SUPELCO®
Solutions within.™

Choosing the Right Adsorbent for your Thermal Desorption Gas Chromatography Applications

AIHA Webinar
November 11, 2015
Jamie Brown
R&D Scientist

sigma-aldrich.com/analytical

SIGMA-ALDRICH®

Topics Discussed:

Adsorbents for Thermal Desorption

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

Active Sampling Conditions

- Flow Rate
- Sample Volume
- Back Pressure
- Humidity

Thermal Desorption For Industrial Hygiene

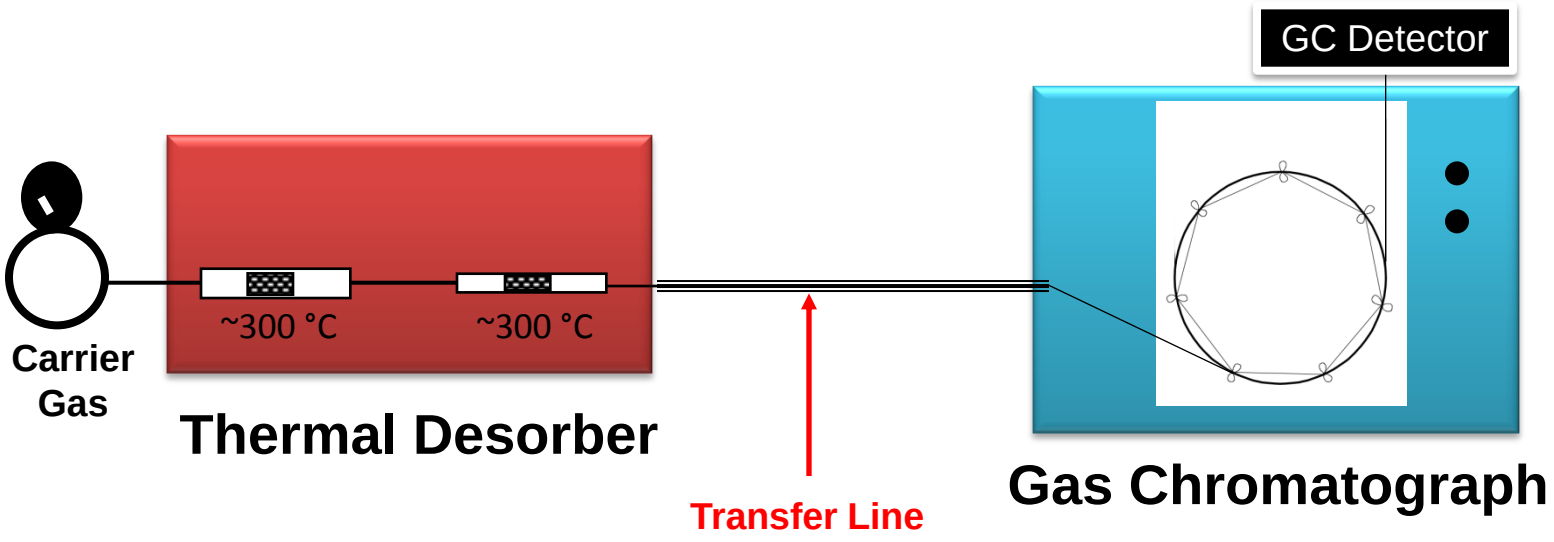
- Advantages of Using Thermal Desorption
- NIOSH 2549 “Thermal Desorption Screening Method”
- Overview of Passive Sampling Options

What is Thermal Desorption?

A sample preparation technique for gas chromatography.

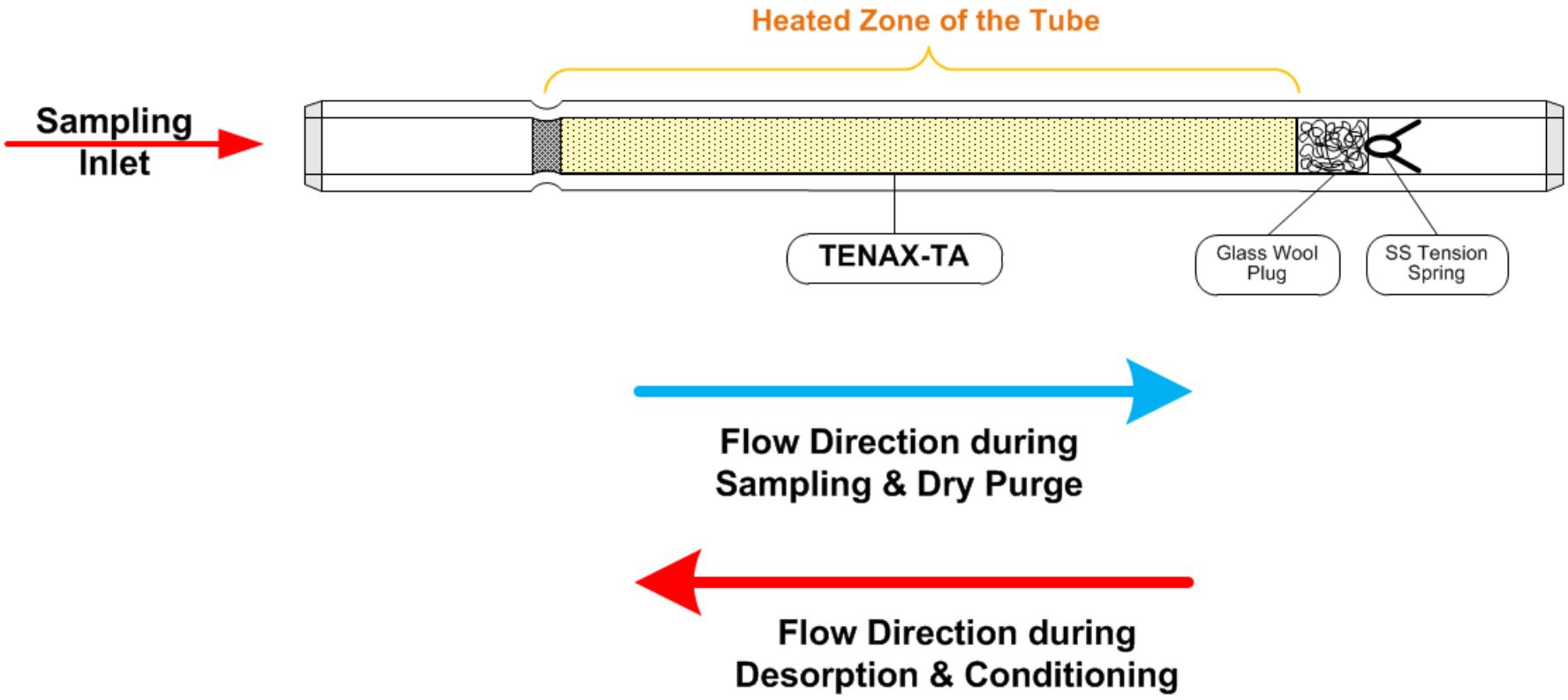
- The sample is collected onto an adsorbent packed glass or stainless steel tube. *The sample is concentrated on the adsorbents.*

- 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.



