VOC Analysis: Critical Success Factors for Purge-and-Trap

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A World of Solutions

Webinar Outline

- Purge-and-trap theory
  - Principle of operation
  - Analytical challenges
- Factors affecting purge efficiency
- Factors affecting trapping efficiency
- Factors affecting desorbtion and baking efficiency
- P&T and water management
- Final comments and Q & A

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Purge-and-Trap Theory: Principle of Operation and Analytical Challenges

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Purge-and-Trap Definition

An analytical technique designed to efficiently extract Volatile Organic Compounds (VOCs) from a matrix and concentrate them for transfer onto a GC analytical column without sacrificing peak shape, recovery, or accuracy.

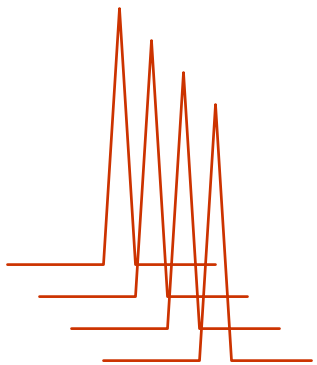

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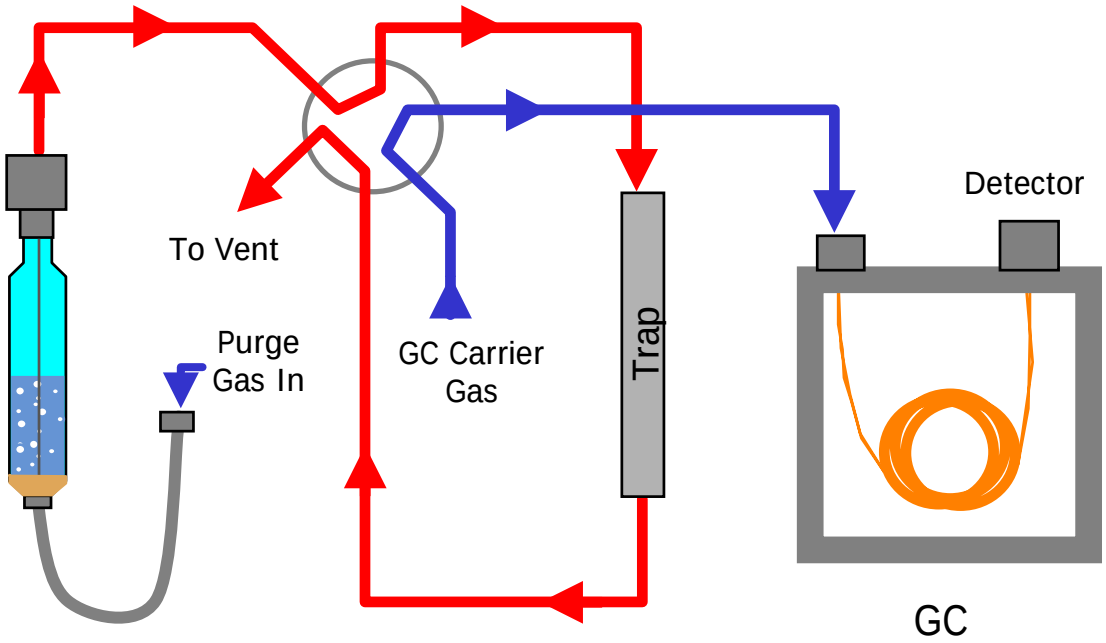
Diagram of Purge State



- Purge gas passes through the sample as finely divided bubbles
- Analytes are transferred out of the matrix and carried onto the trap
- Analytes are captured and concentrated on the trap adsorbent

