Selection of analytical methods and sampling instruments

Sources of information

- OSHA - Salt Lake Technical Center (SLTC)
- SKC methods from OSHA, NIOSH, ASTM, EPA and HSC
- NIOSH Manual of Analytical Methods
  - [http://www.cdc.gov/niosh/nmam/nmampub.html](http://www.cdc.gov/niosh/nmam/nmampub.html)
Considerations for selecting a sampling and analytical method

- Sensitivity
- Interference
- Accuracy and precision
- Sample handling, storage and shipping
- Cost

Sensitivity

- Change in measure signal per unit change in analyte mass (e.g., slope of the calibration curve)
- Low sensitivity – less precision in estimate of mass
Anatomy of an analytical method

- General information on the chemical
  - NAME
  - SYNONYM(S)
  - IMIS
  - CAS
  - NIOSH
  - DOT
  - DESCRIPTION
  - INCOM

- Exposure limits
  - OSHA GENERAL INDUSTRY PEL
  - OSHA CONSTRUCTION INDUSTRY PEL
  - ACGIH TLV
  - NIOSH REL
  - AIHA Weel
Anatomy of an analytical method

- Health factors
  - NTP
  - IARC
  - SYMPTOM(S)
  - HEALTH EFFECTS
  - ORGAN
  - HEALTH GUIDELINE

Anatomy of an analytical method

- Sampling information
- Measurement/analytical information
- Accuracy, interferences other methods, and references
NIOSH Method 1005

METHYLENE CHLORIDE

<table>
<thead>
<tr>
<th>CH₂Cl₂</th>
<th>MW: 84.94</th>
<th>CAS: 75-09-2</th>
<th>RTECS: PA8050000</th>
</tr>
</thead>
</table>

|--------|------------|-------------------------|-------------------------|

OSHA: 25 ppm; STEL: 105 ppm
NIOSH: least feasible carcinogen
ACGIH: 50 ppm; tumor carcinogen
(4 ppm = 34 mg/h)

PROPERTIES:
Liquid, d 1.323 g/ml @ 20 °C, MP 40 °C, BP 95°C, VP 4760 ppm (348 mm Hg) @ 25 °C, nonflammable

SYNONYMS: dichloromethane, methylene dichloride

NIOSH Method 1005

- Field blanks or working blank

SAMPLING

<table>
<thead>
<tr>
<th>SAMPLER</th>
<th>SOLID SORBENT (2 coconut shell charcoal tubes, 100/50 mg)</th>
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<tbody>
<tr>
<td>FLOW RATE</td>
<td>0.01 to 0.2 L/min</td>
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<tr>
<td>VOL-MIN</td>
<td>0.5 L @ 600 ppm</td>
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<td>VOL-MAX</td>
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<tr>
<td>SHIPMENT</td>
<td>separate front and back tubes</td>
</tr>
<tr>
<td>SAMPLE STABILITY</td>
<td>ca. 30 days @ 5 °C [1]</td>
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<td>2 to 10 field blanks per set</td>
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IH&S 725 Dr. Myers C.I.H.
NIOSH Method 1005

### MEASUREMENT

- **Technique:** Gas Chromatography, FID
- **Analyte:** Methylene chloride
- **Description:** 1 mL
- **Injection Volume:** 1 µL
- **Temperature:** Injection: 250 °C; Detector: 300 °C
- **Column:** 80 to 100 °C at 10 °C/min
- **Carrier Gas:** Helium, 2.4 ml/min
- **Column:** Porapak T x 8 ft, 0.32-mm ID, 0.25-µm film, 3% polyethylene glycol, Silicone, or equivalent
- **Calibration:** Solutions of methylene chloride in CS₂

### Measurement Range
- **LOQ:** 0.1 µg per sample
- **LOD:** 0.025 µg per sample
- **Precision:** 0.036 [1]

### Working Range
- **Range:** 1.4 to 3600 µg per sample

### Bias
- **Overall Precision:** ±15.6%
- **Accuracy:** ±0.75%

### Applicability:
The working range for GC-FID analysis is 1.4 to 740 ppm (1.2 to 1000 mg/m³). An electron capture detector (ECD) also may be used to obtain lower levels of detection and quantitation with conditions for using an ECD are listed in the APPENDIX.