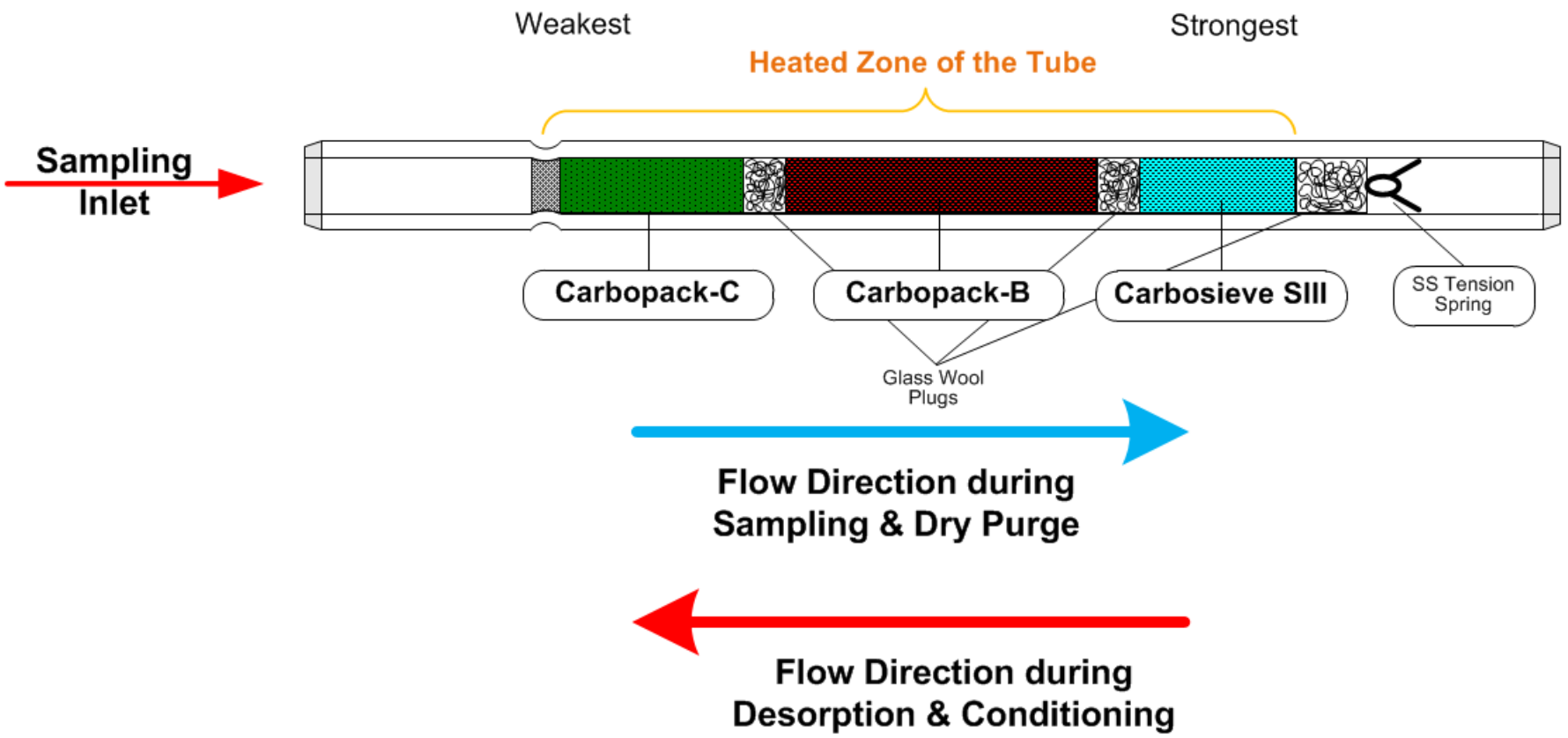
Single-Bed Thermal Desorption Tube

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
- Amendable to Passive Sampling

Disadvantages

- Cannot see the adsorbent(s)

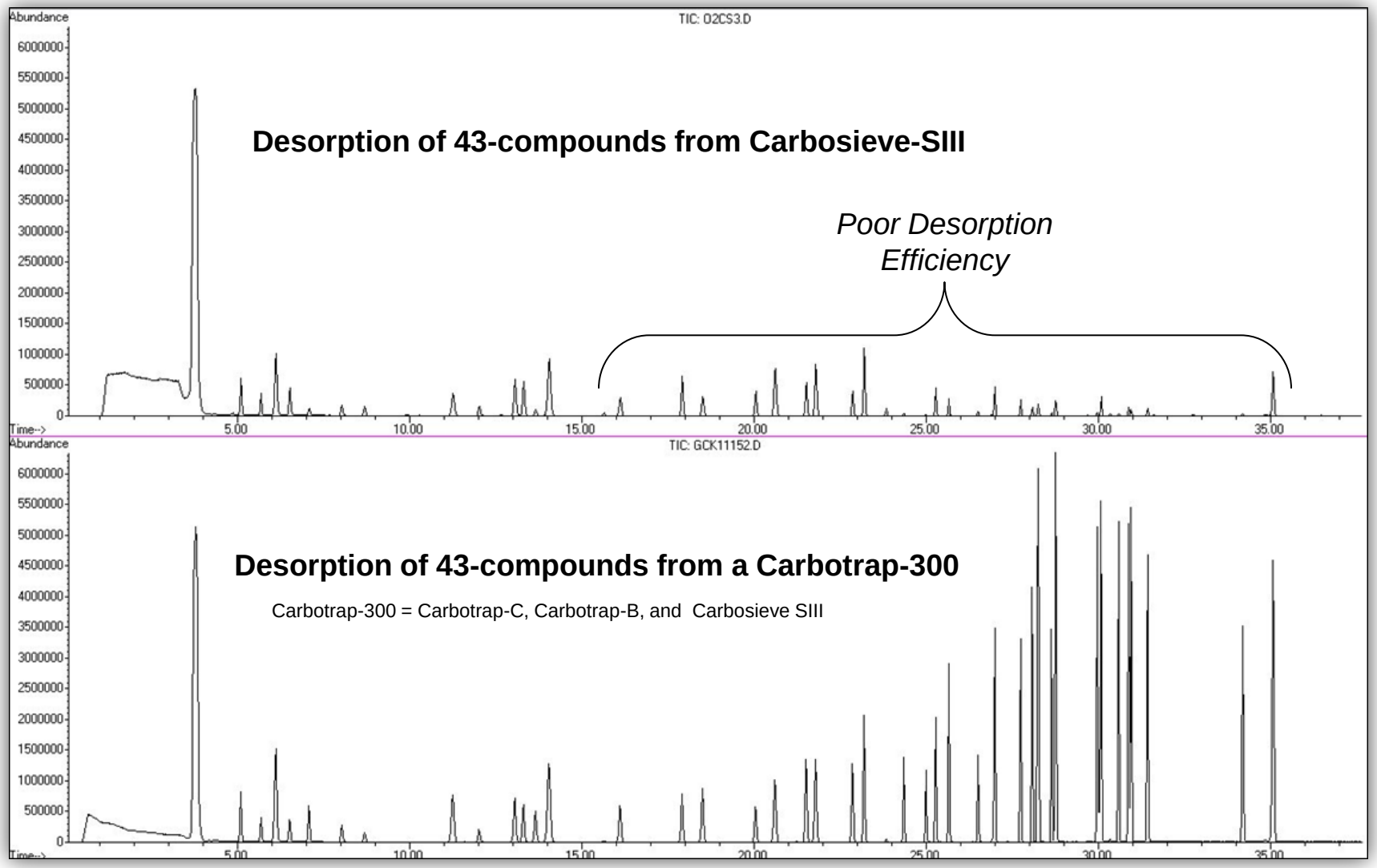
Adsorbent Characteristics for Thermal Desorption

- 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?



SIGMA-ALDRICH®

Terms Defined

Surface Area:

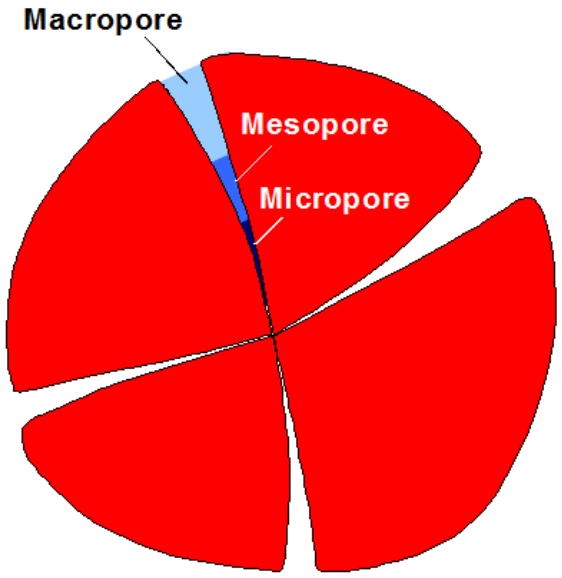
- Surface Area provides a general idea of the adsorbent strength, but it doesn't provide the whole picture. Other characteristics such as: pore size, pore shape, and porosity can also play a role in the adsorbent's ability to retain and release different compounds.

- *General Rule: The higher the surface area value, the stronger the adsorbent. However when the surface area is >800 m^2/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 m^2/g
- Hydrophobic

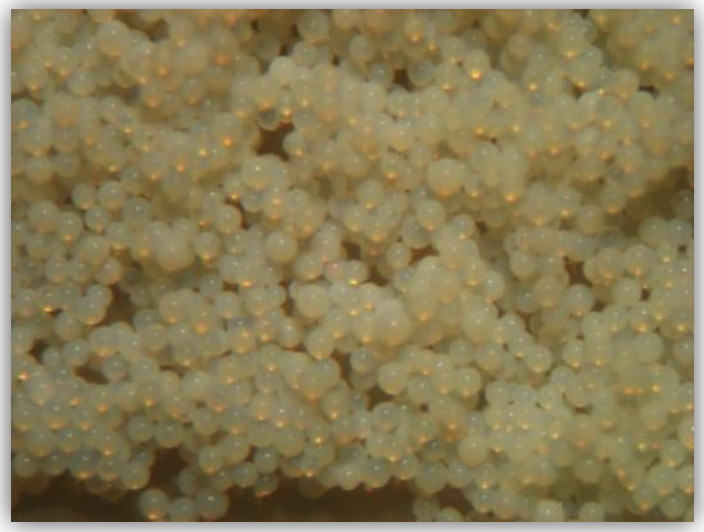
Porous Polymers (cont.)

