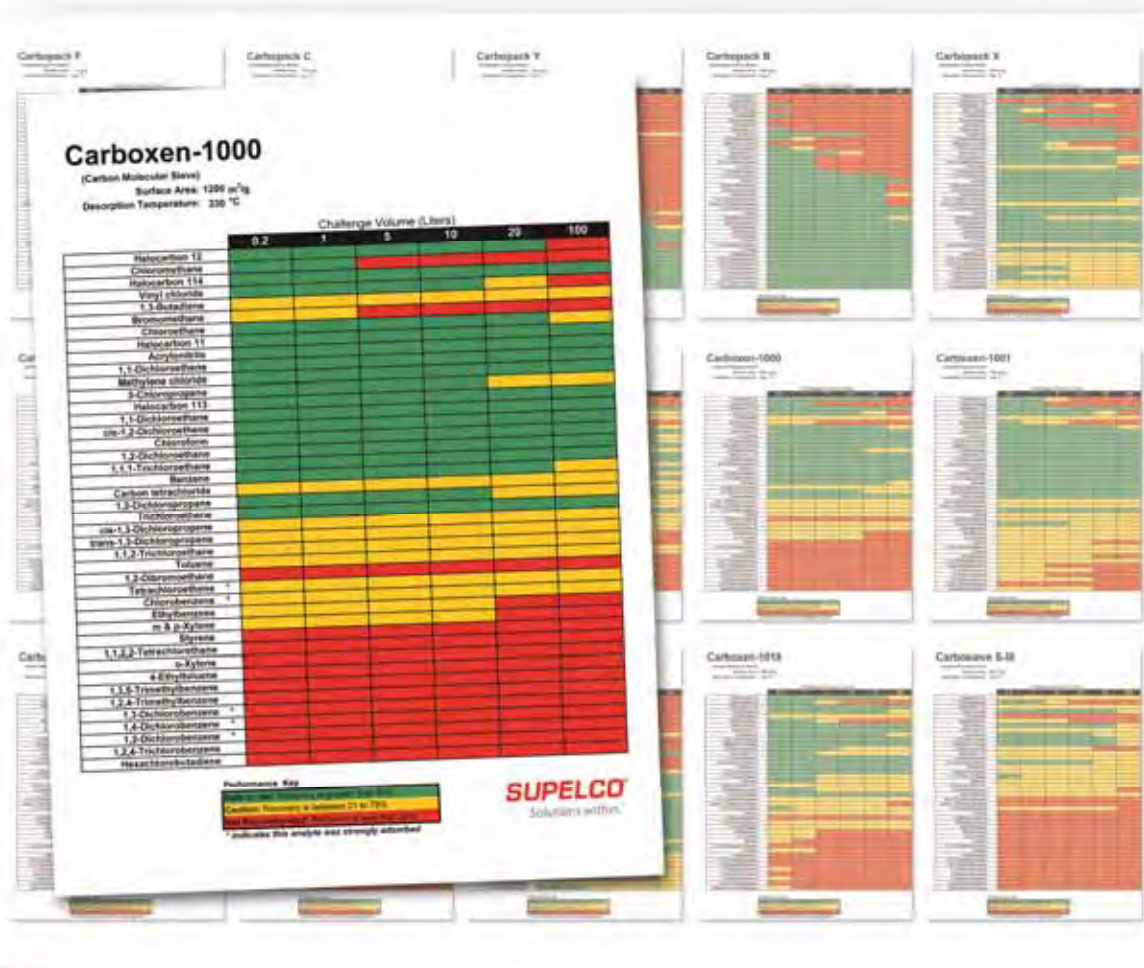
1. Before sampling, Weigh the adsorbent tube and record its tare weight.
2. After sampling, reweigh the tube. If the difference is greater than 1 mg - dry purge is required.
3. Purge the tube with clean nitrogen or helium at ~50 mL/min.
4. After 0.5 Liter has passed through, remove the tube, and reweigh the tube.
5. Repeat every 0.5 Liter until the tube weight is within 1 mg of its tare weight prior to sampling.

Most GC systems can handle < 1 mg (1 μ L) of water if the thermal desorber is splitting some of the sample.

Adsorbent / Thermal Desorption Literature (cont.)

"A Tool for Selecting an Adsorbent for Thermal Desorption"

www.sigmaaldrich.com/air-monitoring



Conclusions

There are three main types of adsorbents used in thermal desorption:

- Porous Polymers
- Graphitized Carbons
- Carbon Molecular Sieves

There are many factors to consider when choosing an adsorbent:

- Single Bed, or Multi-Bed Tubes
- Range of compounds to be sampled
- Sampling flow rate
- Sample volume
- Dry Purge volume

Trademarks

Carbotrap® , Carbopack™ , Carboxen® , Carbosieve® – Sigma Aldrich, USA

Chromosorb® - Imerys Minerals California, Inc. USA

HayeSep® - Hayes Separations, USA

PoraPak™ - Waters Associates, USA

Tenax® - Buchem B.V., Netherlands

Acknowledgments

William Betz - Associate Fellow R&D Scientist
Olga Shimelis - Principal R&D Scientist
Kristen Schultz - Air Monitoring Product Manager
Errol Fernandes - e-Business Product Manager
&
Separation Science



SUPELCO

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Q&A

Follow up questions on thermal desorption or air monitoring?

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