

# Sampling for Gases and Vapors

Evaluating the Occupational  
Environment  
Spring 2004

## Gases and Vapors

- Gases: don't exist in liquid state at STP
  - e.g.: nitrous oxides, ozone, carbon monoxide
- Vapors: may exist in liquid state at STP
  - e.g.: toluene, benzene, other solvents; mercury
- Distinction moot unless liquid is sprayed.

## Methods of Sampling

- Grab sampling
  - Evacuated flask: heavy walls, air removed. A valve is opened to allow workroom air to fill the flask. Analysis in laboratory, or with suitable field instruments.
  - Wash bottle, carboy, or other rigid-walled container. Flush container with workroom air to obtain a sample. Flush the bottle with 10 - 15 times the bottle volume. Water filled bottle is alternative.

## Methods of Sampling

- Plastic bags, made of Tedlar, polyester, polyvinylidene chloride, other plastics. Useful sizes 5 - 15 L. Bags must be tested for leaks before use; polymer selection will consider storage, permeability, and reaction with bag walls and memory effects.

## Methods of Sampling

- Continuous (Integrated) sampling
  - Absorbers: dissolving gas in a liquid. Absorption theory states that gases and vapors will go into solution up to an equilibrium concentration. Reducing volatility (lower T) and increasing solute volume (bubblers) increases equilibrium concentration. These factors also serve to increase sample efficiency. Can also alter design of sampler.

## Methods of Sampling

- Continuous (Integrated) sampling
  - Chemical reactions are often used to stabilize substance before it leaves the liquid. (reduce volatility, e.g.)

## Methods of Sampling

- Samplers: gas washing bottles (impingers), fritted bubblers, spiral and helical absorbers, and glass-bead columns.
  - Examples: MeOH, ButOH in H<sub>2</sub>O; Esters in alcohol examples of use for simple gas bubble (midget impinger). Reactive samplers also use the midget impinger, e.g. TDI hydrolyzed to toluene diamine; ammonia neutralized by sulfuric acid. Cold traps use acetone in dry ice.

## Methods of Sampling

- Solid Adsorbents (gas onto a solid)
  - Activated charcoal
    - can be efficiently desorbed with carbon disulfide. Optimal for nonpolar solvents.
    - Method
    - Breakthrough

## Methods of Sampling

- Silica gel
  - Polar contaminants: amines, some inorganics
- Other sorbants include synthetic polymers like XAD and Tenax. Consistent in quality but more expensive. Useful for low concentrations and unusual chemicals.

## Methods of Sampling

- Thermal desorption is gaining popularity, since it avoids use of CS<sub>2</sub>; accepted in Europe, slowly gaining acceptance in the US.

## Calculations

- Calculations: to find concentration:

$$C = \frac{m_1 - m_{blank}}{SExV} \text{ (impinger)}$$

$$C = \frac{m_1 + m_2 + m_{blank}}{(DExV)} \text{ (sorbenttube)}$$

$$C_{corr} = C \left( \frac{760}{T} \right) \left( \frac{T}{298} \right)$$

## Diffusive Samplers

- Depend on flow of pollutant across a quiescent layer of air, or a membrane. Synonymous with passive dosimeter. Uses no pump to draw air across adsorbent.
- Diffusion depends on well-established rules from physical chemistry, known as Fick's law. Two equations are used to predict solvent uptake

## Diffusive Samplers

$$F = \frac{D(C_a - C_o)}{L}$$

$$\frac{M}{At} = (D) \left( \frac{C_a - C_o}{L} \right)$$

$$Mass = \frac{D(A)}{L} t (C_a - C_o)$$

- F is flux units mg/cm<sup>2</sup>/sec
- L is length of diffusion path, cm
- D is diffusion coefficient, cm<sup>2</sup>/sec

## Diffusive Samplers

- Equations allow prediction of how much mass will be collected by the sampler; sample rate and efficiency are dictated by design of the device.

## Diffusive Samplers

- Factors affecting performance:  
Independent of pressure, proportional to  $T^{1/2}$ . Humidity may reduce efficiency of charcoal samplers. Transients (peak exposures) do not affect performance, so long as sampling time is more than several minutes. Face velocity not too low or too high.

