Sampling and Analysis for Organic Gases and Vapors

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Introduction

- Quick review of Organic Chemistry
- Classes of Organic Compounds
  - Covalent bonding of CHOX Molecules

Classes of Organic Chemicals

- Functional Groups: HCs (Aliphatics, Aromatics, Halogenated), alcohols, acids, carbonyls (aldehydes, ketones), amines, sulfurous, polyfunctional, monomers, polymers

Air Concentrations

- Measured in terms of parts per million (ppm)
- or Milligrams per cubic meter (mg/m^3)

Sampling: Reference

Air Sampling Instruments,
ACGIH, Chapter 17, 1995

Collection (Perkins 468-473)

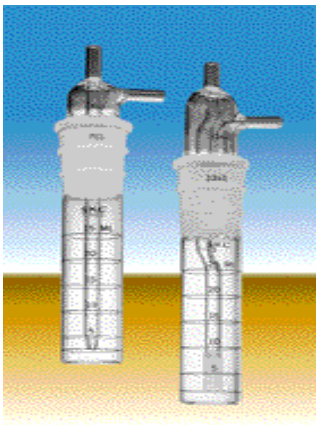
- **From Air (Grab Samples)**
  - **Bags,**
  - **Tanks,**
  - **Bottles,**
  - **Flasks,**
  - **balloons,**
  - **canisters**
- **vs. Bulk Samples**

Bags

Concentration Methods of Collection

- Trapping in Cold traps (ASI, Ch. 17)
- Impingers and Bubblers (Perkins 474-478)
- Adsorbent Tubes (Perkins 426-459)
- Adsorbent Badges (ASI, Ch. 17)
- Reactive Chemical Collectors

Impingers and Bubblers



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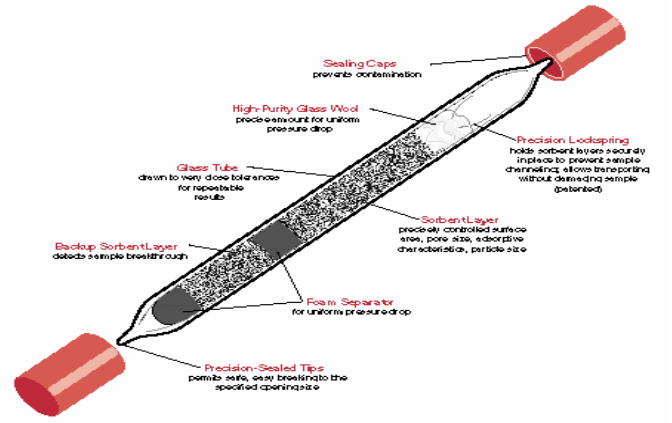
Adsorbent Tubes

- Tube

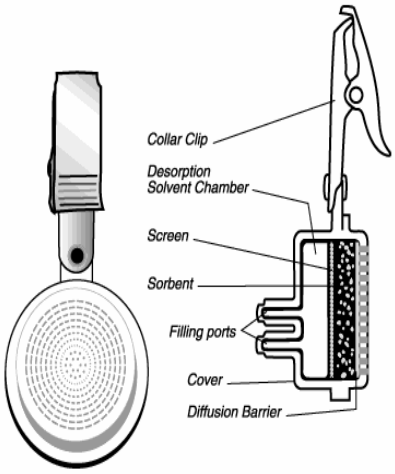


Passive Devices: Reference

- (Perkins 480-486, 500-505) (Air Sampling Inst., 377)

Passive Devices

- Diffusion Driven Monitors
- Laws that govern their sampling rates



Passive Devices

- Formaldehyde Sampler

Chemical Reactants

- React and retain the Vapors from the air
- Convert to a non-volatile form
- Can be reversible or non-reversible
- Can be suspended in liquid or solid media

Analysis

- The collected and concentrated analytes are analyzed by standard instrumental techniques.

Wet Chemistry and Spectrophotometry

- (Perkins--page 379)
- Colorimetry
  - Transmittance vs. Absorption
    - A = - log 1/T
  - Linearity of Concentration vs. Absorbance
    - C = abC
  - Instrumentation: Sources, Optics, Detectors, Monochrometers

Wet Chemistry and Spectrophotometry (Continued)

- Colorimetry (Cont'd)
  - **Examples (Ozone, NO2, Formaldehyde)**
  - **Samples vs. Standard Curves and Regression Equations**
  - **Visible light and UV Light**

Fluorimetric Analysis

- Analytes reacted with fluorescent dyes
- Fluorescence proportional to Concentration
- Quite Specific to the Analyte
- Very sensitive (and Low Detection Limits)
- Instruments designed to ignore incident radiation but to sense fluorescence radiation
  - More energetic exciting / lower energy emitted

