jsb


# Purge &Trap / Headspace

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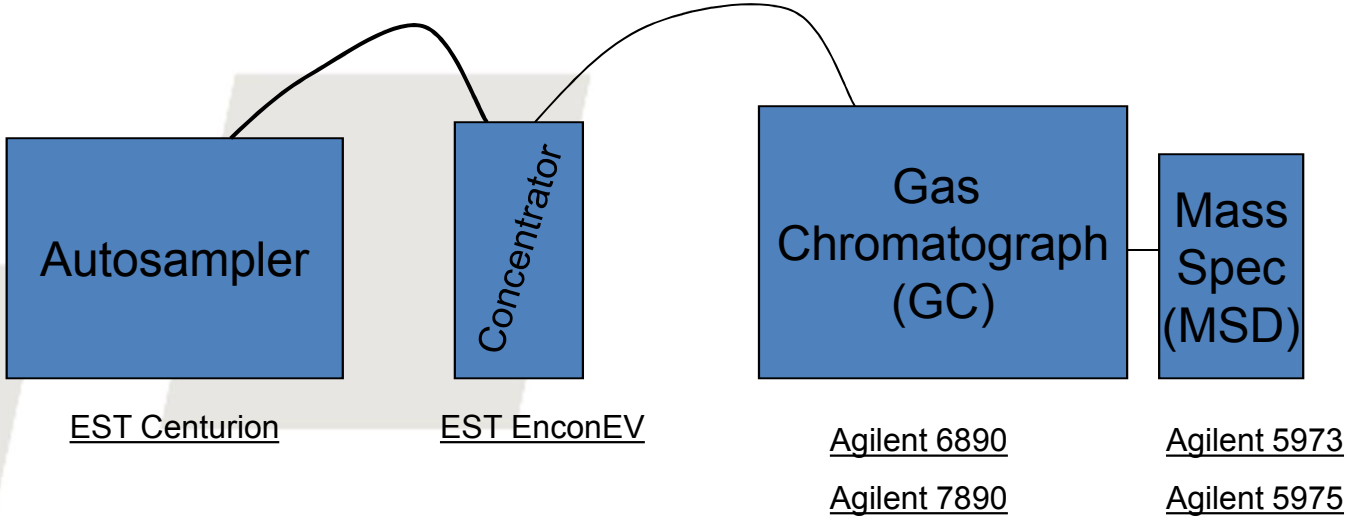
Basics

