Real-Time Detection: 1953

Sampling
Gases and Vapors

**Gas:** A state of matter characterized by very low density and viscosity...ability to diffuse readily into other gases, and ability to occupy with almost complete uniformity the whole of any container.

**Vapor:** An air dispersion of molecules of a substance that is a liquid or solid in its normal state (i.e., at room temperature and 1 atm)

Hawley’s Condensed Chemical Dictionary
Sampling from the Gas Phase

Sampling from gas phase involves diffusion—the velocity of airstream sampled must be low enough to allow diffusion of analyte onto the surface of sorbent before contaminated air passes through tube.

High surface area sorbent is better.

Flow rates for gas phase sampling are frequently low (<0.1 liter/min), although this varies.

“Passive dosimetry” relies completely on diffusion (no airflow through sorbent) - sampling rate for given analytes (mL air/mil) determined empirically.
Diffusion in Gas Phase Sampling

Air Flow

Extraction from gas phase

Solvent desorption

Desorption for Analysis
Sampling Tube Sorbents

Charcoal: activated charcoal is the most widely used solid sorbent in IH applications - nonpolar

Silica gel: polar, hygroscopic material - humidity is important factor

Porous polymers: e.g. “Tenax” a polymer of 2,6-diphenyl-p-phenylene oxide - high thermal stability, less reactivity, also less surface area compared to charcoal

Coated materials (on-tube derivatization): e.g. aldehyde collection with coated resin
Charcoal Tubes

Coconut shell carbon often used -high surface area in microporous structure, very non-polar, also somewhat reactive (limits usefulness with reactive compounds, e.g., aldehydes), has high capacity
Impingers

Filter (traps aerosol)

Impinger (traps gas phase contaminants)

Impinger use is currently limited: solvents in glass sampling devices for assessment of worker exposure make IHs nervous
Impingers

Smith-Greenburg: 1 ft³ (28.3 L)/min

Midget: 0.1 ft³ (2.83 L)/min
Passive Samplers

Assumption: infinite analyte concentration gradient from workplace air to sorbent bed, **Ficks’ Law of diffusion** rates applies (holds until sorbent nears saturation)
What is a Diffusive Sampler?

It is an air-sampling device that samples at rates controlled by molecular diffusion of gases and vapors through a membrane and a static air layer without the use of a sampling pump.
Advantages of Diffusive Sampling

- Convenient, no sampling pump
- Small and intrinsically safe
- Can be used by relatively untrained personnel
- Promoted as equivalent, alternative, supplemental to active sampling
Derivatization: how and why

Why?

Trap active analytes (e.g., aldehydes)

Tame poor analytes (often to lower boiling point for improved GC, e.g., methylation of organic acids)

2-Hydroxymethylpiperidine + Aldehyde → Stable derivative

NIOSH Method 2539, Aldehyde screening uses resin particles coated with 2-hydroxymethylpiperidine
Important Sample Collection Terms

Breakthrough

Sorbent tubes have front and back sections - breakthrough is defined as collection of >10% of front section mass in rear section, caused by sampling too rapidly or saturation of sorbent material.

Collection Efficiency

The ability of sorbent material to scrub analyte from sample stream - effected by temperature, humidity, and presence of other contaminants.
Sampling Tube Anatomy

glass wool separates front & back sections of large Tenax tube

Dark foam rubber separates front & back sections of small Tenax tube

dark foam rubber separators not visible in large charcoal tube

air flow direction (front to rear)
Desorption

Desorption Efficiency

*Refers to the ability to remove the analyte from the sorbent material, given in terms of % recovered from a spiked tube*

Solvent choice

*CS₂ is frequently used to desorb non-polar analytes from tubes*

*CS₂ is very non-polar*

*CS₂ gives very little signal with flame ionization detector (FID), a common GC detector for organic vapors*
A Tale of Two Analytes

\[ \begin{array}{c}
\text{H}_3\text{C} & \text{C} & \text{C} & \text{H}_2 & \text{C} & \text{C} & \text{CH}_3 \\
\text{H}_3\text{C} & \text{C} & \text{C} & \text{H}_2 & \text{C} & \text{C} & \text{H}_2 \\
\end{array} \]

**n-Hexane**

**NIOSH Method 1500 “Hydrocarbons, 36-126°C”**

- Coconut shell charcoal, 100 mg front/50 mg rear
- GC/FID, CS\(_2\) desorption
- Sampling flow rate 0.01-0.2 L/min

mw: 86g/mole
bp: 68.7 °C

**Methanol**

\[ \begin{array}{c}
\text{H}_3\text{C} & \text{—OH} \\
\end{array} \]

**NIOSH Method 2000**

- Silica gel, 100 mg front/50 mg rear
- GC/FID, H\(_2\)O/isopropanol (95:5) desorption
- Sampling flow rate 0.02-0.2 L/min

Mw: 32g/mole
bp: 64.5 °C
A Tale of Two Analytes

**n-Hexane**

mw: 86g/mole  
bp: 68.7 °C

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H₃C—OH  
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NIOSH Method 2000

Silica gel, 100 mg front/50 mg rear  
GC/FID, H₂O/isopropanol (95:5) desorption  
Sampling flow rate 0.02-0.2 L/min
Filtration

Trivia:

PVC vs. MCEF
Colorimetric Tube Detection

“Hoolamite“ (I$_2$O$_5$ + fuming sulfuric acid) for detection of CO in the 1920s, first described by Hoover and Lamb - still used for CO detection by most major tube manufacturers.

NIOSH began certifying detector tube performance in 1973: ±25% at 1, 2, and 5x test standard, and ±35% at 0.5x.

NIOSH exited this area in 1983, and SEI (non-governmental institute) began 3rd party program to fill this void.
What is a detector tube?

• An hermetically sealed glass tube containing an inert carrier material which is impregnated with one or more chemicals changing color when a specific type of contaminant is present.

• The length of stain indicates the amount or concentration of material present.
hermetically sealed glass tube
end of color stain
P/N
no. of strokes
tube name and type
quality control number
airflow direction
Advantages and Limitations of Colorimetric Tube Detection

Advantages: no batteries, no calibration, always ready to use

Limitations: cross-sensitivities, no alarms, no datalogger, must understand the basis of color change, some subjectivity involved in reading a colorimetric tube
Detector Tube Certification Program

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