Occupational Health & Safety

- Recognition of Hazard
  - Process information
  - MSDS evaluation (toxicity, VP, OEL etc)
  - Manner of use (intensity and duration)
  - Symptoms
- Evaluation of Hazard
- Control or Prevention of Hazard
- Training of Workers

How Can We “Evaluate” Hazards?
How Can We “Evaluate” Hazards?

- Air Sampling
- Biological Sampling
  - Urine
  - Blood
  - Breath
- Dermal/Surface Wipe Sampling

If You Can’t Sample All the People All the Time…Then What?

- Prioritize Sampling strategy decisions…
  - Toxicity
  - Tendency to become airborne (VP, how used)
  - Amount used
  - Number of people exposed
  - Duration of use
Biological Sampling

- Means to evaluate internal exposure (dose) of worker to chemical agent
  - Measure concentration of chemical in biological media (urine, blood, hair, nails, breath) reflecting:
    - Amount recently absorbed eg. solvents
    - Amount stored in body (body burden) eg. lead, pesticides
    - Amount of active chemical bound to site of action eg. DNA adducts
  - Concentration of metabolites in biological media

- When to use biological sampling?
**When to Use Biological Sampling?**

- When legally mandated (lead)
- When routes of exposure other than inhalation are important
  - skin designation in TLV’s
- When concern about effectiveness of PPE
- If heavy workload potentially increasing inhalation of airborne exposures.
- Documentation of unanticipated exposures esp if no air monitoring

**OSHA Lead Standard**

- Air standard 50 ug/m³.
- If air conc over 30 ug/m³ for more than 30 days per year need to have blood sampling and air monitoring at least every 6 months.
- If blood lead > 40 ug/dl (dl=100ml blood) must have blood sampling every 2 months.
- If blood lead > 50 ug/dl must be removed from exposure until reduced to 40 ug/dl.
  - OSHA requires workers pay and seniority must be maintained for up to 18 months while on medical removal.
ACGIH Biological Exposure Indices (BEI’s)

• 38 substances as of 2002
• Specify time of sampling
  – End of shift, end of workweek, preshift etc
• Blood, urine and exhaled breath
• Background endogenous levels for many

Biological Sampling Examples

• Toluene
  – Toluene in blood …end of shift
  – Toluene in exhaled air…end of shift
  – Hippuric acid in urine…end of shift
• Lead
  – Lead in blood…time not critical
  – Zinc protoporphyrin…time not critical
Why do Air Sampling?

- Evaluate employee exposures
  - Compliance
  - Health complaints
  - Baseline levels
  - Prioritize controls
- Identify tasks or processes as source of peaks
- Evaluate impact of change
  - Process change
  - Engineering controls
- Check before entry (confined space/hazmat)
- Warn of peak release
Sampling involves…

- Sampling strategy
  - Where, when and whom to sample
  - How many and how long to sample
- Interpretation of results
  - Comparison to standards
  - Comparison to previous or published results
- Choice of measurement and analytical method
- Calibration and Quality Control

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Sampling Plans

- Why?
- Where?
- When?
- Who?
- How long?
- How many?
- How use?
Sampling Plans

- **Why?** Compliance/Confined space/Eval control
- **Where?** BZ, Area of operation, General room air
- **When?** Shift, season
- **Who?** Operator, indirect (bystander), remote
- **How long?** Peak vs Task vs TWA….constraints of method
- **How many?** Average? Single point(before/after)
- **How use?** Compare to what?
Sampling involves…

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Info on sample media, sample volume and analytical method

Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
4676 Columbia Parkway
Cincinnati, OH 45226-1998
http://www.cdc.gov/niosh/nmam/nmampub.html

OSHA Analytical Methods Manual
Occupational Safety and Health Administration
OSHA Salt Lake Technical Center
P. O. Box 65200
1781 South 300 West
Salt Lake City, UT 84165-0200

Annual Book of ASTM Standards
American Society for Testing and Materials
100 Barr Harbor Dr.
West Conshohocken, PA 19428
How Long to Sample?

Vol-Min of Analytical Method based on:
- Samples should collect enough analyte to exceed the Limit of Detection (LOD) or Limit of Quantification (LOQ)
  - LOD: the lowest concentration that can be detected; 3 Standard Deviations of Blank value
  - LOQ: the lowest concentration that can be quantified with confidence; 10 Standard Deviations of Blank value

Vol-Max of Analytical Method based on:
- Samples should collect less analyte than the amount producing Breakthrough:
  - the amount of analyte which overloads the collection material resulting in the “escape” of analyte from the sample.
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Formula</td>
<td>C2H4O2</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>60.05 g/mol</td>
</tr>
<tr>
<td>Melting Point</td>
<td>-16.8 °C</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>117.9 °C</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>1.071 g/cm³</td>
</tr>
<tr>
<td>Density</td>
<td>1.071 g/cm³</td>
</tr>
<tr>
<td>Color</td>
<td>Clear</td>
</tr>
<tr>
<td>Odor</td>
<td>Ammoniac</td>
</tr>
</tbody>
</table>