EST analytical

# System Configuration

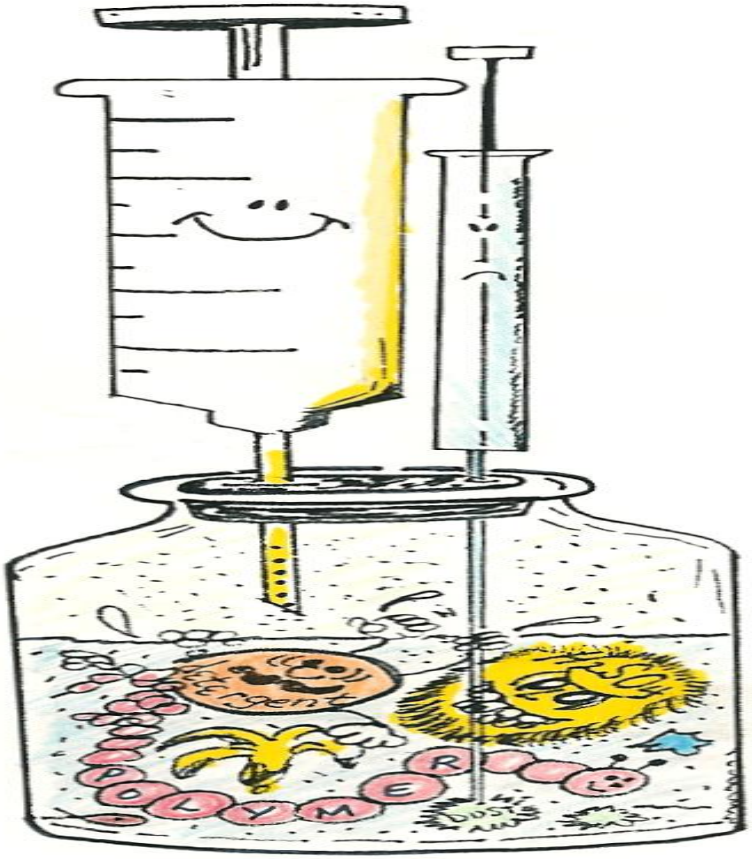



VOC System Configuration Options with EST Analytical Products

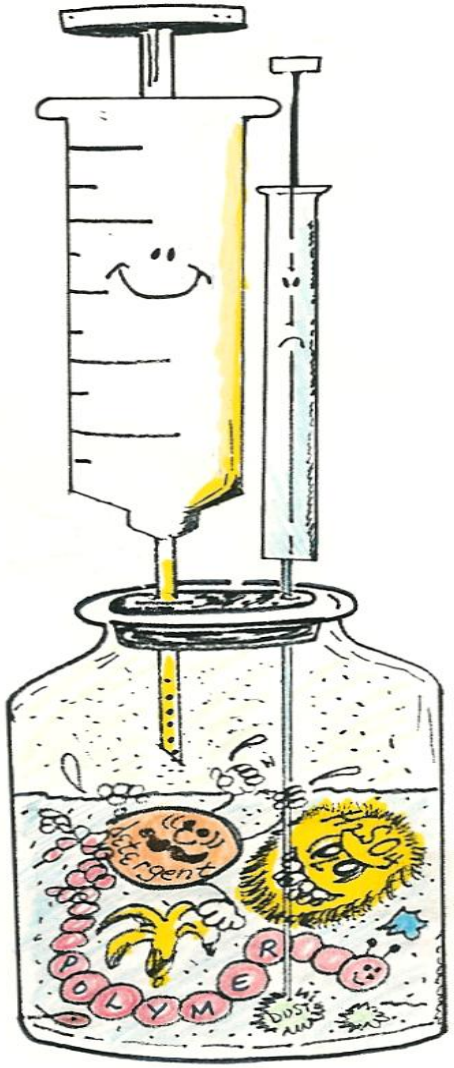
# Definition of VOC

- A volatile compound is any compound that has a boiling point below 180 deg C.
- Preferred for Purge and Trap (P/T)
  - Low boiling point
  - Insoluble or slightly soluble in water