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 m^2/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

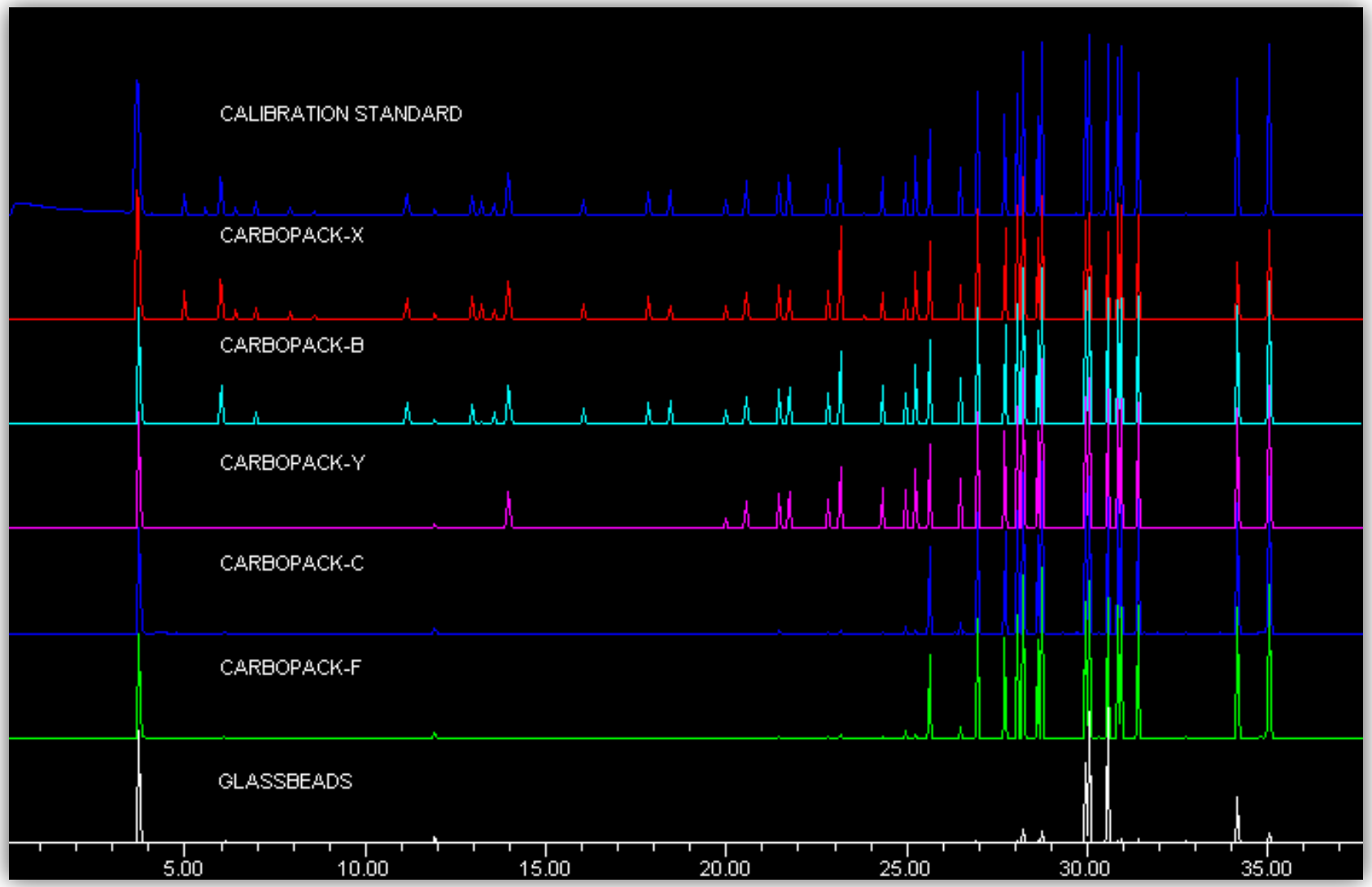
Typical Characteristics

- Granular - Flat Grey/Black in color
- Surface area: 5 to 240 m^2/g
- Designed to retain and release mid to large molecular weight compounds
- Hydrophobic
- High Purity - Low Background

Adsorptive Strength of Graphitized Carbon Blacks

		Relative Adsorption Strength
Carbopack F	5 m^2/g	Weakest
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	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

Standard Test Sieves

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

Large

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 m^2/g
- Designed to retain and release small molecular weight compounds

Adsorptive Strength of Carbon Molecular Sieves

Relative Adsorption Strength

Weakest

Carbosieve-G (1160 m^2/g)

Carboxen-1012 (1500 m^2/g)

Carboxen-564 (400 m^2/g)

Carboxen-1000 (1200 m^2/g)

Carboxen-1001 (500 m^2/g)

Carboxen-569 (485 m^2/g)

Carboxen-1003 (1000 m^2/g)

Carboxen-1018 (675 m^2/g)

Carbosieve-SIII (975 m^2/g)

Carboxen-1021 (1160 m^2/g)

Strongest

Other Adsorbents

Glass Beads 5 m^2/g ("good pre-filter")

<u>Adsorbents rarely used for Thermal Desorption</u>

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

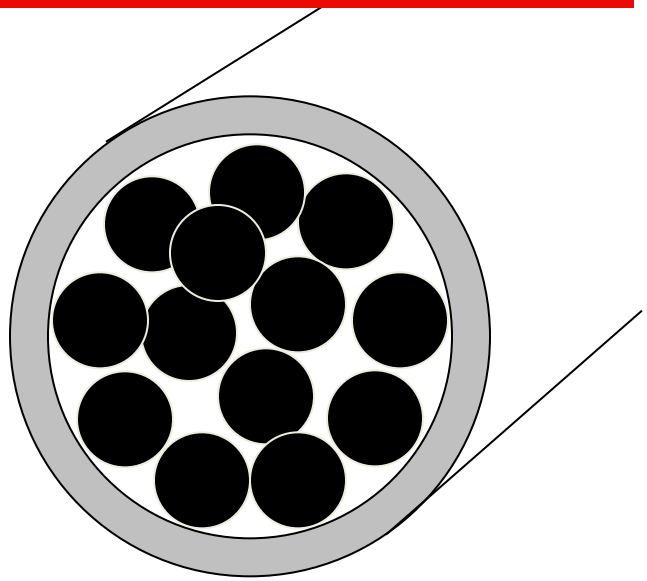
Adsorbent Mesh Size

Does Adsorbent Mesh Size Matter ?

Mesh Size vs. the Tube Inside Diameter

Poor

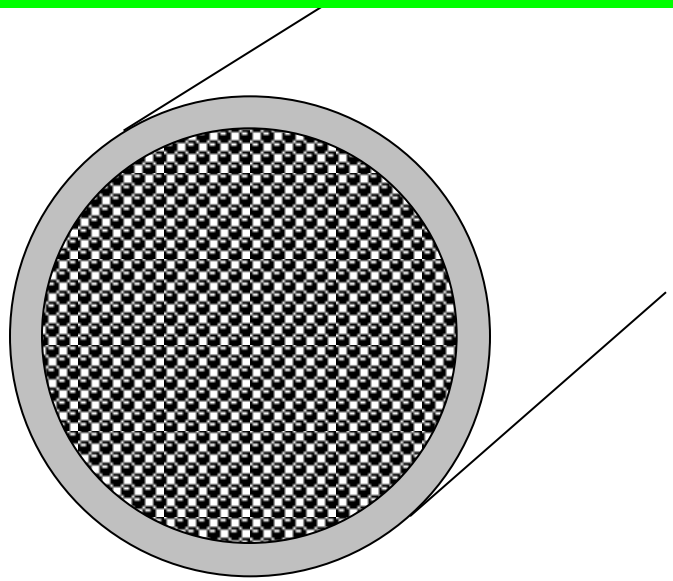
Compounds can travel around the adsorbent