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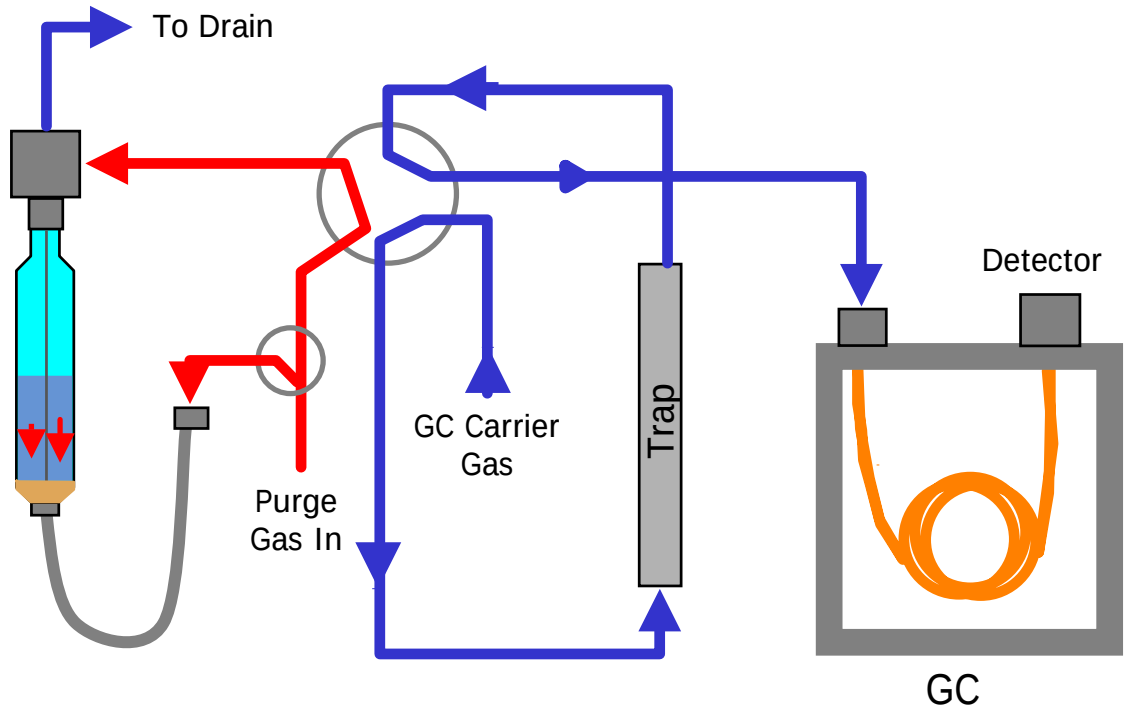
Diagram of Desorb State



- 6-port valve rotates to place the trap in-line with the GC carrier gas
- Trap is heated rapidly to thermally desorb analytes
- GC carrier gas transfers analytes to the GC column
- P&T system drains sample, and pathway is rinsed with clean water

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P&T Analytical Challenges

- Complex compound lists with multiple chemistries
- Wide concentration range
- Multiple sample matrices
- Water considerations
- Dirty or foaming samples
- Complex hardware with multiple system components
- High sample load; limited resources

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Factors Affecting Purge Efficiency

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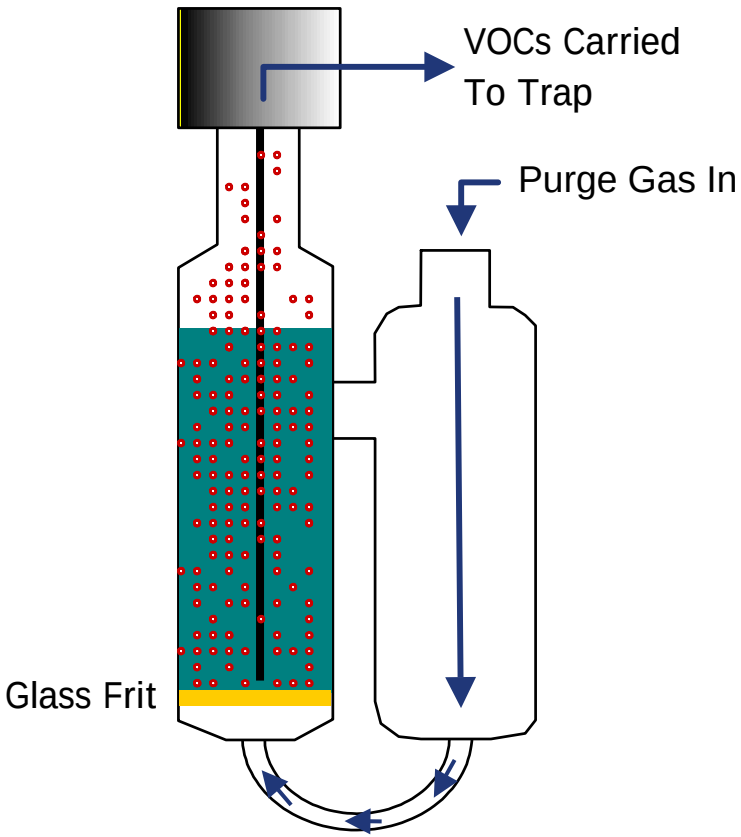
Factors Affecting Purge Efficiency

- Volume of the purge gas
  - Flow rate * purge time = volume
  - Too little volume = low recovery of heavies
  - Too much volume = breakthrough of gases
- Height of the sample column
- Type of sparger
  - Needle sparger vs. frit sparger
- Sample temperature
  - Ambient adequate for most compounds
  - Heating will improve purge efficiency of the polar compounds and the heavies
  - Some matrices may need more heating