# Analytical Evaluation of various Headspace Vapor Injection Techniques



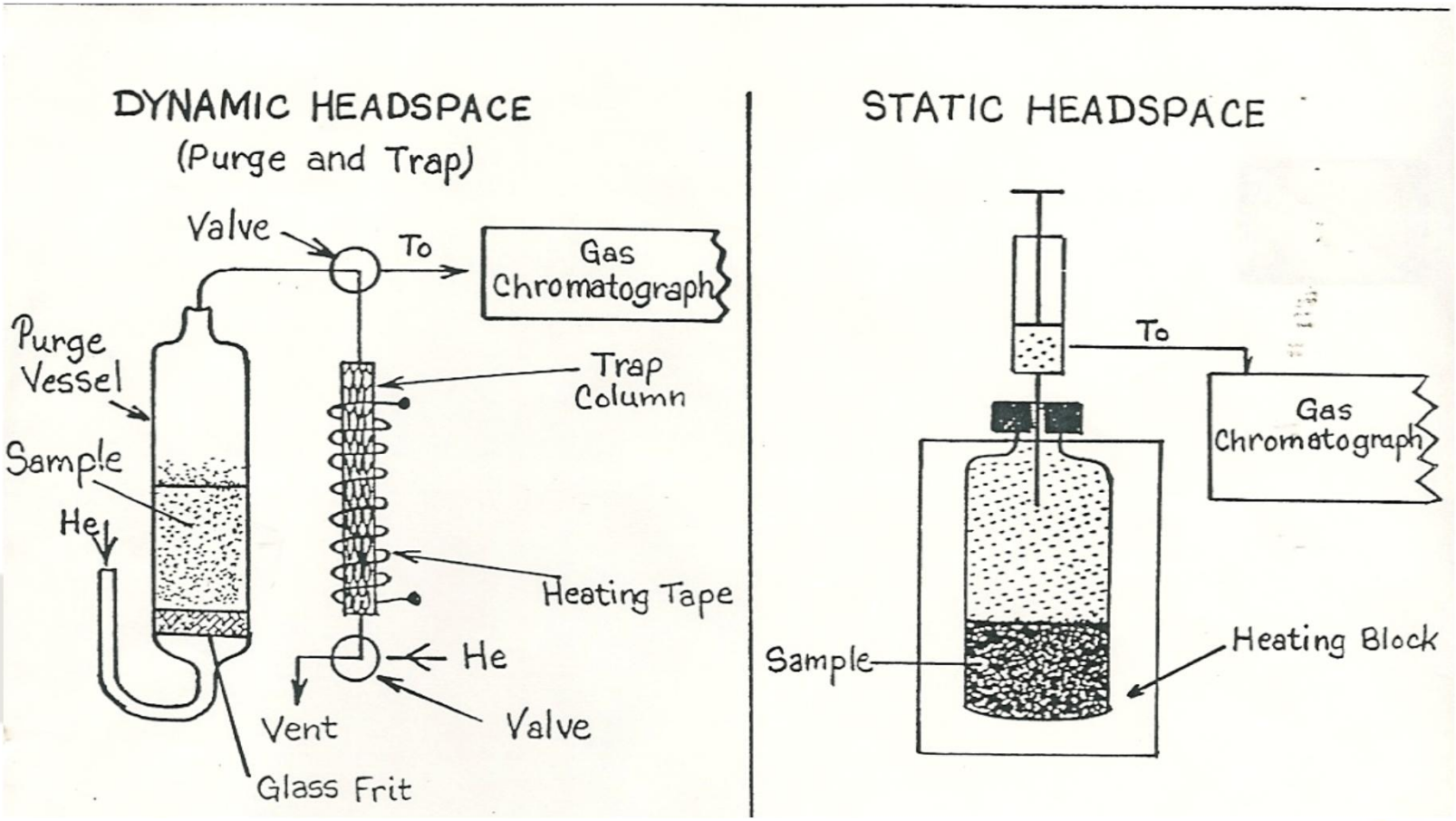
# Headspace vs. Direct Injection




1. Perfect filter
2. High sensitivity
3. Superior versatility
4. GC protection
5. Excellent repeatability

# Dynamic and Static Headspace

# Dynamic and Static Headspace



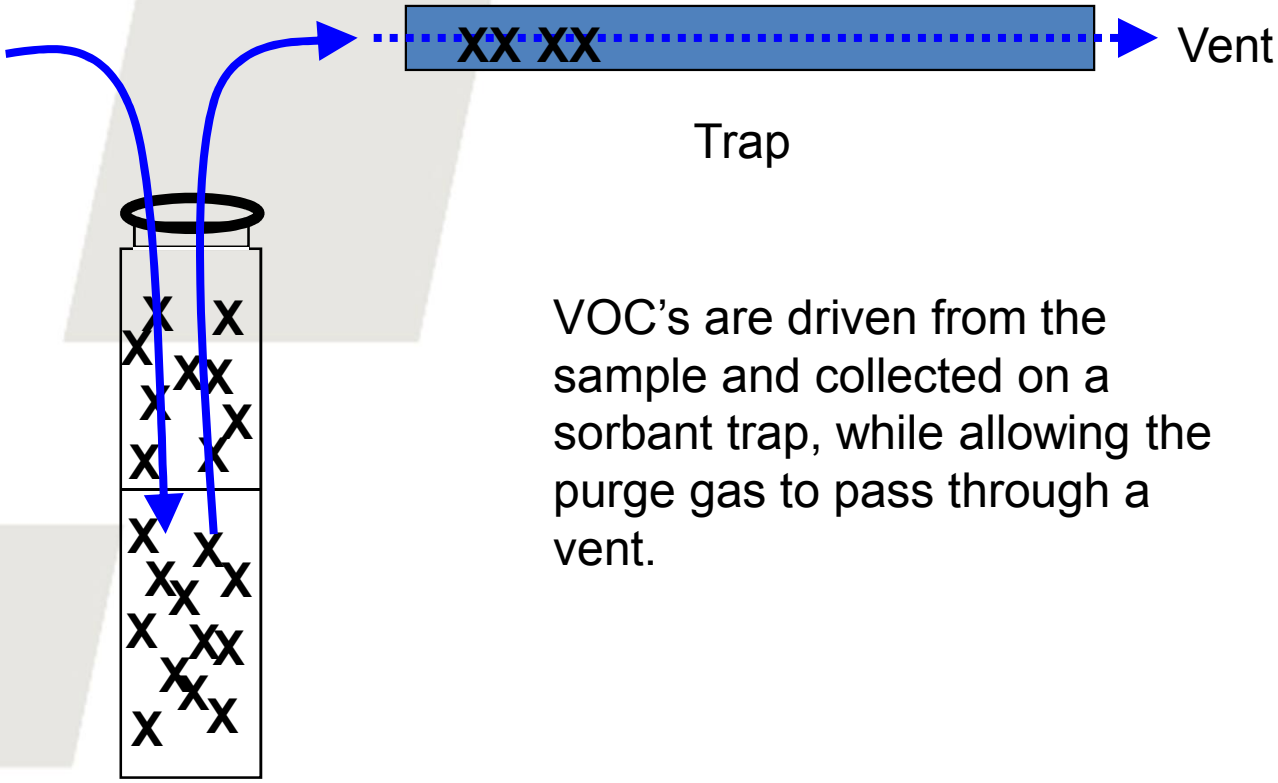
# Differences in Techniques

- Purge and Trap
  - Gas Extraction
  - More Water transferred to GC/MS
  - Chance for a “foaming sample”
  - GC could be waiting for P&T
  - Some Carry-over
- Headspace
  - Heated extraction
  - Less water transferred to GC/MS
  - No chance of a “foaming sample”
  - Always ready when GC is ready
  - Little Carry-over