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

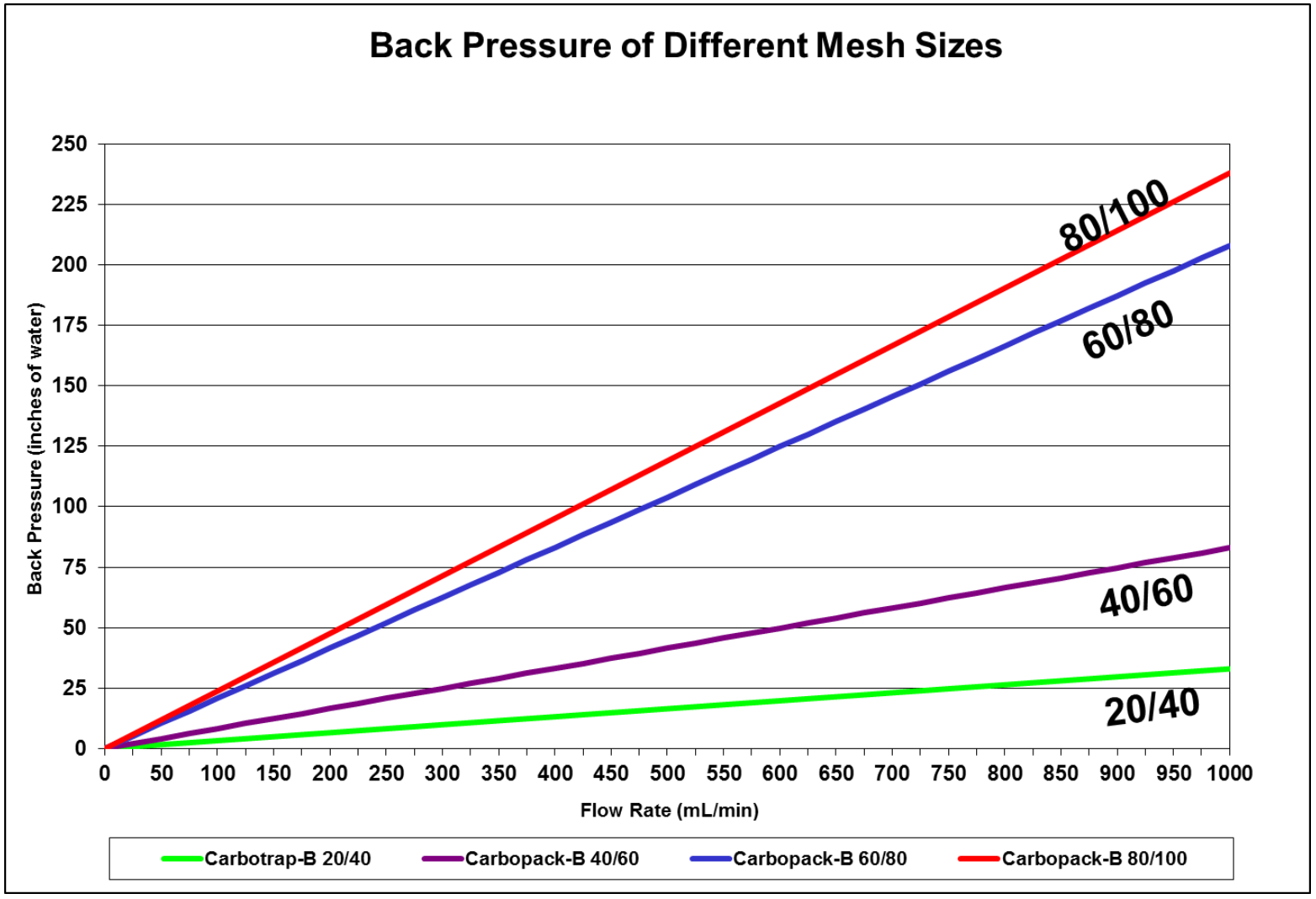
- Best ratio is between 0.10 to 0.25

	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

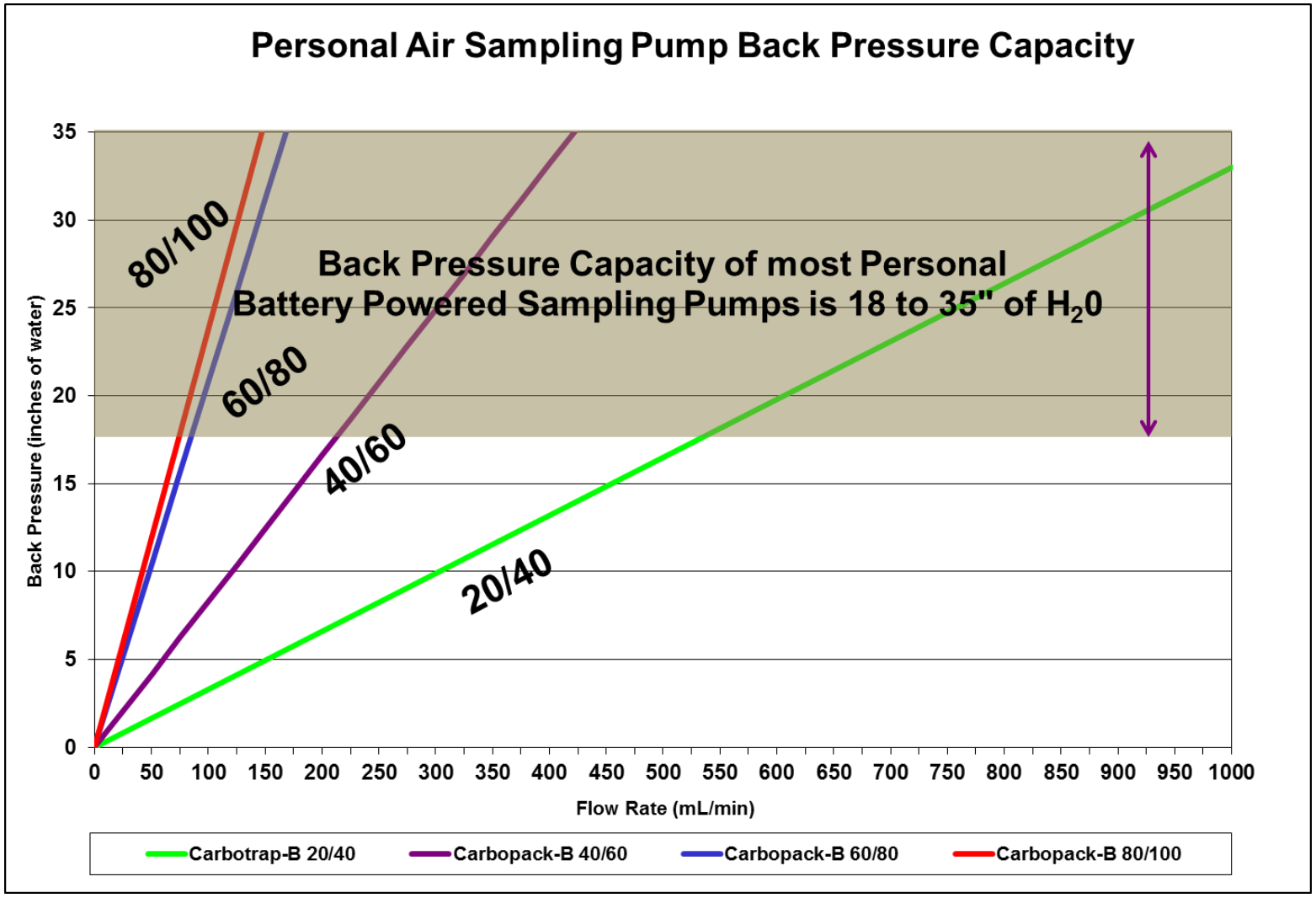
Mesh Size is too large >0.26 - Channeling may occur
Mesh Size is within range >0.10 <0.25 - Optimum Ratio
Mesh Size is smaller than required <0.10 - Excessive back pressure