## Diffusive Samplers

- Calculation

$$C = \frac{m_1 + m_2 - m_{blank}}{DE \times V}$$

## Real Time Monitoring

- Continuous monitors measure and report instantaneous observations of concentration. Supplemented by a means of recording data, a plot of air concentration vs. time can be generated.

## Real Time Monitoring

- Technologic developments
  - Digital meters replacing analog meters
  - Data logging built in
  - Miniaturization
  - Multipoint monitoring

## Stationary Monitoring Systems

- Uses
  - Warning or alarm systems
  - Monitor operation of controls
  - Identify problem areas
  - Generate a record of concentration
  - Define exposure problems

## Real Time Monitoring

- Description
  - Multipoint monitor vs. single point
  - Sensor(s)
  - Response time

## Advantages, Disadvantages

- Real time data at several locations
- Capable of warning of leaks before personnel are injured
- Provide history of exposure data
- Expensive
- Complicated
- Area monitor (not personal)

## Personal Monitoring Systems

- Personal dosimeters: data logging, computer interface, instantaneous response
- Personal alarm monitors: intended to warn if air concentrations get too high.

## Advantages, Disadvantages

- Portable
- Easy to use, stable and accurate
- Can be specific to vapors of concern
- Can monitor rapidly fluctuating concentrations
- Can provide detailed exposure profile for an individual worker
- Limited number of chemicals can be monitored this way.
- Increased maintenance (over pump/filter)

## Direct-reading Instruments Characteristics

- Specific or nonspecific: advantages and disadvantages to each, depends on the use of instrument

## Direct-reading Instrument Characteristics

- Terms, accessories
  - Remote probes
  - Data storage, transfer
  - Alarm (variable settings)
  - Ease of operation (some devices are complex)
  - Response time (lag time)
  - Saturation
  - Sensor (sensor life)
  - Probe
  - Active/passive collection

## Direct-reading Instruments: Characteristics

- Hazardous atmospheres: instrument should be rated as intrinsically safe, if flammable air concentrations may be encountered. RF shielding may be needed.

## Direct-reading instruments

- Calibration: conduct before each use, preferably with same contaminant as being monitored, else a reliable standard. Use prepared standards, or generate your own. Calibrate flow of pump, if it is included. Calibration of aerosol monitors is more complex; may require factory calibration (periodic)

## Direct-reading Instruments

- Recording data: strip chart recorder; data logger; computer.

## Recording Data

- Strip chart recorder is traditional method. Generates hard copy of instrument response.
  - Chart paper is specific for instrument.
  - Chart speed is constant, used as a timer.
  - Input voltage allows for a range of switch settings; allow for full-scale response at highest anticipated concentration.
  - Modern strip chart recorders: data analysis, programmability.
  - Maintenance: zero instrument before use, check span. Replace paper as needed, check chart speed. Observe performance of the pens.

## Recording Data

- Data loggers allow collection of digitized information. They connect to the voltage output from monitors. Data logger may be contained in monitor, or be a separate unit.

## Recording Data

- require proper connections between monitor and data logger.
- loggers can be programmed to record at specific times, and to analyze data collected.
- Calibration is needed, for monitor/data logger combination.
- Data logger can be connected to a computer or a printer, to generate hard copy. Connection to a computer allows analysis of data, using a spreadsheet. Software packages, knowledge of how to connect devices.

## Recording Data

- Dedicated printers: printers intended for use with specific pieces of equipment. Allows a simple method of generating hard copy, user needs little knowledge of how to connect devices together.

## Principles of Detection

- Electrical Methods: Chemical and/or physical properties change electrical parameters in a gas or liquid. Amount of change is proportional to the concentration of the contaminant.

## Principles of Detection

- Conductivity: nonspecific method; electrolytes in aqueous solution change solution's conductivity. Change is proportional to all ions present. Most useful when one contaminant predominates. Temperature regulation is required. Contaminants: H<sub>2</sub>S, SO<sub>2</sub>, NH<sub>3</sub>. Some devices can detect Cl<sub>2</sub>, CO<sub>2</sub>, and halogenated hydrocarbons.

## Principles of Detection

- Potentiometry (measure potential difference): Gases react with chemicals in solution to change the pH of the solution. pH change is sensed electrically (ion flow); although reaction is not specific, choice of reagents can improve specificity. Contaminants: Carbon monoxide, oxygen, carbon dioxide, many others.

## Principles of Detection

- Voltometry: polarized electrodes. Analyte moves to an electrode, gets oxidized, and resultant current is measured.