**SAMPLING**

- Technique: Gas Chromatography w/ FID
- Column: 4% Carbowax 20M on Chromosorb W-100/80
- Flow Rate: 40 ml/min
- Injection Volume: 0.5 μl

**MEASUREMENT**

- Analysis: Ammonia
- Description: 1 ml rinse and stand 40 min
- Calibration: Standard solution of 0.01M Ammonia

**ACCURACY**

- Standard Deviation: ±0.005 mg/sample
- Precision: ±0.005 mg/sample
- Overall Precision: ±0.01 mg/sample
Calculating Sample Time

1. Choose sampling volume from method
   - Eg. Min vol 20 liters and Max vol 300 liters
   - Pick 100 liters

2. Choose sampling flow rate from method
   - Eg. 0.01-1.0 liters/minute
   - Pick 0.5 liters/minute

3. Determine sampling time
   - # minutes = 100 liters x \( \frac{\text{minute}}{0.5 \text{ Liters}} \)
   - Ans. 200 min

Calibration of Sampling Pumps

- Bubblemeter
  - Manual or Electronic
- Graphite Piston
- Rotometer
Other Quality Control Issues in Sampling

- **Interferences**: Collect information on other contaminants present. Bulk samples.

- **Blanks**
  - Field blank is treated like sample but no air drawn through. Determines contamination for media, handling, storage and shipping. Minimum 1-2, 10-20% better to max of 10

- **Storage**
  - Tightly sealed, cooled if possible, shortest possible storage time
Aerosol Sampling

AEROSOLS ARE DESCRIBED BY:
• 1) SHAPE and SOURCE
  • Dusts: solid particles formed by mechanical or organic processes 0.1-100 μm.
  • Fibers: solid particles whose length is much greater than width
  • Fumes: solid particles formed by condensation, 0.01-5 μm
  • Mists: liquid droplets formed mechanical processes by condensation, up to 5 μm

Aerosol Sampling

AEROSOLS are described by:
2) COMPOSITION
   Inorganic Aerosols
      Metals, Silicates, Crystalline silica, Asbestos
      Acids/Bases
   Other
      Portland cement, Limestone, PNOC/PNOR
   Organic Aerosols
      Naturally occurring (Animal dander, Flour dust, Textile fibers)
      Human made (Combustion products, Pesticides)
Aerosols are described by:

3) SIZE (as Aerodynamic Diameter)

- 2 particles of same volume behave differently in air if they have different densities (Settling velocity greater for heavier particle) **AERODYNAMIC DIAMETER**

Normalizes for shape & density by estimating diameter of particle as if it was spherical in shape and had a unit density (1 g/cm³).

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Regions of the Respiratory Tract

(a) Nasopharyngeal (NP) region
(b) Tracheobronchial (TB) region
(c) Pulmonary (P) region

- (a) the NP region conditions inhaled air to body temperature and essentially 100% relative humidity and efficiently removes larger particles; 
- (b) the TB region conducts inhaled air quickly and evenly from the mouth and nose to the pulmonary spaces; 
- (c) the P region performs the gas exchange function of respiration.
Collection Efficiency As a Fraction of Total Aerosol of Samplers

Size Selective Aerosol Standards

- The ACGIH TLV Committee, the International Organization for Standardization and the European Standardization Committee have agreed that:

  Standards for particulate matter and health related air sampling should account for particle size as well as mass concentration because of:

  1) effects of particle size on the deposition site within the respiratory tract, and

  2) the tendency for many occupational diseases to be associated with material deposited in particular regions of the respiratory tract.
The **Particle Size-Selective Standards and Sampling Criteria:**

**1. Respirable Particulate Mass Standards**
for materials that are hazardous when deposited within the gas exchange region of the lung. (Insoluble materials; Materials that cause regional effects like emphysema or fibrosis)

**2. Thoracic Particulate Mass Standards**
for materials that are hazardous when deposited anywhere within the lung airways or gas exchange region of the lung. (Cause regional health effects like bronchitis, asthma, bronchogenic cancer; includes respirable size particles and effects)

**3. Inhalable Particulate Mass Standards**
for those materials which are hazardous when deposited anywhere in the respiratory tract. (Soluble and cause systemic effects; Toxic after oral ingestion via respiratory clearance; Toxic at deposition sites in head and upper airways; Includes thoracic size particles and effects)
Aerosol Sampling

- There are a few size-selective OSHA PEL’s covering the respirable fraction. They include crystalline silica, PNOS/PNOR, coal dust, zinc oxide & others.
- However, historically, most sampling in the U.S. has been done with open or closed face 37mm sampling cassettes at variable flow rates. These samples are called “total” dust samples.
- These samplers are neither “total” nor do they meet the size selective sampling criteria. Nevertheless, most OSHA compliance sampling is done this way.
- The U.S. is in transition regarding aerosol sampling.