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

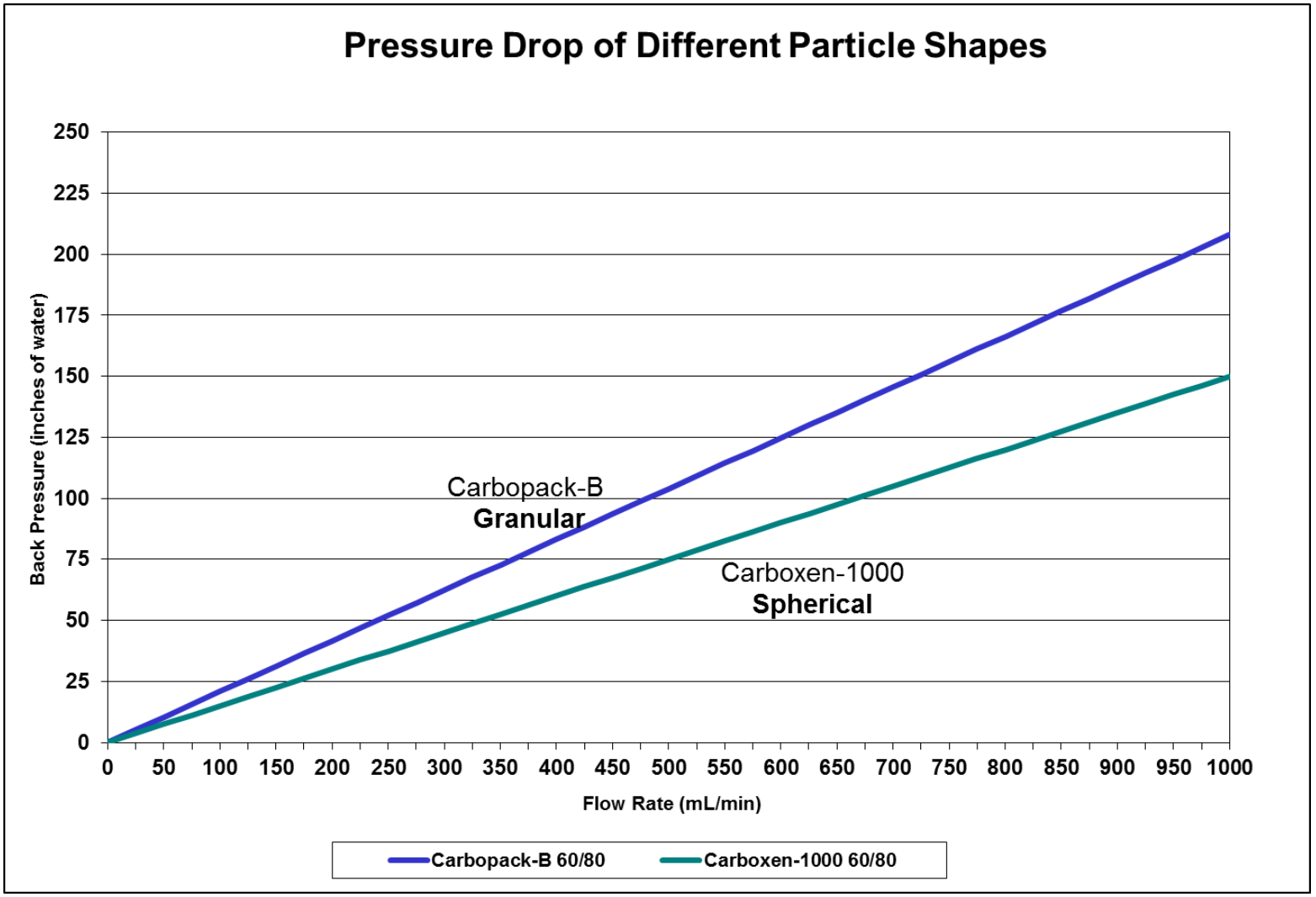
Mesh Size - How it affects Back Pressure



Mesh Size - Air Sampling Pump Capacity



Shape of the Adsorbent Particle



Flow Rate and Sample Volume

Sampling Flow Rates (Good Starting Point)

Typically range is between 10 and 250 mL/min.

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

Sample Collection Volume

Recommended Sample Volumes:

Single Bed Tubes using Hydrophobic Adsorbents

- 1 - 10 Liters

Multi-Bed Tubes using Carbon Molecular Sieves

- 1 - 5 Liters

Sample Flow Rate x Sampling Time = Sampling Volume

Humidity and Thermal Desorption

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.

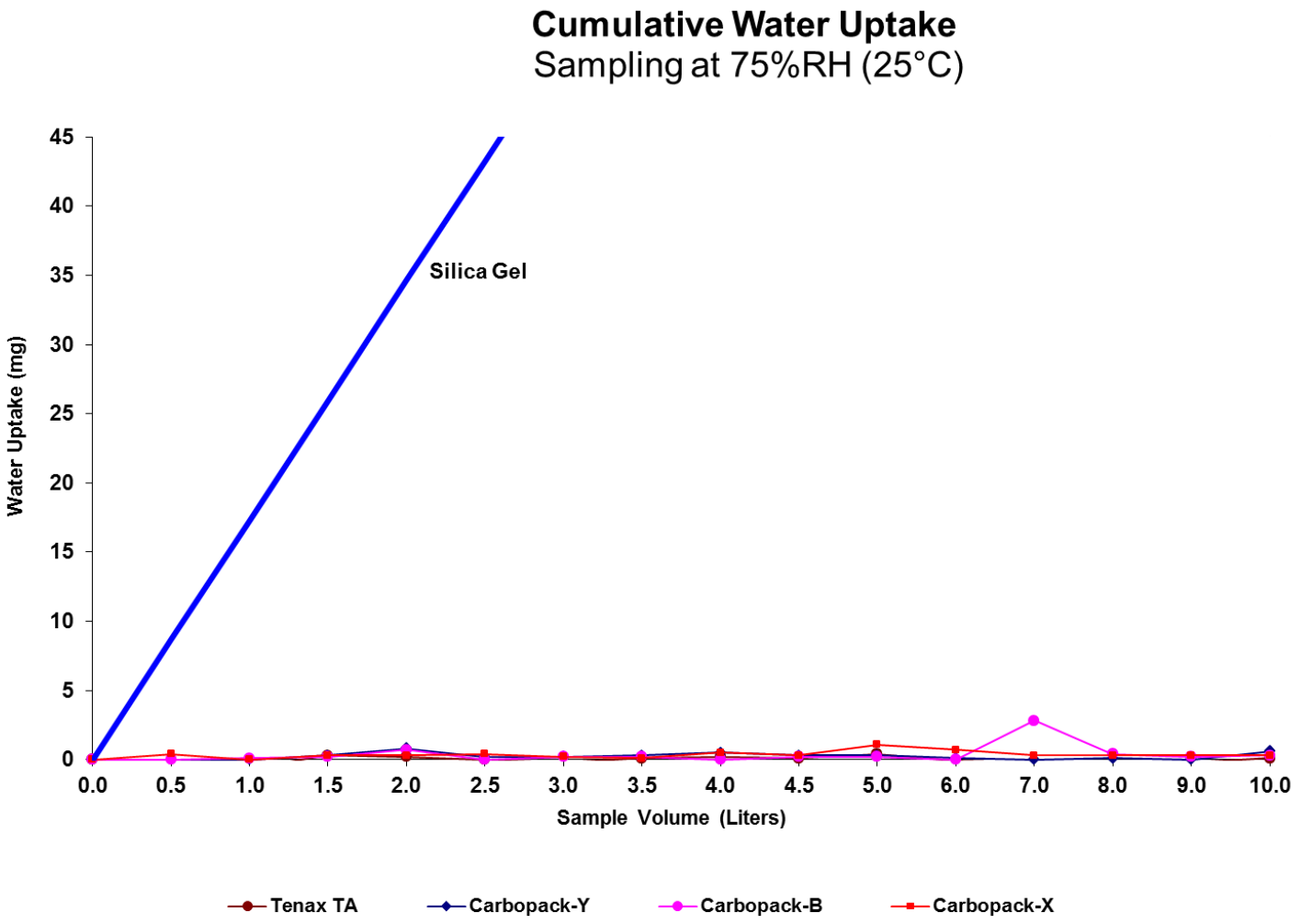
Some adsorbents are more hydrophobic than others.

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

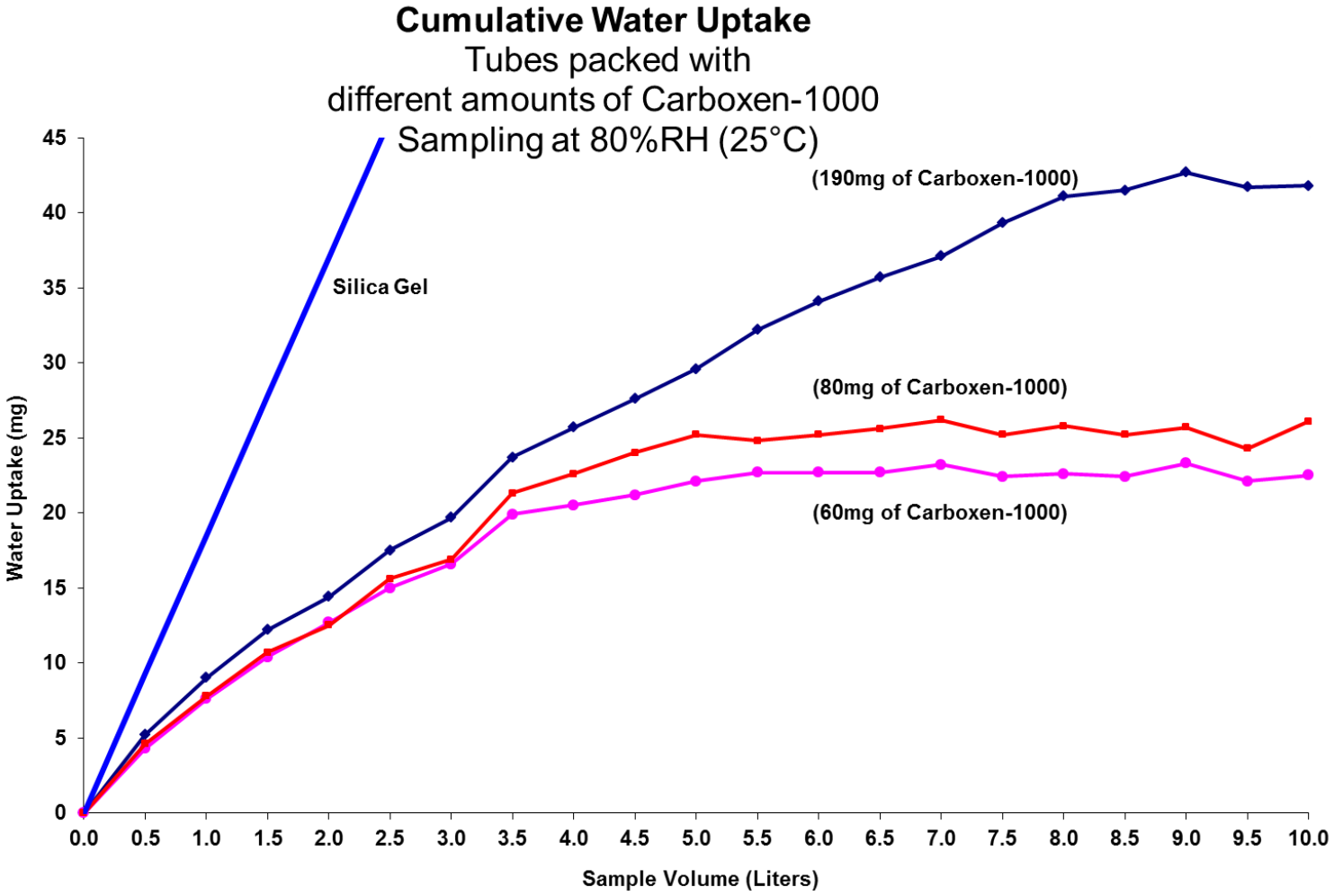
Carbon Molecular Sieves are still classified as hydrophobic.