# Why Purge and Trap?

- Increased Sensitivity
  - Provides a means to deliver increased mass quantities of VOC's onto a GC column.
- Inability of GC Applications to tolerate water injections.
  - Many columns and detectors are adversely affected by the presence of water.
- Delivers sample in a vapor form.

# Basic Operation – Step 1

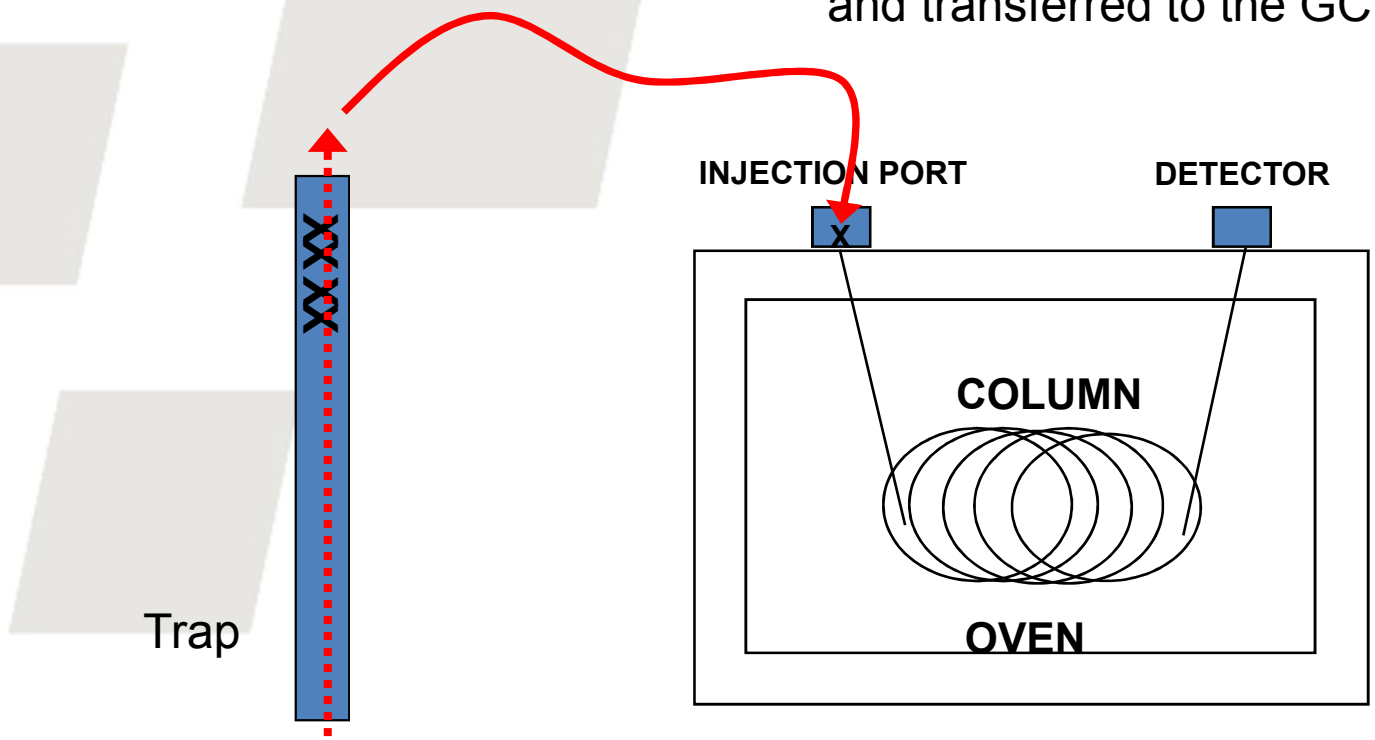



VOC's are driven from the sample and collected on a sorbant trap, while allowing the purge gas to pass through a vent.

