

Selection of analytical methods and sampling instruments

Lecture Notes

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Sources of information

- OSHA - Salt Lake Technical Center (SLTC)
 - <http://www.osha.gov/dts/sltc/>
- SKC methods from OSHA, NIOSH, ASTM, EPA and HSC
 - <http://www.skcinc.com/guides.html>
- NIOSH Manual of Analytical Methods
 - <http://www.cdc.gov/niosh/nmam/nmampub.html>

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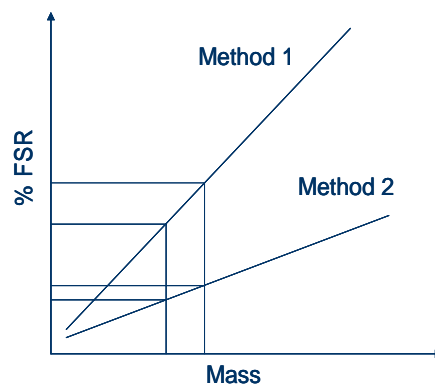
Considerations for selecting a sampling and analytical method

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

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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



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Anatomy of an analytical method

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

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Anatomy of an analytical method

- Exposure limits
 - OSHA GENERAL INDUSTRY PEL
 - OSHA CONSTRUCTION INDUSTRY PEL
 - ACGIH TLV
 - NIOSH REL
 - AIHA Weel

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Anatomy of an analytical method

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

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Anatomy of an analytical method

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

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NIOSH Method 1005

METHYLENE CHLORIDE

1005

CH₂Cl₂

MW: 84.94

CAS: 75-09-2

RTECS: PA8050000

METHOD: 1005, Issue 3

EVALUATION: FULL

Issue 1: 15 August 1984
Issue 3: 15 January 1998

OSHA: 25 ppm; STEL 125 ppm
NIOSH: lowest feasible; carcinogen
ACGIH: 50 ppm; suspect carcinogen
(1 ppm = 3.47 mg/m³)

PROPERTIES: liquids, d 1.323 g/mL @ 20 °C; BP 40 °C; MP -95 °C; VP 47 kPa (349 mm Hg) @ 25 °C, nonflammable

SYNONYMS: dichloromethane, methylene dichloride

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NIOSH Method 1005

SAMPLING

SAMPLER: SOLID SORBENT
(2 coconut shell charcoal tubes, 100/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: 0.5 L @ 500 ppm
-MAX: 2.5 L

SHIPMENT: separate front and back tubes

SAMPLE STABILITY: ca. 30 days @ 5 °C [1]

BLANKS: 2 to 10 field blanks per set

- Field blanks or working blank

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NIOSH Method 1005

MEASUREMENT

TECHNIQUE:	GAS CHROMATOGRAPHY, FID
ANALYTE:	methylene chloride
DESORPTION:	1 mL CS ₂
INJECTION VOLUME:	1 µL
TEMPERATURE-INJECTION:	250 °C
-DETECTOR:	300 °C
-COLUMN:	80 to 150 °C at 10 °C/min
CARRIER GAS:	Helium, 2.4 mL/min
COLUMN:	capillary, 30 m x 0.32-mm ID, 0.25-µm film polyethylene glycol, Stabilwax, or equivalent
CALIBRATION:	solutions of methylene chloride in CS ₂
RANGE:	1.4 to 2600 µg per sample [1]
ESTIMATED LOD:	0.4 µg per sample [1]
PRECISION (\hat{S}_r):	0.026 [1]

- Measurement range
- LOQ
- LOD
- Precision

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NIOSH Method 1005

ACCURACY

RANGE STUDIED:	1700 to 7097 mg/m ³ [2]
BIAS:	-4.1%
OVERALL PRECISION ($\hat{S}_{r,t}$):	0.076 [1, 2]
ACCURACY:	±15.8%

- Working range
- Bias
- Overall precision
- Accuracy

APPLICABILITY: The working range for GC-FID analysis is 0.4 to 749 ppm (1.4 to 2600 mg/m³) for a 1-L air sample [1]. An electron capture detector (ECD) also may be used to obtain lowest feasible level of detection and quantitation [3]. 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. Alternate chromatographic columns are Carbowax-PEG and DB-1 fused silica capillary columns. The capacity of the charcoal