Frit Sparging



- Purge gas passes through a glass frit at the bottom of the sample column
- Finely divided bubbles of purge gas pass through the sample, stripping the volatile analytes from the matrix and carrying them into the headspace above the sample
- Flow of the purge gas transfers the VOCs onto the analytical trap

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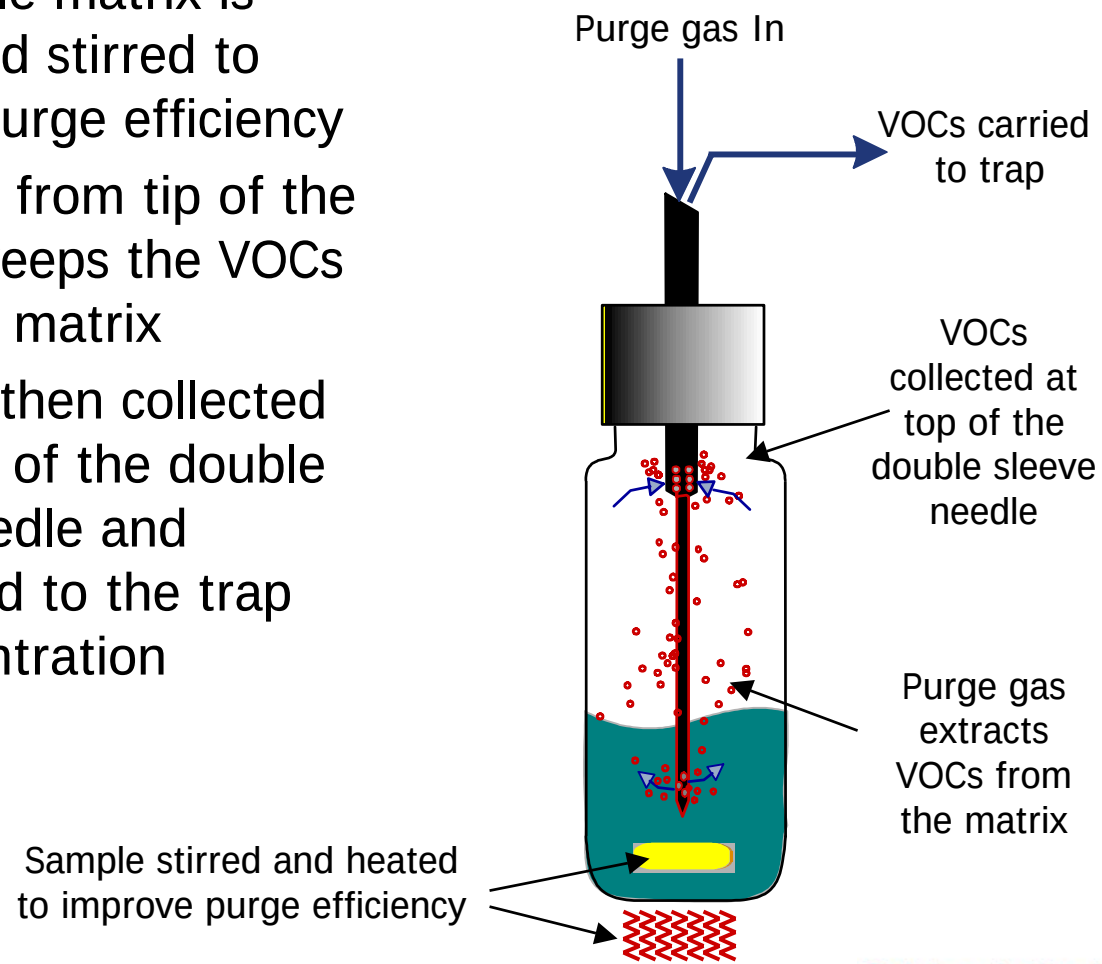
Needle Sparging

- The sample matrix is heated and stirred to improve purge efficiency
- Purge gas from tip of the needle sweeps the VOCs out of the matrix
- VOCs are then collected at the top of the double sleeve needle and transferred to the trap for concentration



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Frit Sparging vs. Needle Sparging

	Frit Sparging	Needle Sparging
Advantages	• Finely divided bubbles increase surface contact between purge gas and sample matrix, leading to higher purge efficiency	• Disposable glassware is good for “dirty” samples • Accommodates any matrix
Disadvantages	• The frit is difficult to clean when it is contaminated by a dirty sample	• Larger bubbles have less surface contact with the matrix, leading to lower purge efficiency • Shorter sample column