Respirable Sampling Methods

50% Cutpoint of AMMD

Cyclones
Thoracic Sampling Methods
50% cutpoint AMMD 10 um

BGI cyclone
Thoracic
(1.6 lpm)
& Respirable
(4.2 lpm)

Inhalable Sampling Methods
50% Cutpoint AMMD of 100 um

IOM
Samplers for Ambient Air

- PM 10-Particulate
  Matter less than 10 um in aerodynamic diameter
- PM 2.5-Particulate
  Matter less than 2.5 um in aerodynamic diameter

Analysis of Aerosols

- Analysis of Aerosols includes:
  - Determine mass concentration
    \[ \text{mg/m}^3 = \frac{\text{post weight} - \text{pre weight (mg)}}{\text{sample air volume (liters)} \times 0.001 \text{m}^3/\text{liter}} \]
  - Determine fiber count
    - Based on size and shape count # fibers by phase contrast microscope
  - Determine chemical composition
    - Metals and elements usually by Atomic Absorption Spectroscopy (AA)
    - Silica by Xray diffraction
    - Inorganic ions by ion specific electrodes
  - Filters chosen based on analyte and analysis method
When is Gravimetric Analysis Used?

- **Coal dust, oil mist, welding fume**
- **General dust**
  - ACGIH: Particulate Not Otherwise Specified (PNOS) (previously called PNOC(classified)): (no TLV, insoluble and low toxicity...not cytotoxic, genotoxic or chemically reactive with lung tissue, do not emit ionizing radiation, cause immune sensitization or toxic effects other than by inflammation or “lung overload”) 10 mg/m$^3$ inhalable; 3 mg/m$^3$ respirable
  - OSHA: Nuisance Dust, Particulate Not Otherwise Regulated (PNOR) (includes all inert or nuisance dusts, whether mineral, inorganic or organic, not listed specifically by substance name): 15 mg/m$^3$ total; 5 mg/m$^3$ respirable
  - These should only be applied to dusts which do not have specific toxic effects. Even so, high concentrations of PNOR/PNOS dusts can reduce lung health

When is Microscopy Used?

- Asbestos samples are counted under phase contrast microscope
- Count fibers that are:
  - > 5 um
  - Have 3:1 length to width ratio
- Count 20-100 fields or 100 fibers (whichever greater)
When is Xray Diffraction used?

- Crystalline materials are analyzed by XRD
- Current standards for respirable crystalline silica
  - NIOSH
    - Quartz REL = 0.05 mg/m$^3$ = 50 ug/m$^3$
  - ACGIH:
    - Quartz TLV = 0.1 mg/m$^3$ = 100ug/m$^3$
    - (0.05 mg/m$^3$ for cristobalite & tridymite)

\[
\frac{\text{mg silica}}{\text{air sampled (m}^3\text{)}} = \text{air conc}
\]

OSHA Permissible Exposure Limit (PEL) for Crystalline Silica

Respirable Crystalline Silica (as respirable dust conc)=

\[
\frac{10 \text{ mg/m}^3}{\% \text{ Quartz} + 2(\% \text{ Cristobalite}) + 2(\% \text{ Tridymite}) + 2}
\]

Requires 2 analyses:

\[
\% \text{ SiO}_2 \text{ of each type} = \frac{\text{mg weight of each type silica (XRD or IR analysis)}}{\text{mg weight of all dust on sample (gravimetric)}}
\]
When is Atomic Absorption Spectroscopy (AA) used?

- When analyzing for metals or elements
  - Lead, Chromium, Aluminum etc
- Can not differentiate compounds with same element
  - Chromium (III) from Hexavalent Chromium
  - Arsenic from arsenic trioxide ($\text{As}_2\text{O}_3$) or organo-arsenics
- To analyze for multiple elements use ICP-AES (inductively coupled plasma-atomic emission spectroscopy)

Atomic Absorption measures ELEMENTS

- $\text{Na}_2\text{B}_4\text{O}_7$ is measured as Boron (B)
- $\text{Fe}_2\text{O}_3$ is measured as Iron (Fe)
<table>
<thead>
<tr>
<th>Personal Sample of Worker Buffing (Polishing) Aluminum Parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>• PVC filter in inhalable (IOM) sampler used to collect and weigh particulate generated in operation. Concentration estimated as 6.26 mg/m³</td>
</tr>
<tr>
<td>• Particulate sample contains:</td>
</tr>
<tr>
<td>– Aluminum particulate (TLV 10 mg/m³)</td>
</tr>
<tr>
<td>– Red Rouge Abrasive particulate (buffing compound contains wax and chromium oxide TLV chromium 0.5 mg/m³)</td>
</tr>
<tr>
<td>– Buffing Disc Particulate (polishing wheel contains wool fibers)</td>
</tr>
<tr>
<td>– Cigarette smoke particulate (from worker and co-workers contains nicotine, carbon, polyaromatic hydrocarbons etc)</td>
</tr>
<tr>
<td>– General workroom particulate from nearby operations including oil mist from stamping operation etc.</td>
</tr>
<tr>
<td>• Is the operation in compliance with standards including PNOS/PNOR?</td>
</tr>
<tr>
<td>• Further sampling/analysis?</td>
</tr>
</tbody>
</table>