Purge Gas

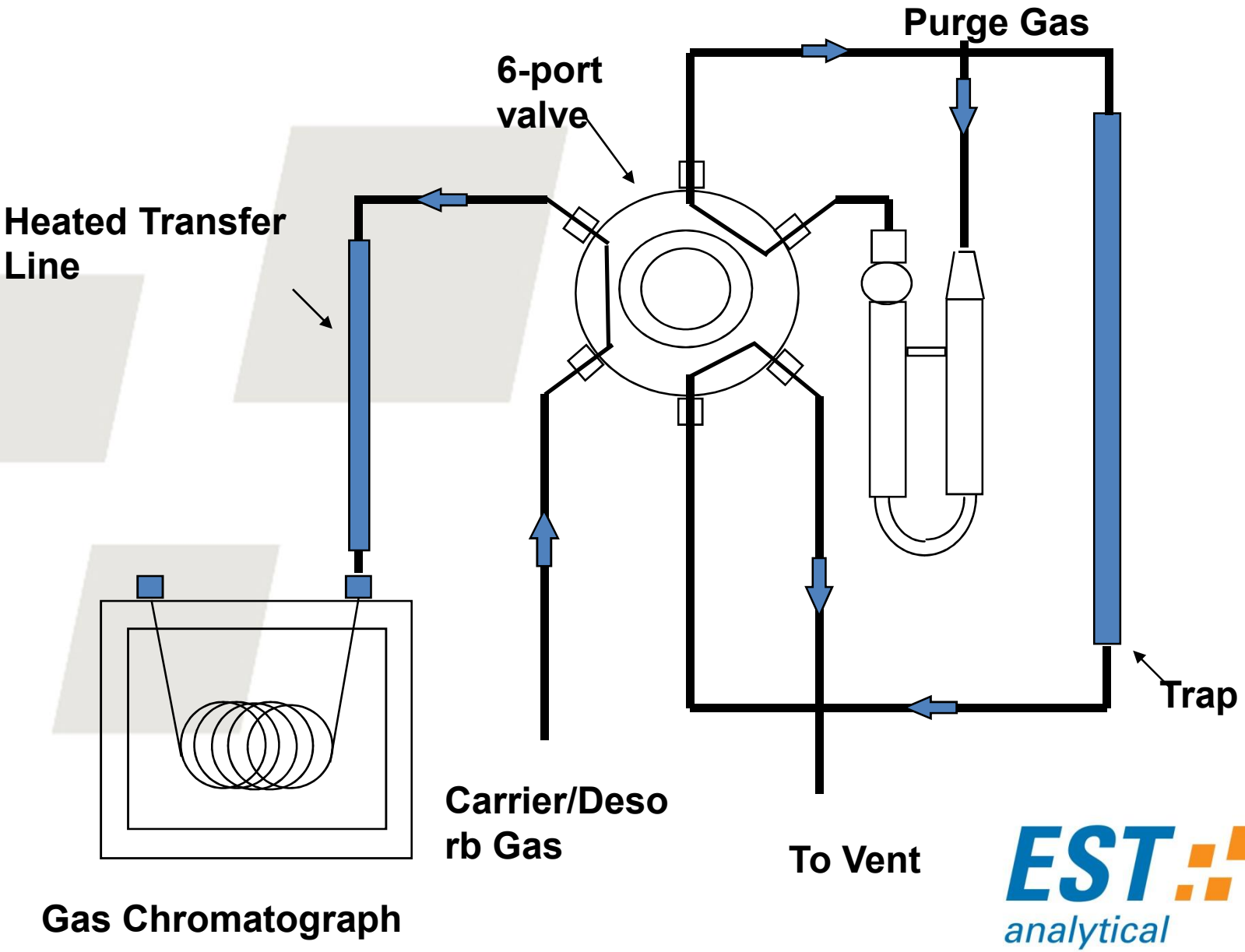
# Basic Operation – Step 2

The trap is heated and the VOC's are backflushed off the trap by the carrier gas and transferred to the GC.




Desorb Gas

# Basic P/T Flow Path



# Basic Operation

1. A measured amount of sample is placed in a purge vessel and purged with an inert gas.
2. The volatile analytes (VOC's) are driven from the sample and collected on a sorbant trap, while allowing the purge gas to pass through a vent.
3. The trap is heated and the VOC analytes are backflushed (**Desorbed**) off the trap by the carrier gas and transferred to the GC.
4. Once the analytes pass through the inlet and enter the column, separation and detection is performed by normal GC operation.

