Methylene Chloride

CAS number:	75-09-2
OSHA PEL:	25 ppm (87 mg/m^3) 8-Hour TWA PEL, 12.5 ppm (43 mg/m^3) 8-Hour TWA Action Level, 125 ppm (434 mg/m^3) 15-Minute STEL, General Industry, Construction, Shipyard
Procedure:	Collect samples by drawing workplace air containing methylene chloride vapor through two Anasorb 747 synthetic charcoal sorbent tubes connected in series. Extract samples with 60/40 (v/v) *N,N*-dimethylformamide/carbon disulfide (DMF/CS$_2$) and analyze by gas chromatography (GC) using a flame ionization detector (FID).
Recommended sampling time and sampling rate:	240 min at 50 mL/min (12 L, 8-Hour TWA) 15 min at 50 mL/min (0.75 L, 15-Minute STEL)
Limit of quantitation: Reporting limit:	0.22 ppm (0.77 mg/m^3, 8-Hour TWA), 3.6 ppm (12 mg/m^3, 15-Minute STEL) 0.48 ppm (1.7 mg/m^3, 8-Hour TWA), 7.7 ppm (27 mg/m^3, 15-Minute STEL)
Uncertainty (u):	8.6% (8-Hour TWA) 9.3% (15-Minute STEL)
Special requirements:	Immediately after sampling, separate and cap the two sampling tubes to prevent post-sampling migration.
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1   Introduction

The methodologies described in this method replace OSHA's use of OSHA Method 80.[1] That method requires the collection of samples using Carbosieve S-III sorbent tubes with a sampling time and rate of 60 minutes at 50 mL/min, extraction using 99/1 (v/v) CS_2/DMF in the presence of anhydrous sodium sulfate, and analysis by GC-FID.

2   Sampling Procedure

Follow all safety practices that apply to the work area where sampling occurs. Wear eye protection when breaking off ends of flame-sealed glass sampling tubes.

2.1   Apparatus

Two single section 8-mm x 110-mm glass sampling tubes packed with 20/40 mesh Anasorb 747 sorbent are required for sampling. The front tube contains 400 mg and the back tube contains 200 mg. Connect the tube in series with a 1-inch length of ¼ -inch i.d. silicone tubing. The sorbent is held in place with glass wool on the inlet side and a foam plug on the outlet side. Commercially available tube sets were purchased from SKC Inc. (catalog no. 226-82) for method development. Sorbent tubes are provided to OSHA field activities through official sampling media procurement channels, and sorbent tubes are labeled with expiration dates. Store unused sorbent tubes at room temperature prior to use, and discard sorbent tubes when expiration dates are exceeded.

A sampling tube holder, such as SKC Inc. tube cover D (catalog no. 224-29D), is used to protect a sampled worker from the sharp ends of the glass sampling tubes.

A personal sampling pump calibrated to within ±5.0% of the recommended flow rate with a representative sampling device in-line is used to draw air through a sampling tube. When possible, sample over the duration specified for the specific exposure limit.

2.2   Reagents

None Required

2.3   Technique

Immediately before sampling, break off the ends of the flame-sealed tubes to provide an opening approximately half the internal diameter of the tube. Connect the outlet end of the 400-mg tube to the inlet end of the 200-mg tube with a 1-inch length of ¼-inch i.d. silicone tubing. Place tubes into a sampling tube holder to minimize the hazard to the worker from the broken ends of the tubes. All tubes submitted for analysis (including field blanks) should be from the same lot.

Attach the tube holder (with the adsorbent tubes) to the sampling pump so that the inlet side adsorbent tube is in the worker's breathing zone during sampling. Position the sampling pump, tube holder, and tubing so they do not impede worker performance or safety of an employee being sampled. The air being sampled should not pass through any hose or tubing before entering the inlet sampling tube.

Sample at 50 mL/min for 240 min (12 L) or 50 mL/min for 15 min (0.75 L) for methylene chloride.

After sampling for the appropriate time, seal each tube with plastic end-caps. Seal each sample end-to-end with a Form OSHA-21 as soon as possible.

Submit at least one field blank sample with each set of samples. Handle the field blank sample in the same manner as the other samples except draw no air through it.

Record sample air volume (liters), sampling time (min) and sampling rate (mL/min) for each sample, along with any potential interference on the Form OSHA-91A.

Submit samples to the laboratory for analysis as soon as possible after sampling. If a delay is unavoidable, store the samples in a refrigerator as a precaution.