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

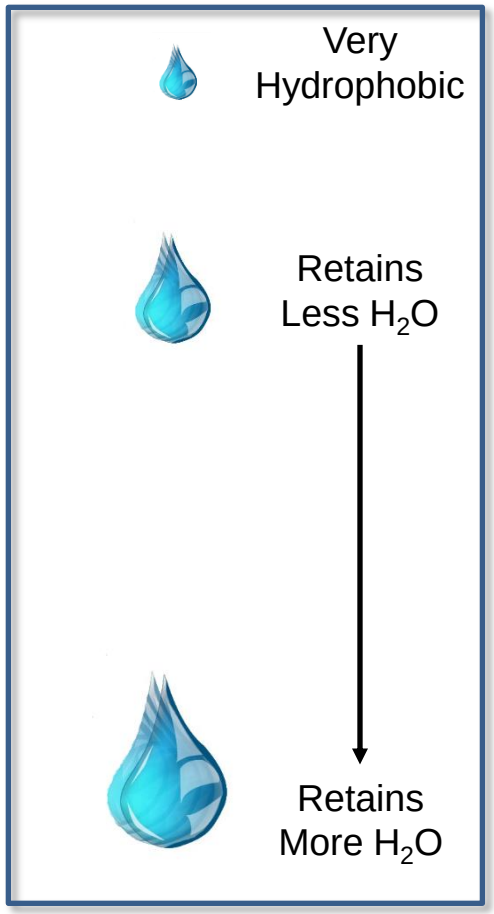
Water vapor retained by Carbopack(s) & Tenax-TA



Water vapor retained by Carboxen-1000



Relative Hydrophobicity



Glass Beads

Graphitized Carbon Blacks

Porous Polymers

Carboxen 569,1001,1003

Carboxen 563

Carboxen 564

Carboxen 1000

Carboxen 1012

Carboxen 1018

Carboxen 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 what dry purge volume is needed

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 up to <1 mg (1µL) of water if the thermal desorber is splitting some of the sample.

Thermal Desorption For Industrial Hygiene

Advantages of Using Thermal Desorption "Compared to Solvent Desorption"

- Wider range of analytes can be collected on a single tube
  - *Multiple Adsorbent Beds can be packed in the same tube*
- Thermal desorption offers more sensitivity than solvent extraction
  - *Typically 2 - 3 orders of magnitude (since no solvent dilutions occurs)*
- Desorption efficiency are typically <95%
- No hazardous extraction solvents are required
- No solvent interference during analysis
- Cost savings - tubes are reusable
- Sample prep is automated by the thermal desorber
- Both Active and Passive Sampling Tubes are available

NIOSH 2549 for Volatile Organic Compounds

NOISH 2549 is an active air sampling method that uses a multi-bed adsorbent tube.

- Aromatic & Aliphatic Hydrocarbons
- Chlorinate Hydrocarbons
- Ketones & Alcohols
- Glycol Ethers
- Terpenes
- Acetates
- Aldehydes

VOLATILE ORGANIC COMPOUNDS (SCREENING) **2549**

FORMULA see Table 1 MW: see Table 1 CAS: see Table 1 RTECS: see Table 1

METHOD: 2549, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 May 1996**

OSHA:
NIOSH: varies with compound
ACGIH:

PROPERTIES: See Table 1

SYNONYMS: VOCs; See individual compounds in Table 1

SAMPLING		MEASUREMENT	
SAMPLER:	THERMAL DESORPTION TUBE (multi-bed sorbent tubes containing graphitized carbons and carbon molecular sieve sorbents [See Appendix])	**TECHNIQUE:**	THERMAL DESORPTION, GAS CHROMATOGRAPHY, MASS SPECTROMETRY
FLOW RATE:	0.01 to 0.05 L/min	**ANALYTE:**	See Table 1
VOL-MIN:	1 L	**DESORPTION:**	Thermal desorption
-MAX:	6 L	**INJECTION VOLUME:**	Defined by desorption split flows (See Appendix)
SHIPMENT:	Ambient in storage containers	**TEMPERATURE-DESORPTION:**	300 °C for 10 min.
SAMPLE STABILITY:	Compound dependent (store @ -10 °C)	**-DETECTOR (MS):**	280 °C
BLANKS:	1 to 3 per set	**-COLUMN:**	35 °C for 4 min; 8 °C/min to 150 °C, 15 °C/min to 300 °C
ACCURACY		**CARRIER GAS:**	Helium
RANGE STUDIED:	not applicable	**COLUMN:**	30 meter DB-1, 0.25-mm ID, 1.0-µm film, or equivalent
BIAS:	not applicable	**CALIBRATION:**	Identification based on mass spectra interpretation and computerized library searches.
OVERALL PRECISION ($\hat{S}_{rT}$):	not applicable	**RANGE:**	not applicable
ACCURACY:	not applicable	**ESTIMATED LOD:**	100 ng per tube or less
		PRECISION ($\hat{S}_r$):	not applicable

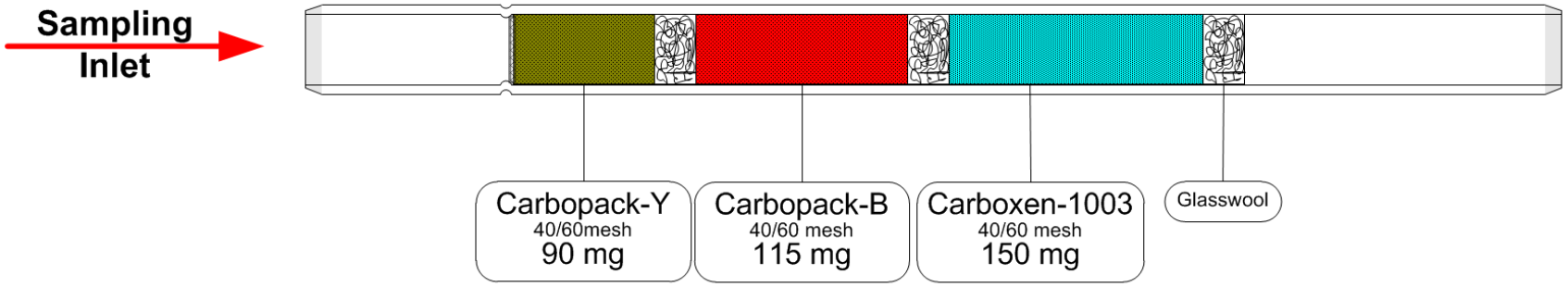
APPLICABILITY: This method has been used for the characterization of environments containing mixtures of volatile organic compounds (See Table 1). The sampling has been conducted using multi-bed thermal desorption tubes. The analysis procedure has been able to identify a wide range of organic compounds, based on operator expertise and library searching.

INTERFERENCES: Compounds which coelute on the chromatographic column may present an interference in the identification of each compound. By appropriate use of background subtraction, the mass spectrometrist may be able to obtain more representative spectra of each compound and provide a tentative identity (See Table 1).