OTHER METHODS: This revises NMAM 1005 (dated 8/15/94) [5]. If sampling in an atmosphere with high relative humidity ($\geq 80\%$), a tube with larger bed of charcoal is recommended. OSHA Method 59 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 80% relative humidity [4]. OSHA Method 80 uses a carbon molecular sieve sampler and GC-FID analysis, and has been evaluated at 10 ppm and 500 ppm [6].

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Sampling considerations - time

SAMPLING

SAMPLER:	SOLID SORBENT (2 coconut shell charcoal tubes, 100/50 mg)
FLOW RATE:	0.01 to 0.2 L/min
VOL-MIN:	0.5 L @ 500 ppm
-MAX:	2.5 L
SHIPMENT:	separate front and back tubes
SAMPLE STABILITY:	ca. 30 days @ 5 °C [1]
BLANKS:	2 to 10 field blanks per set

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

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Sampling consideration - mass

SAMPLING

SAMPLER:	SOLID SORBENT (2 coconut shell charcoal tubes, 100/50 mg)
FLOW RATE:	0.01 to 0.2 L/min
VOL-MIN:	0.5 L @ 500 ppm
-MAX:	2.5 L
SHIPMENT:	separate front and back tubes
SAMPLE STABILITY:	ca. 30 days @ 5 °C [1]
BLANKS:	2 to 10 field blanks per set

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

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Sampling consideration - mass

SAMPLING

SAMPLER:	SOLID SORBENT (2 coconut shell charcoal tubes, 100/50 mg)
FLOW RATE:	0.01 to 0.2 L/min
VOL-MIN:	0.5 L @ 500 ppm
-MAX:	2.5 L
SHIPMENT:	separate front and back tubes
SAMPLE STABILITY:	ca. 30 days @ 5 °C [1]
BLANKS:	2 to 10 field blanks per set

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

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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 chose for this assessment?

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Let's run a little what if

PPM	% PEL	mg/m3	Sample Time min	Flow Rate LPM	Mass Collected mg
2.5	10%	8.7	30	0.01	0.0026
2.5	10%	8.7	30	0.05	0.0131
2.5	10%	8.7	30	0.10	0.0261
2.5	10%	8.7	30	0.15	0.0392
2.5	10%	8.7	30	0.20	0.0522

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What can you conclude?

MEASUREMENT	
TECHNIQUE:	GAS CHROMATOGRAPHY, FID
ANALYTE:	methylene chloride
DESORPTION:	1 mL CS ₂
INJECTION VOLUME:	1 µL
TEMPERATURE-INJECTION:	250 °C
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-COLUMN:	80 to 150 °C at 10 °C/min
CARRIER GAS:	Helium, 2.4 mL/min
COLUMN:	capillary, 30 m x 0.32-mm ID, 0.25µm film polyethylene glycol, Stabilwax, or equivalent
CALIBRATION:	solutions of methylene chloride in CS ₂
RANGE:	1.4 to 2600 µg per sample [1]
ESTIMATED LOD:	0.4 µg per sample [1]
PRECISION (S):	0.026 [1]

- 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.

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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?

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Answer #1

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Accuracy (A)

$$A = \frac{(C_m - C_t)}{C_t} * 100\%$$

Where

A = accuracy in percent

C_m = measured value

C_t = true value

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Bias (K)

- The ratio of the measured value to the true value

$$K = \frac{C_m}{C_t}$$

K is related to A by

$$A = |K - 1| * 100\%$$

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Precision (σ_c)

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

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

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

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

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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.

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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?

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Determination of accuracy

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

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Determination of bias

- What is the bias in the new procedure?

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Determination of precision

- What is the precision of the procedure?

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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

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What is the coefficient of variation for Bill's weighing procedure?

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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

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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

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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.

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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.

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Answer for #2

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