## Principles of Detection

- Coulometry: Maintain a current in a cell; chemicals react in solution.  
Contaminants: oxygen, ozone, H<sub>2</sub>S, nitrogen oxides, sulfur dioxide, HCN.

## Principles of Detection

- Ionization: Generate ions in a chamber, measure the number of ions collected on an electrode. Method is nonspecific, in that any chemical species ionized will be measured. Two types: flame ionization detector (FID) and photo ionization detector (PID).  
Contaminants: organic solvents, in a number of ranges (ppm to % LEL).

## Principles of Detection

- Thermal methods: use thermal properties of a gas to measure concentration.
  - Conductivity: Nonspecific method measuring thermal conductivity of a gas.
  - Combustion: Nonspecific method that measures the heat released during combustion. Principle is to measure the change in electrical resistance across a heated filament. Instruments may be refined using particular filaments or oxidation catalysts. Very common detection technique.

## Principles of Detection

- Spectroscopic and Photometric Methods
  - Use of electromagnetic energy (UV, IR, visible) to measure levels of contaminants. Most common method is absorption, but fluorescence, scattering, acoustic techniques are being developed.

## Principles of Detection

- Methods depend on: molecular absorption (energy is absorbed, depending on changes in energy state, or flexing of molecular bonds.); emission (absorbed energy is emitted as energy level drops down, may be induced chemically or photometrically); scatter (bending of incident radiation, or emission at a different wavelength).

## Principles of Detection

- Infrared Photometry
  - Nondispersive: employ a band of IR light, and select regions for analysis by employing lasers (specific wavelengths), selective detectors, or selective filters to tune at specific wavelength. CO<sub>2</sub> is often measured with NDIR.

## Principles of Detection

- Dispersive: employ a grating or prism to separate broadband light into component wavelengths. Instruments can scan across IR region, to analyze for unknown gases.

## Principles of Detection

- Chemical compounds absorb energy at characteristic wavelengths, depending on chemical structure. IR absorption can be used to identify pure chemical compounds, or for air analysis.

## Principles of Detection

- Ultraviolet photometers: measure absorption of UV radiation at particular wavelengths. Select wavelength depending on substance being detected. Mercury absorbs UV at 254 nm. Reduction of UV energy is a measure of mercury concentration.

## Principles of Detection

- Chemi-electromagnetic methods (chemical reaction followed by a measurement of electromagnetic radiation)
  - Colorimetry: Gas is sampled in a liquid or solid matrix, and color change takes place. Choice of reactants can make monitor specific to vapor of concern. Analysis involves selection of a choice of sensing cell and wavelengths to measure. Response time can be quite slow. One commercially available instrument: can measure SO<sub>2</sub>; nitrogen oxides; ammonia, chlorine, TDI, formaldehyde, cyanide, others.

## Principles of Detection

- Photometric (Chemiluminescent): substances are induced to emit electromagnetic radiation
  - Ozone reacts with Rhodamine B (a dye), and light at 585 nm is emitted. This emission can be detected by a photomultiplier tube, and is proportional to the mass of ozone in the detector.

## Principles of Detection

- Ozone reacts with ethylene and nitrogen oxide; each reaction results in specific light emission that can be measured proportionately to the mass of ozone or nitrogen oxide in the system.

## Principles of Detection

- Colorimetric indicators
  - Development of detector tubes
- Colorimetric indicators may use liquid reagents, chemically treated papers or solid reagents. Some simple laboratory methods have been packaged for field use; simple instructions can allow field analysis of reactive chemicals (e.g.: TDI, chromates, nitrogen oxides)

## Principles of Detection

- Chemically treated papers may react with specific chemicals to give a single color change or a range of colors, indicating concentration in air. Sampling by diffusion (may be prone to error) or with use of a pump. Commercial instruments use a paper tape to indicate concentration.

## Principles of Detection

- Detector tubes contain specific chemicals in a small tube; reagents react with chemicals in the sampled air to provide a color change (most commonly length-of-stain indication) to define contaminant concentration.

## Principles of Detection

- Applications: qualitative, quantitative evaluation of workroom air; air pollution studies subject to detection limitation; explosive atmosphere evaluation.

## Principles of Detection

- Because of limitations and sources of error, qualified persons should make interpretations of results; despite simplicity, unskilled users may derive misleading results.