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Advantages to Sample Heating

- Transfer of VOCs from the matrix to the purge gas can be affected by sample temperature
  - Heating the sample increases the rate at which the VOCs are transferred to the purge gas
- Improves purge efficiency for all compounds, particularly the polar, water-soluble compounds
  - Alcohols, ethers, ketones, etc.
- Assures all samples are purged at the same temperature
  - Purge efficiency will be consistent from sample to sample
  - %RSD will be lower for calibration
  - Avoids variation due to ambient laboratory temperatures
  - Particularly important when the samples are held at 4 °C in the autosampler until analysis

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Disadvantages to Sample Heating

- Whenever the sample is heated additional water will be transferred to the analytical trap
- Must employ effective water management strategy

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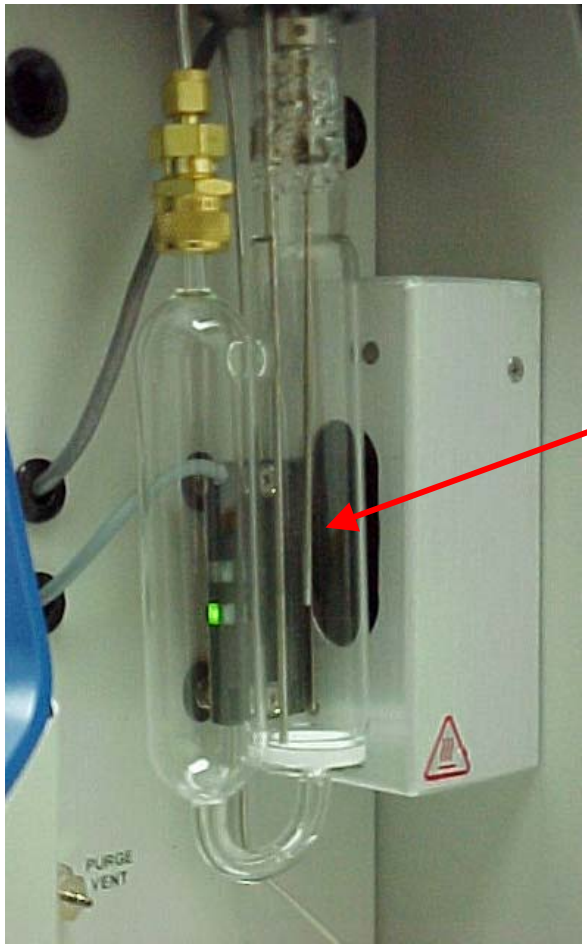
Sample Heating Techniques

- Sleeve or jacket style heater
  - Sample heating rate can be slow
  - Difficult to control the temperature of the sample, since the thermocouple is usually in the sleeve and not in the sample
  - Can obscure view of the sample
- Infra-sparge sample heater
  - Sample is brought to the desired temperature very quickly
  - Temperature is accurately controlled because the thermocouple is submerged within the sample
  - Does not obscure view of the sample
- Recommended sample temperature is 40-45 °C

Infra-sparge™ Sample Heater



- The Infra-sparge sample heater uses infrared light
  - Extremely rapid heating
- The thermocouple is submerged in the sample for precise control

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Factors Affecting Trapping Efficiency

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Factors Affecting Trap Efficiency

- Selection of proper trap for your application
- Correct trap operating conditions (temperature and flow rate) during Purge, Desorb, and Bake
- Routine maintenance

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Trap Selection

- Selection of the proper adsorbent for the application
  - Match adsorbent to compound list
  - BTEX or VPH use Tenax®-only trap
  - Multiple layer traps common for the standard methods
- Hydrophobic vs. hydrophilic
  - If using a hydrophobic material it may require the dry purge state to help remove water
  - Hydrophilic materials (e.g. silica) cannot be dry purged
- Operational temperature range
  - Does it trap effectively at ambient temperatures?
  - Does it release the analytes easily during desorb?
  - Will it be stable through multiple heating/cooling cycles?

Trap Selection (cont.)