OTHER METHODS: Other methods have been published for the determination of specific compounds in air by thermal desorption/gas chromatography [1-3]. One of the primary differences in these methods is the sorbents used in the thermal desorption tubes.

Tube Configuration Specified in NIOSH 2549

Carbotrap-349

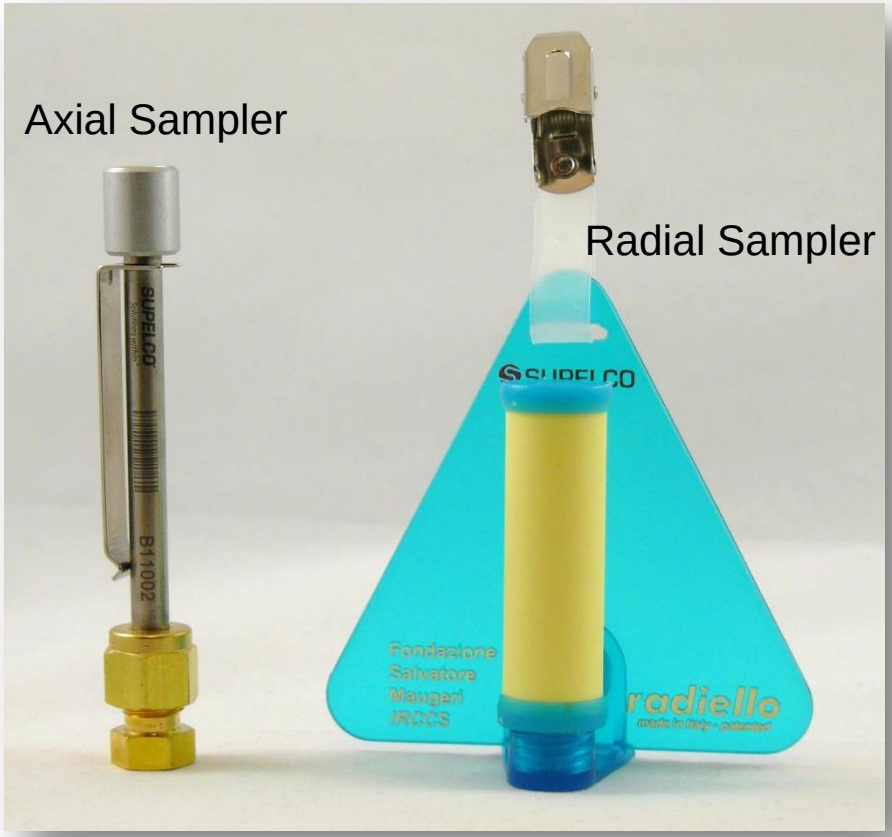


This adsorbent configuration will retain & release a wide range of compounds.

Flow Rate to use : 10 to 50 mL/min

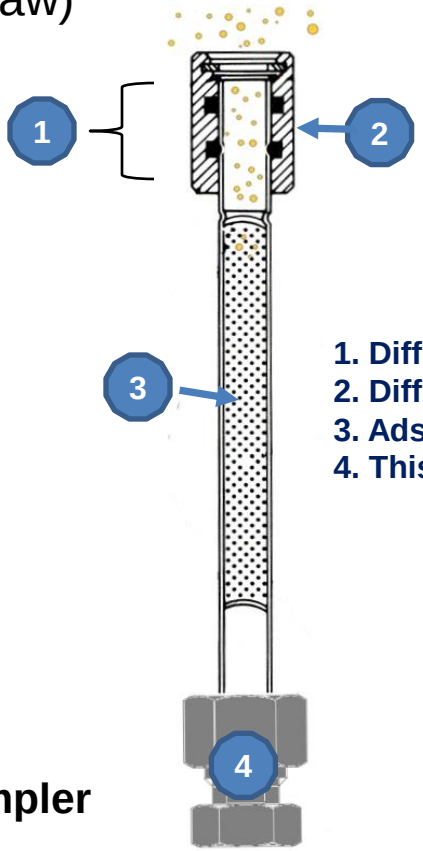
Sample Volume to collect: 1 to 6 Liters

Passive Sampling Options for Thermal Desorption



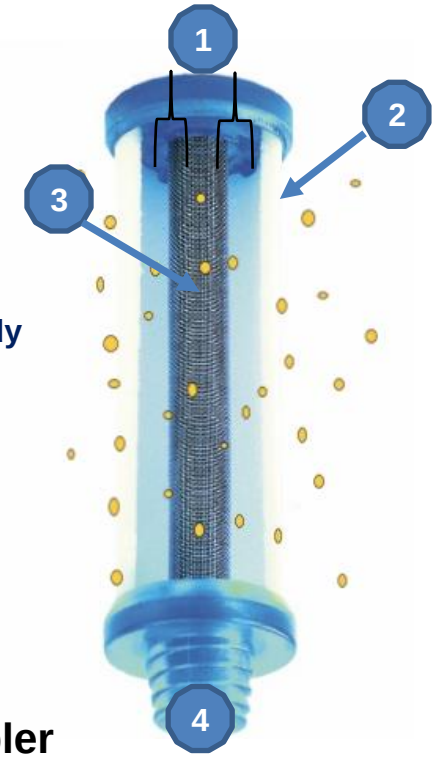
How it works (Passive Sampling)

The air sample is collected by the natural movement of the contaminant molecules across a concentration gradient of the air gap and onto the adsorbent. (Fick's Law)



Axial Sampler

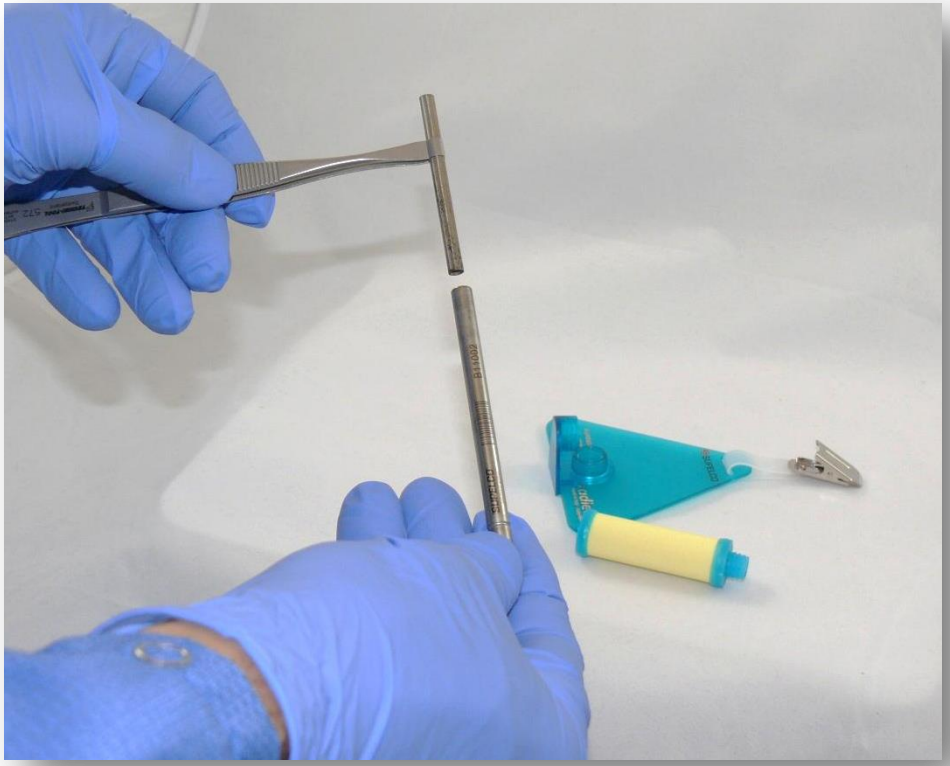
1. Diffusion Path "Air Gap"
2. Diffusion Sampling Cap, or Diffusive Body
3. Adsorbent, or Adsorbent Cartridge
4. This end is sealed during sampling