### Interferences:
No specific interferences were identified. However, any compound with a similar retention time may interfere. Alternative chromatographic columns are Carbowax, PEG, and DB-1 fused silica capillary columns. The capacity of the charcoal

### Other Methods:
This method NIOSH 1005 (dated 8/1994) [5]. If sampling is in an atmosphere with high relative humidity (≥75%), a filter with a larger bed size of charcoal is recommended. OSHA Method 88 uses a sampler with three sorbent sections, each containing 350 mg of charcoal, and has been evaluated for a 10-L air sample at 1 ppm of methylene chloride with 75% relative humidity [4]. OSHA Method 88 uses a carbon molecular sieve sampler and GC-FID analysis, and has been evaluated at 10 ppm and 100 ppm [6].
### Sampling considerations - time

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- What is the minimum and maximum sampling time under these sampling parameters?  
  - Minimum =  
  - Maximum =

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### Sampling considerations - mass

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- What is the minimum and maximum mass collected on the tube under these sampling parameters?  
  - Minimum =  
  - Maximum =
Sampling consideration - mass

- What is the minimum and maximum mass collected on the tube if the concentration is at the PEL concentration?
  - Minimum =
  - Maximum =

Sampling consideration – time and mass

- You want to determine if the exposure to methylene chloride, associated with a task that takes 30 minutes to complete, is over 10% of the PEL value.
- What minimum sample rate would you choose for this assessment?
Let’s run a little what if

<table>
<thead>
<tr>
<th>PPM</th>
<th>% PEL</th>
<th>mg/m³</th>
<th>Sample Time</th>
<th>Flow Rate</th>
<th>Mass Collected</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>10%</td>
<td>8.7</td>
<td>30</td>
<td>0.01</td>
<td>0.0006</td>
</tr>
<tr>
<td>2.5</td>
<td>10%</td>
<td>8.7</td>
<td>30</td>
<td>0.05</td>
<td>0.0131</td>
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<td>2.5</td>
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<td>8.7</td>
<td>30</td>
<td>0.10</td>
<td>0.0261</td>
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<tr>
<td>2.5</td>
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<td>8.7</td>
<td>30</td>
<td>0.15</td>
<td>0.0392</td>
</tr>
<tr>
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<td>8.7</td>
<td>30</td>
<td>0.20</td>
<td>0.0522</td>
</tr>
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What can you conclude?

- Assuming a concentration of at least =>10% of the PEL a sample rate of 0.01 LPM would provide sufficient mass of methylene chloride for quantification.
Problem #1

Given the sampling conditions we just established and using a flow rate of .15 LPM the laboratory reports back to you that your collected mass is less than the LOD of the method. What can you say about the possible exposure level?

Answer #1
**Accuracy (A)**

\[
A = \left( \frac{C_m - C_t}{C_t} \right) \times 100 \%
\]

Where
- \(A\) = accuracy in percent
- \(C_m\) = measured value
- \(C_t\) = true value

**Bias (K)**

- The ratio of the measured value to the true value

\[
K = \frac{C_m}{C_t}
\]

\(K\) is related to \(A\) by

\[
A = |K - 1| \times 100\%
\]
Precision ($\sigma_c$)

- Standard deviation of repeated measurements of the same observable with the same measurement method

$$\sigma_c = \frac{1}{\sqrt{n}} \sum_{i=1}^{n} (C_i - \overline{C})^2$$

where: $C_i$ is the $i^{th}$ measurement of observable $C$ and

$$\overline{C} = \frac{1}{n} \sum_{i=1}^{n} C_i$$

Example 1

Bill Hygienist has developed a new procedure for his technicians to weigh filters and wants to measure the precision of the procedure. He has six different technicians weight the same filter on six different days.
Filter weight data

- $W_i$
  - T1: 2.466 mg
  - T2: 2.440 mg
  - T3: 2.457 mg
  - T4: 2.448 mg
  - T5: 2.461 mg
  - T6: 2.452 mg

- What is the mean?
- What is the sample standard deviation?

Determination of accuracy

- Given the true weight of the filter is 2.450 mg what is the accuracy of Bill’s new procedure?
Determination of bias

- What is the bias in the new procedure?

Determination of precision

- What is the precision of the procedure?
Coefficient of Variation (CV)

Expressed as a fraction

$$CV = \frac{S}{X}$$

Expressed as a percent

$$CV\% = \frac{S}{X} \times 100$$

- Where:
  - $S$ = standard deviation
  - $X$ = mean or analytical result

What is the coefficient of variation for Bill’s weighing procedure?
Relative Standard Deviation ($S_r$)

Expressed as a fraction

$$S_r = CV \times X$$

Expressed as a percent

$$S_r = \frac{CV\% \times X}{100}$$

- Where $X =$ mean or analytical result

Ok – so why is this important?

- Because what the laboratory reports back to you is not an absolute number – there really is some variability around its value
Ok – what do we do?

- Using the coefficient of variation (termed precision on NIOSH analytical methods) we can report that variability in our estimate as a relative standard deviation.

Problem # 2

- Given we collect a dust sample. Using Bill’s weighing procedure a laboratory technician reports back a mass weight gain of 1.564 mg. Report the relative standard deviation on the reported mass.
Answer for #2