- Three traps most commonly used with the OI concentrators are:
  - #7: Tenax only
  - #10: Tenax, silica gel, carbon mole sieve
  - #11: VOCARB
- The VOCARB trap is usually the trap of choice when Dry Purge is the principle method of water removal
- OI concentrators employ active water management during desorb, either the three-layer trap or the VOCARB trap can be used

#10 (3-Layer) Trap

Advantages	Disadvantages
Low operating temperatures • 20 °C at Purge • 180 °C at Desorb Preheat • 190 °C at Desorb • 210 °C at Bake	If you have been using a different instrument or a different type of trap some of the peak shapes may be slightly different
Fast cool-down and short cycle time	
Works for most USEPA methods	
Does not require a Dry Purge step	

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VOCARB Trap

Advantages	Disadvantages
Hydrophobic character aids water management	High operating temperatures • 20 °C at Purge • 230 °C at Desorb Preheat • 240 °C at Desorb • 250 °C at Bake
Excellent peak shape and baseline resolution of six early eluting gases	Longer cool down and longer cycle times
Works for most USEPA methods	Requires Dry Purge step to remove water

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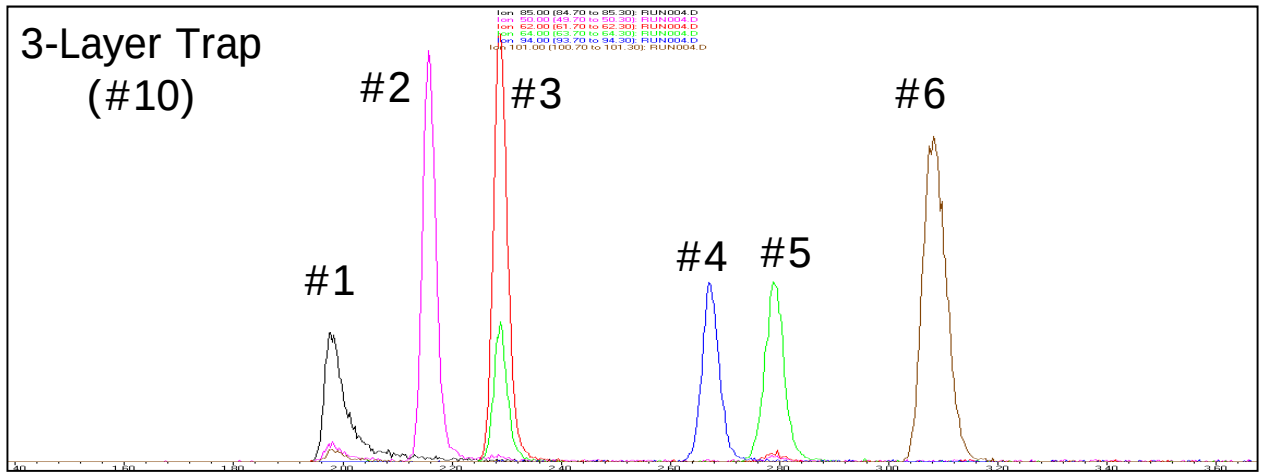
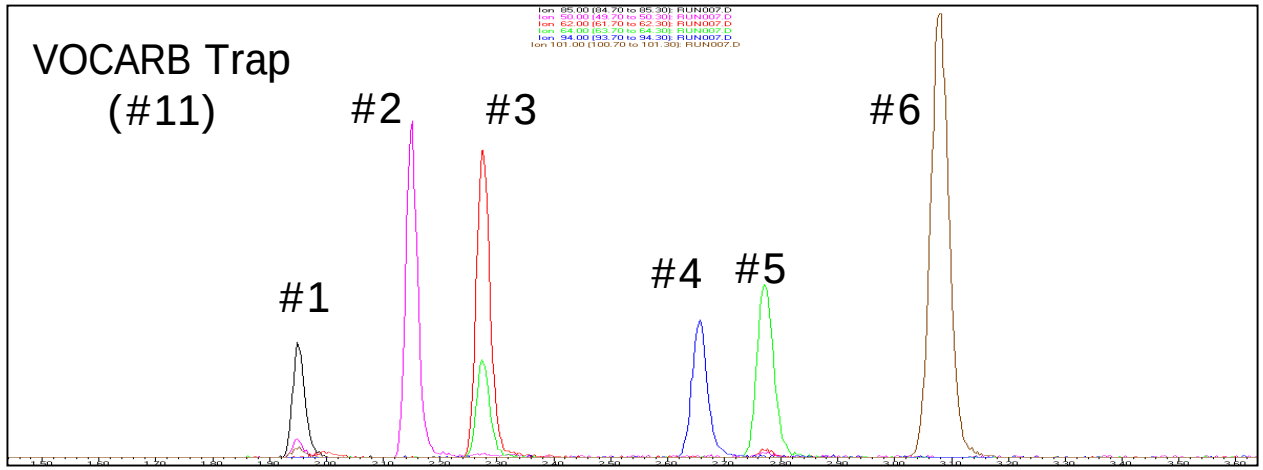
Chromatography of the Gases