Infra Red Spectrophotometric analysis

- (Perkins pages 379-381 & 610-626)
  - Collected Samples of Air
    - by Grab Sample or continuous Flow
  - Utilize either Dispersive or Non-dispersive
  - Employs long path amplification

Characteristics of Infra Red Absorption Spectra

- Molecular Bonds in Motion
- Broad bands of absorption in the IR Region
  - Range from 2 to 16 µ (600 to 4000 cm^{-1})
- Absorption Bands relate to the bond energy of the molecules
- Spectra are characteristic of each compound or class of compounds

Infra Red Instrumentation

- Components--Sources, Detectors, Cells, Windows, Monochromator
- Non-dispersive Field Instruuments
  - Example:
    - Horiba--Carbon Dioxide Monitor

Infra Red Instrumentation

- Field Instruments--Dispersive
  - Single Beam, Long Cell, Filter Wheel, Source
  - Stable, low resolution, Qualitative, Quantitative
  - Now Electronically Controlled and readout
  - **Example: MIRANS**

Infra Red Instrumentation

- Highly Versitile
- Many Applications
- Instrument of choice for some Applications

Infra Red Instrumentation

- Laboratory Instruments--Bench Top Size
  - High Resolution, Large, complex
  - Wavelength Dispersive--Double beam
    - large, slower, earlier applications
  - FTIR--Fourier Transform IR
    - Faster, Multiple Scans, Single Beam, Highest Resolution

Example IR Spectra

Application of Infra Red

- Identify Unknown Contaminants
- Detect Contaminants in the Field
- Quantify Compounds in Collected Samples
- Resolve Mixtures
  - Unique Absorption Peaks can identify and quantify compounds in simple mixtures
- Long Path & Open Path Monitoring

Gas Chromatographic Analysis for Volatile Organic Compounds

Reference:
(Perkins pgs 370-376)

Sample Collection for GC Analysis

- Desorbed Tubes and Adsorption samplers
  - Solvent or Heat Desorption
  - Injection in the Gas Stream of the GC

GC Instrumentation

- Sample Injection
- Precision Gas Flow Control with Minimum Volume Injection
- Columns (determine separations)
- Detectors (respond to classes of compounds)
- Temperature, Pressure and Flow Control

Characteristics of Chromatograms

- Strip Chart or Integration by Computer
- Analog Plots of Detector Response vs. Time
- Retention Times (Characteristic of Compounds)
- Quantitation by Peak Height or Area
- Computer Integration and Control

Gas Chromatographic Analysis

- Form and Calculation of Results: Standards Relative to Samples
  - Response is proportional to Concentration
  - Standard curve or Regression Curve is prepared from the response of a series of standard concentrations
  - Concentration of Sample is calculated from the comparison to the standard cuurve.

Field Portable GCs

- Reference:
  - (Perkins, pages 649-658)
- Small, transportable
- Limited Application
- Special Purpose

Liquid Chromatography

- High Pressure Liquid Chromatography (HPLC), Perkins pg. 372
- Sample Collection: Adsorption or Chemical Trapping

High Pressure Liquid Chromatography

- Instrumentation
  - Liquid flow and pressure control
  - Liquid chromatographic Columns
  - Detectors--UV, Visible, Fluorescent, Refractive Index
  - Analog Chromatogram Readout

High Pressure Liquid Chromatography

- Solvents
  - Liquid medium for analytes transport through Column
  - Solvent characteristics can determine the resolution of the compounds
  - Programming of solvent mixtuures is used to improve separation and resolution of complex mixtures

High Pressure Liquid Chromatography

- Integrated Results
- Analog Chromatograms
- Peak areas proportional to concentration
- Retention times characteistic of specific compounds

Gas Chromatography/Mass Spectroscopy, (Perkins pg. 374)

- Used for Identification and Quantitation of Trace Contaminants
- Combination of GC and Mass Selective Detection
- Role in Complex Mixtures

GC/MS

- Mass Spectra
  - Fragmentation of Organic Molecules into Recognizable Fractions
  - Characteristic and Unique for Each Compound
  - Nature of Mass Spectra
  - Libraries of Spectra and Computer Matching

GC/MS

- Instrumentation
  - GC
  - Interface
  - MS
    - Quadrupole
    - Time of flight
    - Magnetic focuussing

HPLC/MS

- Applications
  - Utilized for the separation and analysis of semi-volatile compound from mixtuures
  - Examples
    - Pesticides
    - Monomers
    - Oils
    - Biological Metabolites

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