# Headspace Equilibrium

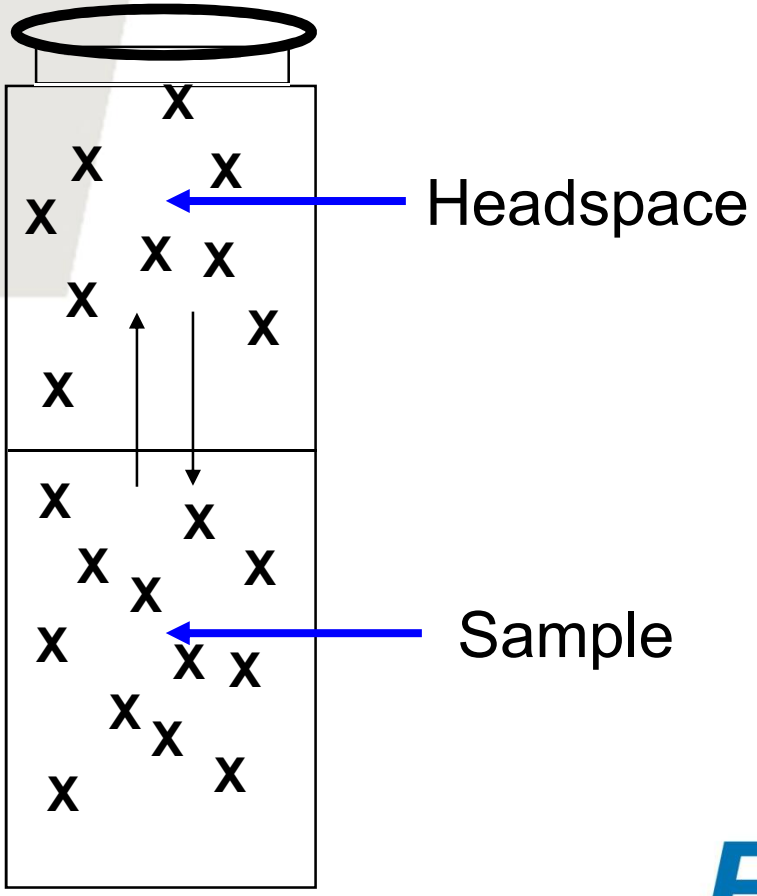
Purge and trap is based on the science of headspace equilibrium. It is this process that allows VOC's to be extracted from the sample.

Headspace is defined as the vapor space above a sample.

VOC's, given time, will migrate out of the sample and into the headspace until an equilibrium is established.

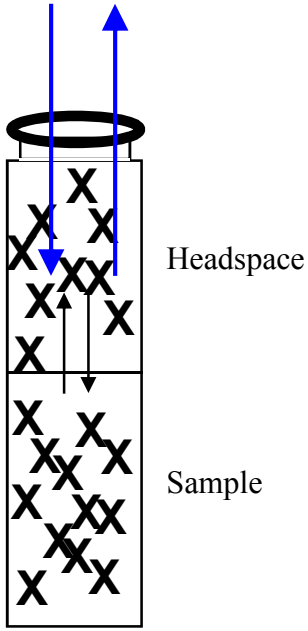
In other words, headspace equilibrium is the result of equal concentrations of VOC's in the sample and the headspace.

# Illustration of Headspace Equilibrium



# Gas Extraction

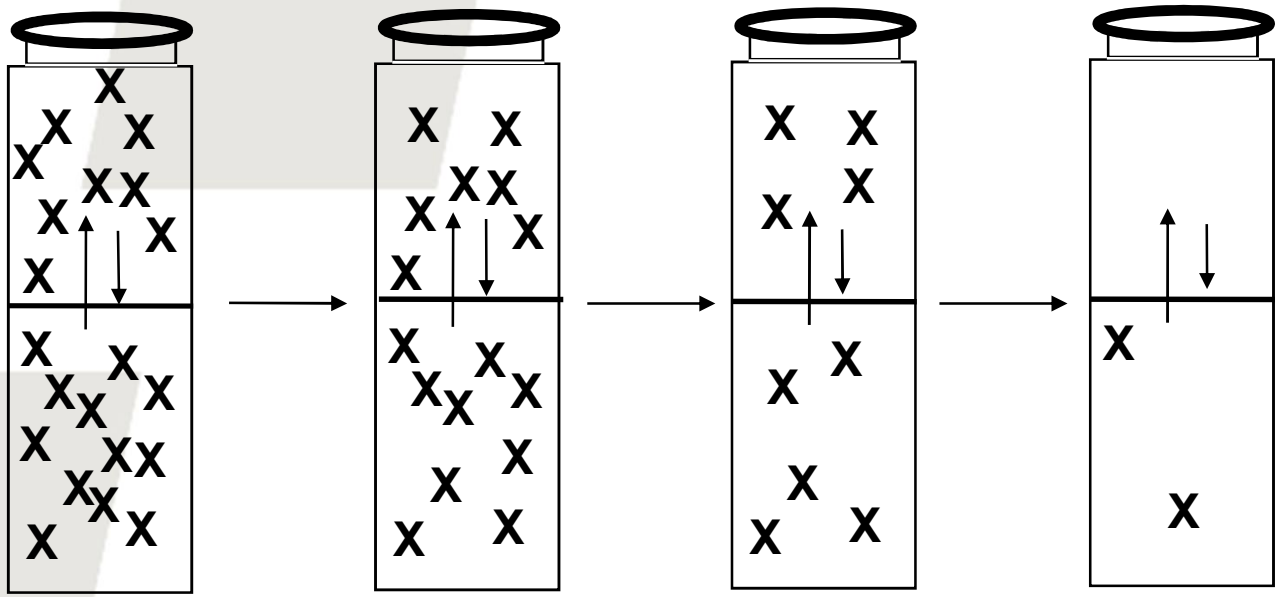
Purge and trap sample analysis is actually a gas extraction, rather than a static headspace technique described by headspace equilibrium.