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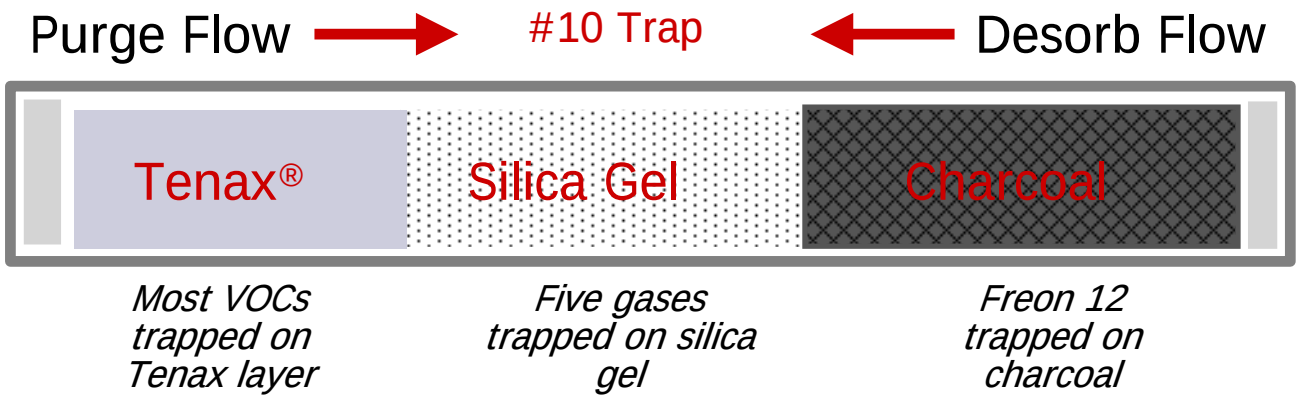
Trap Operating Conditions



- During Purge the trap is at ambient temperature; during Desorb it is heated to release the analytes
- When using a #10 trap, most compounds are trapped on the Tenax and always have very sharp chromatography
- The first five gases are trapped on the silica gel with the H_2O
- Freon 12 is trapped on the charcoal
- A VOCARB trap works the same way, but with different packing materials and distribution

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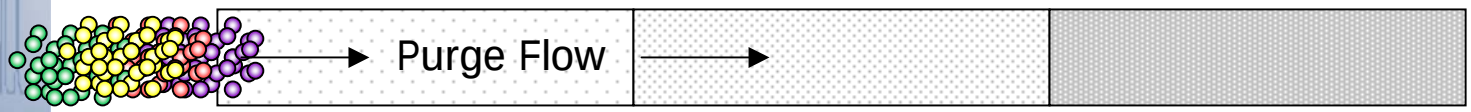
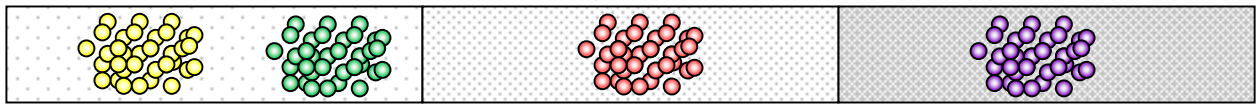
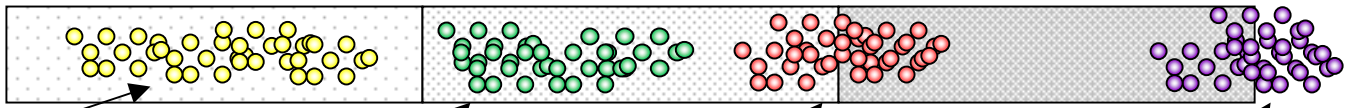
Common Trap Problems



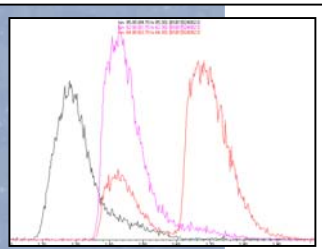
"Normal" analyte distribution . . .



Result of excessive forward flow . . .

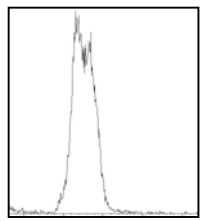


1. Band-broadening = poor peak shape



2. Stronger adsorbent = carryover

3. Straddling 2 adsorbents = split peaks



4. Breakthrough = low recovery

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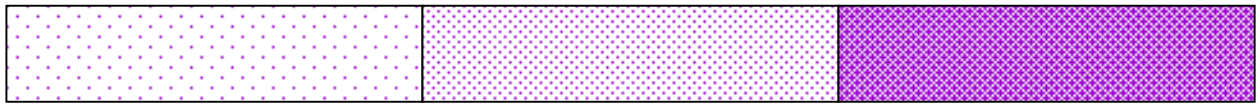
Additional Trap Considerations

"Normal" adsorbent packing . . .