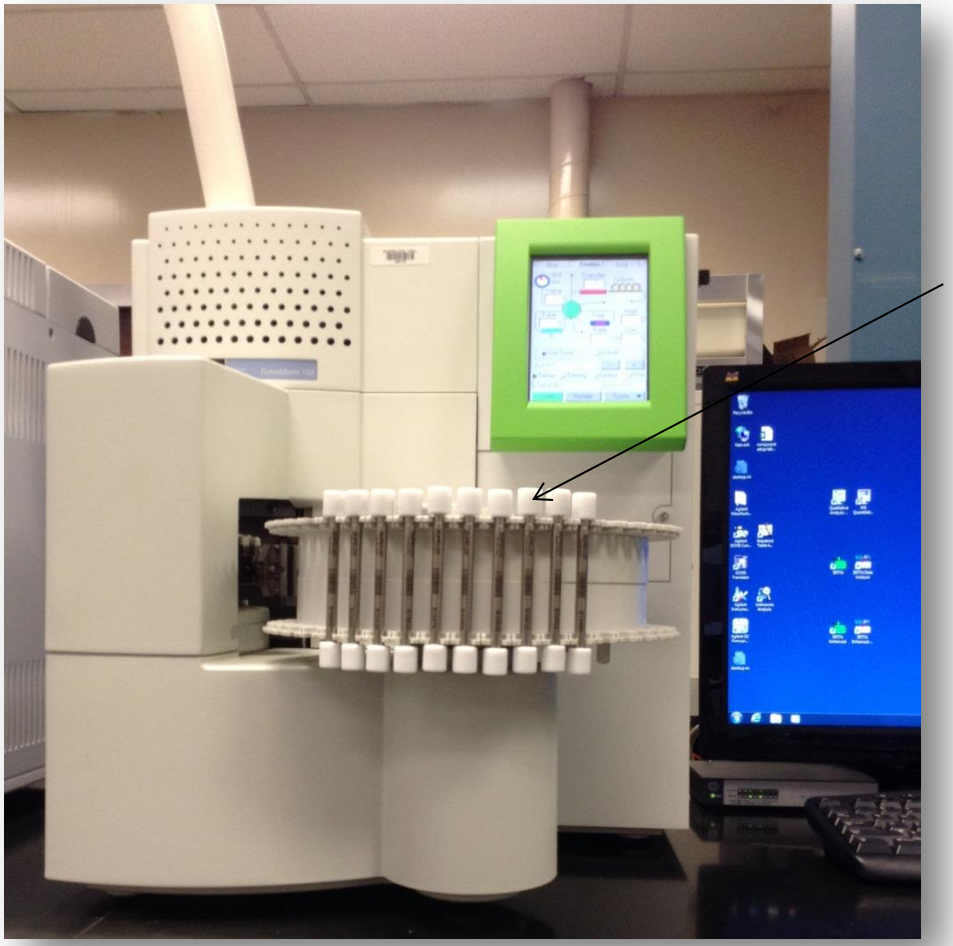
Radial Sampler

Radiello (RAD-145)

After sampling, the RAD 145 adsorbent cartridge is placed in an empty stainless steel thermal desorption tube for analysis.



Tubes are Analyzed on a Thermal Desorber



Other IH Methods Related to Thermal Desorption

ASTM D6196 – Standard Practice for Selection of Sorbents, Sampling, and Thermal Desorption Analysis Procedures for Volatile Organic Compounds in Air

ISO-16017 – (parts 1 and 2) Indoor, Ambient and Workplace Air -- Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography

Health and Safety Executive Methods:

MDHS 72 – Volatile organic compounds in air, using pumped solid sorbent tubes by thermal desorption and gas chromatography,

MDHS 80 – Volatile organic compounds in air, using diffusive solid sorbent tubes by thermal desorption and gas chromatography.

Conclusions

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

- Porous Polymers
- Graphitized Carbon Blacks (GCB)
- Carbon Molecular Sieves (CMS)

There are several factors to consider when choosing an adsorbent:

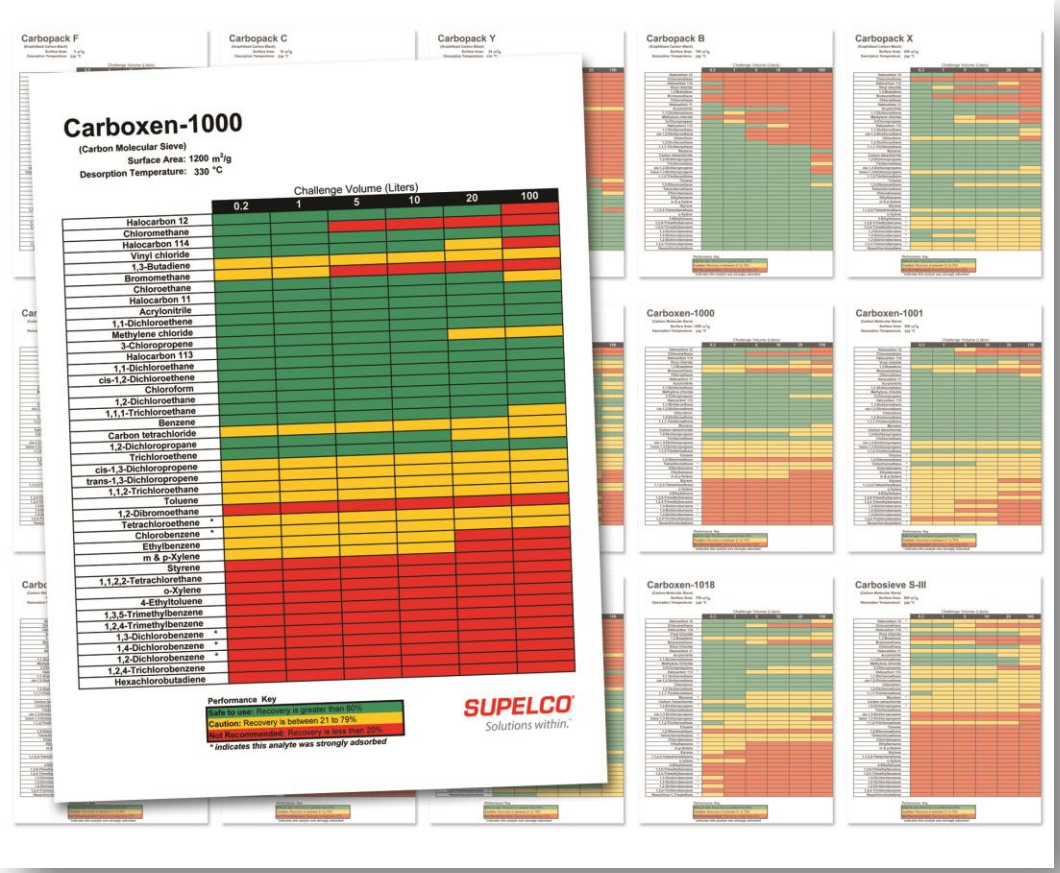
- Single Bed, or Multi-Bed Tubes
- Range of compounds to be sampled
- Sampling flow rate
- Sample volume
- Dry Purge volume

There are several options for available for Passive Sampling

Adsorbent / Thermal Desorption Literature (cont.)

"A Tool for Selecting an Adsorbent for Thermal Desorption"

www.sigmaaldrich.com/air-monitoring



Trademarks

Carbotrap®, Carbopack™, Carboxen®, Carbosieve® , - Sigma Aldrich Co LLC, USA

Chromosorb® - Imerys Minerals California, Inc., USA

HayeSep® - Hayes Separations, USA

PoraPak™ - Waters Associates, USA

Radiello™ - Fondazione Salvatore Maugeri IRCCS, Italy

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

&

American Industrial Hygiene Association (AIHA)

SUPELCO®

Solutions within.™ *Bellefonte, Pennsylvania USA*

SIGMA-ALDRICH®

SUPELCO®
Solutions within.™

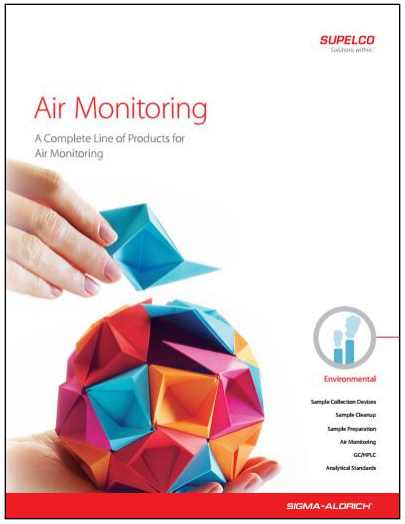
Q&A

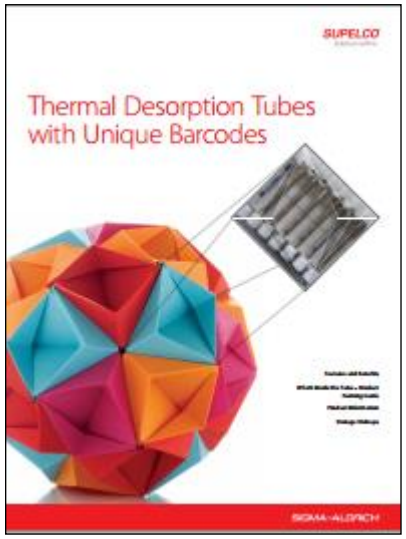
Follow up questions on thermal desorption or air monitoring?

Contact:

Jamie.Brown@sial.com

Kristen.Schultz@sial.com





View the complete portfolio of Air Monitoring products, find product literature, and more at: www.sigmaaldrich.com/air-monitoring

SIGMA-ALDRICH®