Gas extraction refers to the process of continually sweeping the headspace with an inert gas, thus reducing the vapor pressure above the sample.

The reduction in vapor pressure above the sample encourages the migration of VOC's into the vapor phase while eliminating migration from vapor phase to the liquid phase.

# Illustration of Gas Extraction



# Purge Efficiency

Many factors determine how well the VOC's are removed from the water or sample matrix. We will now review these factors that effect the ability of the VOC analyte to transfer from the liquid phase to the gas phase.

Purge Efficiency = The percentage of VOC's transferred from the liquid phase to the vapor phase through the gas extraction process.

# Factors Determining Purge Efficiency

- Vapor Pressure
- Solubility
- Temperature
- Sample Size
- Purge Volume
- Type of Purge Method

# Effects of Vapor Pressure

- The greater the vapor pressure the greater the purge efficiency.

- High vapor pressure analytes migrate into the vapor phase rapidly due to their preference to exist in a vapor state.
  - Example – Dichlorodifluoromethane – high purge efficiency.

# Effects of Solubility

- The greater the solubility in the sample matrix, the lower the purge efficiency.

- Example: Methanol is very soluble in water and the purge efficiency is about 10%. This is the primary reason most VOC stds are prepared in methanolic solutions.

# Effects of Temperature

- The higher the purge temperature, the greater the purge efficiency.
- Increasing the purge temperature, increases the vapor pressure of the VOC's in the sample matrix. (See Effects of Vapor Pressure)
  - Note: For each 10 deg C rise in purge temperature, the amount of water transferred doubles.

# Effects of Purge Volume

- Defined as the total volume of gas used to purge a sample.
- Increasing the purge volume, increases the purge efficiency.
- Purge for 11 min at 40ml/min = 440 ml purge vol

Note: When increasing purge volume, a point is reached where the efficiency gain is insignificant and time required becomes too lengthy.

# Effects of Sample Size

- Increasing sample size actually reduces purge efficiency.
- Large sample volumes require more purge volume to achieve equivalent purge efficiencies to standard sample volumes.

Note: Sensitivity is increased due to increased ng of VOC's transferred.

Equivalent purge volumes result in a 70 to 80% increase in sensitivity with 100% increase in sample size.

# Effect of Purge Method

- Frit Sparger
- Fritless Sparger
- Needle Sparger

Purge Efficiency

Increasing the amount of purge gas which comes into contact with the sample increases purge efficiency.