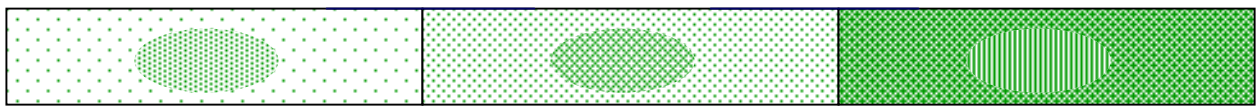


Aging, high flows, or pressure pulses in opposite directions can cause trap degradation, such as . . .

1. "Blurring" of the adsorbent interface

2. Channeling

3. Inconsistent or too tight packing in spots



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Factors Affecting Desorbtion and Baking Efficiency

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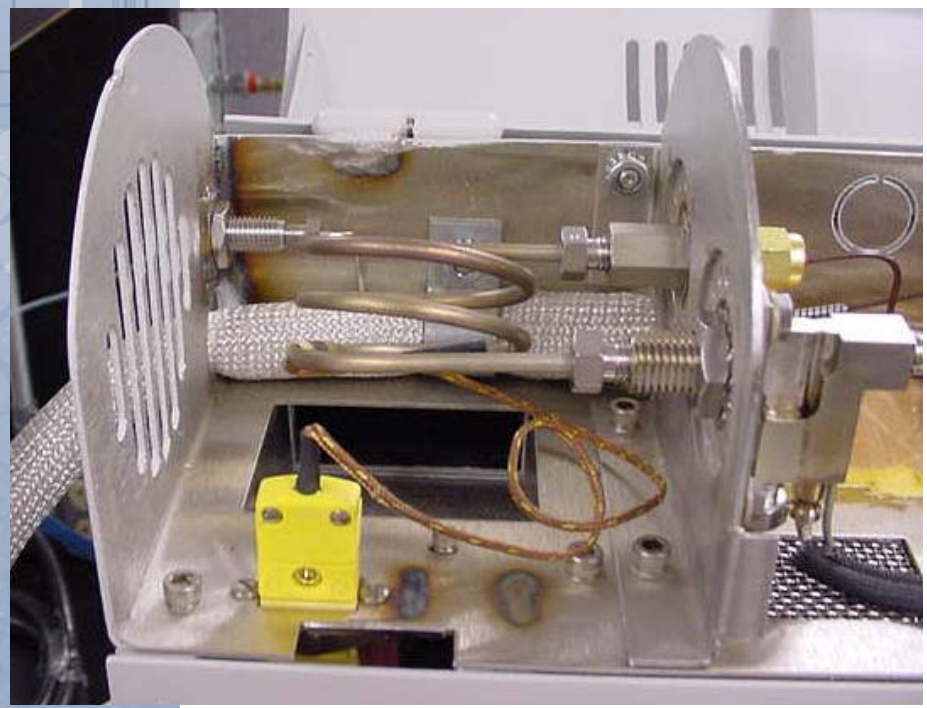
Factors Affecting Desorption Efficiency

- Trap heating rate and final temperature
  - Direct vs. indirect heating
  - Release of analytes from adsorbent
  - Narrow, focused bandwidth
  - Short desorb times
- Desorb flow rate
  - Controlled by column flow rate and split ratio

Indirect Trap Heating

- Some P&T instruments employ indirect trap heating
  - Sleeve, jacket, or heater tape coiled around the trap
- Several drawbacks to the jacket design
  - Inconsistent heating, TC is in the sleeve, not at the trap
  - Slow heating rate of ~300-400 °C/minute
  - Longer cool-down times due to the insulation or heater coal wrapped around the trap

Direct Resistive Trap Heating



- SS trap electrically isolated
- Current applied directly to the trap
- Thermocouple controls temperature of the trap
- Fast heating rate, 900 - 1100 °C/minute
- Accurate, reproducible heating
- Faster cool down
- Shorter desorb times

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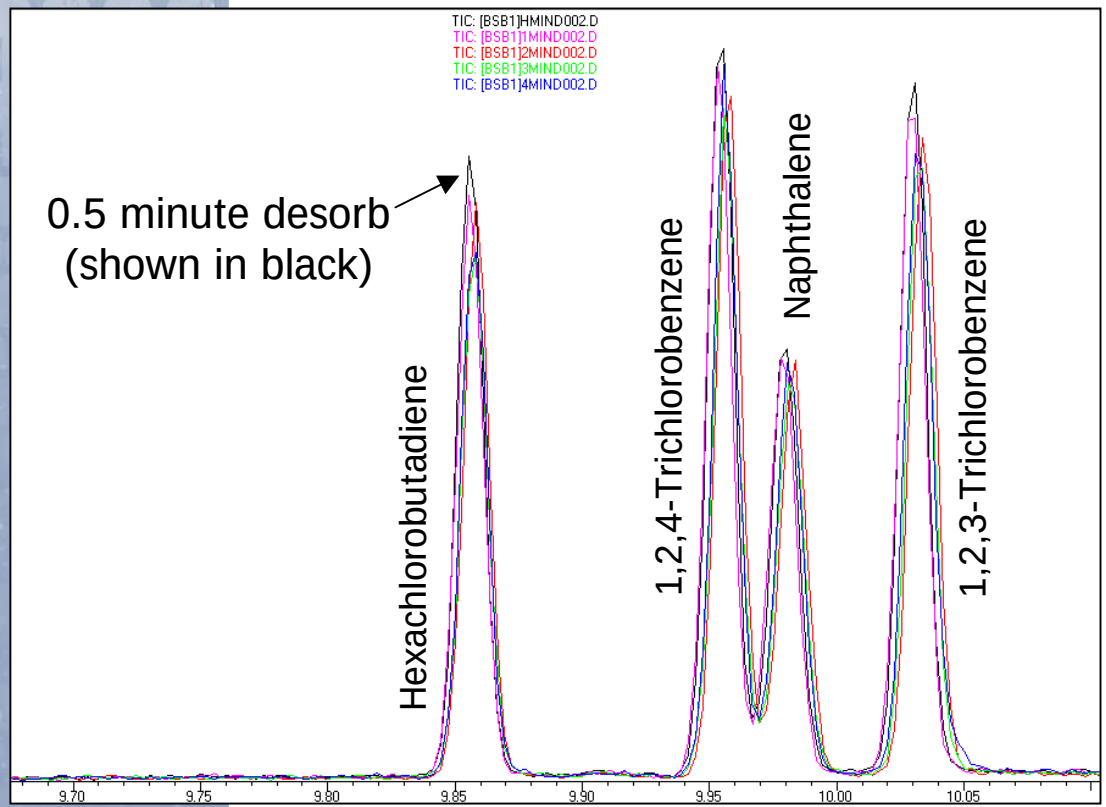
High Recovery With Short Desorb Times

Overlaid chromatograms of the 4 heaviest peaks using desorb times of 4, 3, 2, 1, and 0.5 minutes.



The four heaviest compounds had ~100% recovery with a ½-minute desorb

#10 Trap

45 mL/min flow

½-min desorb

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Desorb Flow Rate

- The faster the desorb flow rate, the more quickly the analytes are transferred to the GC column and the narrower the peaks will be
- Desorb flow rate is controlled by the column carrier gas flow rate and the split ratio
- When using a direct column connection (no split), the column flow is the same as the desorb flow rate
- When using a split flow, the total GC flow will be the desorb flow rate

Factors Affecting Bake Efficiency

- Rapid, accurate heating of the trap to a given temperature
  - Temperature depends on adsorbent type
- Time held at that temperature
  - Complete release of contaminants
- Minimum gas flow
  - Flush contaminants from the sample pathway as they are released

P&T and Water Management

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P&T and Water Management

- Any time you purge an environmental sample, water or soil, moisture will be transferred to the trap along with the analytes
- When developing your method operating conditions you must build in elements that will minimize the amount of water transferred to the GC
- Most VOC analytical systems use several techniques simultaneously to manage the water

P&T and Water Management (cont.)

- If you wish to heat the sample to improve purge efficiency, you will have to be prepared to remove the additional water
- You must know what kind of trap you are using and whether it is hydrophobic or hydrophilic
- You must be able to recognize the affects of water on the GC/MS

Final Comments

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Other Factors Affecting P&T

- The P&T is only one part of a complex, multi-component system used for analysis of VOCs
  - Autosampler with standard addition
  - Purge-and-trap
  - GC, inlet, and column
  - Detector
- Important for analyst to understand how each component works individually, and how they interact, or affect, performance of the others
- All components must be optimized to work together for best results

GC Considerations

- Keep connection at GC inlet warm to prevent cold spot
- Split ratio and column flow control the desorb flow rate
- A small ID liner will help minimize band broadening when desorb flow rate is slow
- Use a column designed specifically for volatiles
- Match the column dimensions to the detector type
- Match the split ratio to the column dimensions
- Cycle time of the system is what will determine productivity, not necessarily the cycle time of any single component

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Q&A

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