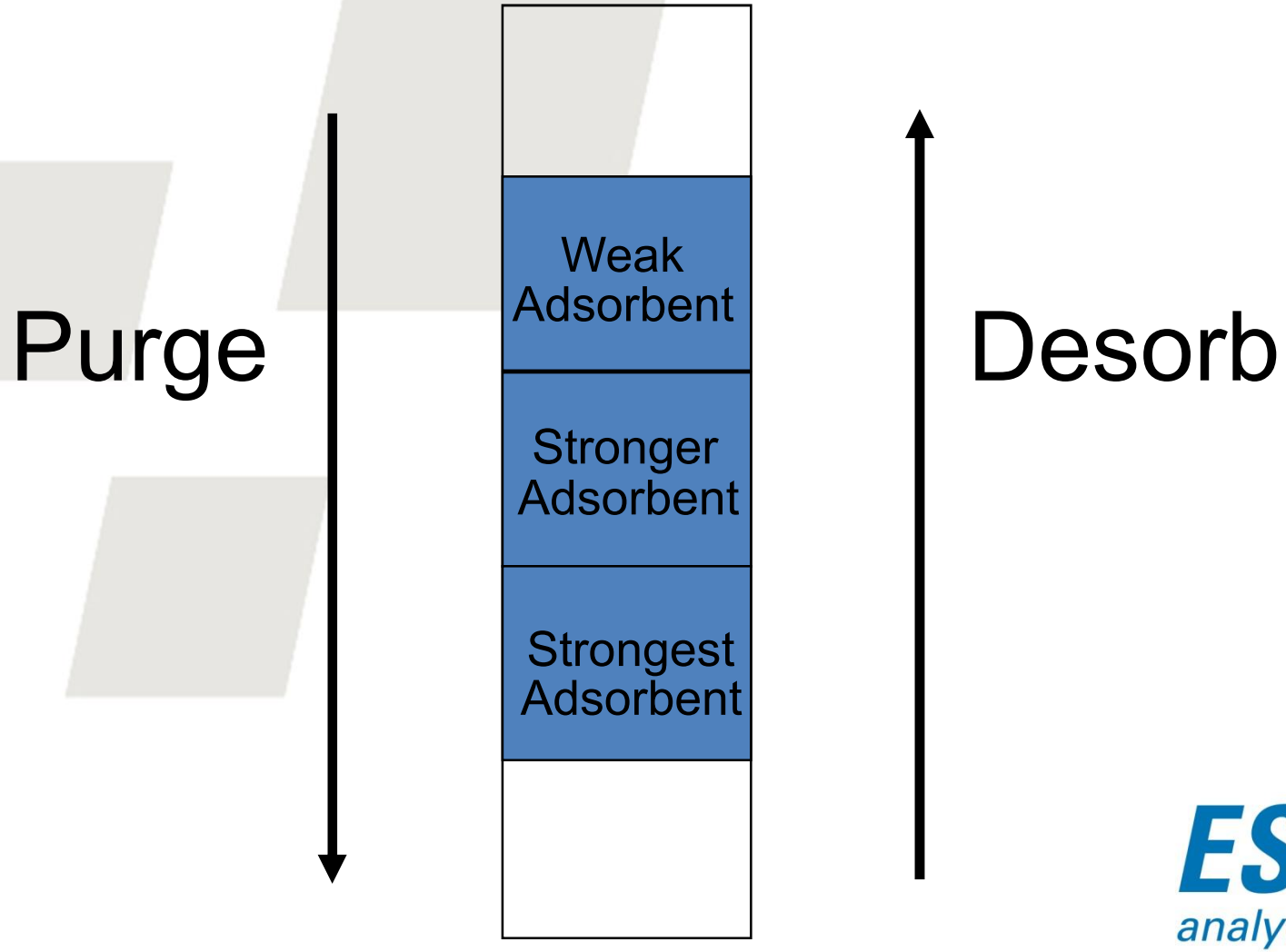
# Review of Purge Efficiency

- Vapor Pressure – High pressure increases efficiency.
- Solubility – Higher solubility decreases efficiency.
- Temperature – Higher temperature increases efficiency – but also increases water transfer.
- Purge Volume – more purge gas increases efficiency
- Sample Size – Greater sample size reduces efficiency if purge volume stays the same.
- Purge Method – Frit sparger is the best technique for the highest efficiency.

# Requirements of a Trap

- Must retain analytes of interest
- Allow oxygen and water to pass through
- Release analytes quickly and efficiently
- Remain stable and not release VOC's upon heating
  - Tenax will release BETX when over heated
- Low reactivity

# Trap Adsorbent Packing



# Common Trap Adsorbents

- Tenax
  - Excellent for non-polar analytes
  - Most common
  - Hydrophobic
- Silica Gel
  - Stronger sorbant than tenax
  - Used in conjunction with tenax
  - Traps polar compounds
  - Hydrophilic
- Carbo Traps
  - Graphitized carbon black
  - Stronger sorbant than tenax
  - High operating temperature
  - Hydrophobic

**Note: - Commonly used traps are a combination of these adsorbents.**

# Common Trap Types

- Trap #1
  - Tenax
- Trap #3
  - Tenax
  - Silica Gel
  - Charcoal
- Vocarb 3000
  - Carbopak B
  - Carboxin 1000
  - Carboxin 1001

# Breakthrough

Note: Potential problem with large purge volumes.

Breakthrough refers to the effect of large purge volumes on retention of VOC's within the trap adsorbent.

When the purge volume is too great, VOC's may pass through the trap and out the vent.

Results in either reduced recovery or complete loss of target analytes.

# Concept of Breakthrough