3   Analytical Procedure

3.1   Apparatus

- Mechanical vial rotator
- One liter amber glass solvent dispenser capable of dispensing 2.00 mL
- Syringes (10 and 250-µL)
- Class A graduated cylinder to deliver (100-mL)
- Class A volumetric pipette (1-mL)
- Class A volumetric flasks (1, 2 and 500-mL)
- Amber glass vials with polytetrafluoroethylene (PTFE)-lined screw caps (2 and 4-mL)
- GC instrument with FID

3.2   Reagents

- Methylene chloride (>99%, analytical grade)
- Carbon disulfide (CS_2, reagent grade or better)
- 1-Octanol (> 99%, analytical grade)
- *N,N*-Dimethylformamide (DMF, reagent grade or better)

3.3   Reagent Preparation

Extraction solvent (60/40 (v/v) DMF/CS_2 with 2.00 µL/mL 1-octanol as an internal standard (ISTD)): To a 500-mL volumetric flask add 300 mL of *N,N*-dimethylformamide, 1.00 mL of 1-octanol, then carbon disulfide to the mark. Immediately mix the solution and transfer to an amber glass solvent dispenser.

3.4   Standard Preparation

Prepare two working standards at approximately 10.1 and 232 µg/µL by injecting 7.6 and 175 µL of neat methylene chloride, respectively, into 1-mL volumetric flasks containing approximately 0.5 mL of the extraction solvent. Fill to the mark with extraction solvent, mix, and transfer to 2-mL amber glass vials. Prepare a calibration standard at approximately 20.2 ug/sample by injecting 2 µL of the 10.1 µg/µL working standard into a 2-mL volumetric flask containing approximately 1 mL of the extraction solvent. Fill to the mark with extraction solvent and mix. Prepare additional calibration standard at approximately 580, 1160, 1740 and 2320 ug/sample by injecting 2.5, 5, 7.5, and 10 µL, respectively, of the 232 µg/µL working standard into 2-mL volumetric flasks containing approximately 1 mL of the extraction solvent. Fill to the mark with extraction solvent and mix. Transfer the five calibration standards to 2-mL amber glass autosampler vials. If sample concentrations are greater than the range of prepared standards, dilute high samples with extraction solvent and reanalyze the diluted samples.

3.5   Sample Preparation

Remove the plastic end-caps from the 400-mg and 200-mg sample tubes. Transfer the respective 400 and 200-mg Anasorb 747 sections into separate 4-mL vials. Discard glass tubes, foam, and glass wool plugs.

Add 2.00 mL of extraction solvent to each vial and immediately seal with PTFE-lined caps.

Extract the samples by rotating vials for 1 hour.

Pour the extraction solution in each 4-mL vial to a 2-mL amber glass autosampler vial and seal with PTFE-lined caps.

3.6   Analysis

Analyze samples using a GC-FID instrument and the analytical parameters described below. Use an ISTD calibration method. Construct an x^{-1} weighted-least-squares linear regression curve by plotting ISTD-corrected response of standard injections versus micrograms of analyte per sample. Confirm the presence of methylene chloride when the OSHA 8-hour time-weighted average (TWA) action level, 8-hour TWA permissible exposure limit (PEL), or the 15-minute short-term exposure limit (STEL) value has been exceeded, as described in Section 3.8. See Figure 1 below for an example chromatogram obtained from a standard containing a methylene chloride mass concentration equivalent to sampling for the recommended time at the OSHA 8-hour TWA. See Figure 2 below for an example calibration curve obtained from injection of calibration standards at concentrations defined in Section 3.4.

<u>GC parameters</u>

column:	Agilent J&W DB-WAX capillary column, 60-m × 0.32-mm i.d., d_f = 0.5-µm (Catalog no. 123-7063, or equivalent)
inlet liner:	Restek Topaz 4.0-mm ID Precision Inlet Liner w/wool (Catalog no. 23305, or equivalent)
carrier:	hydrogen, constant flow 2 mL/min
septum purge:	hydrogen, 3.0 mL/min
injection:	1 µL, split injection, 50:1 ratio
inlet temperature:	235 °C
oven temperature program:	40 °C (hold 4 min), ramp to 70 °C at 5 °C/min (hold 0 min), ramp to 205 °C at 15 °C/min (hold 0 min), ramp to 240 °C at 35 °C/min (hold 0 min)
run time:	20 min
retention times:	4.63 min - CS_2 8.63 min - methylene chloride 16.61 min - DMF 18.50 min - ISTD

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FID parameters

detector temperature:	240 °C
hydrogen flow:	40 mL/min
air flow:	450 mL/min
nitrogen make up flow:	45 mL/min
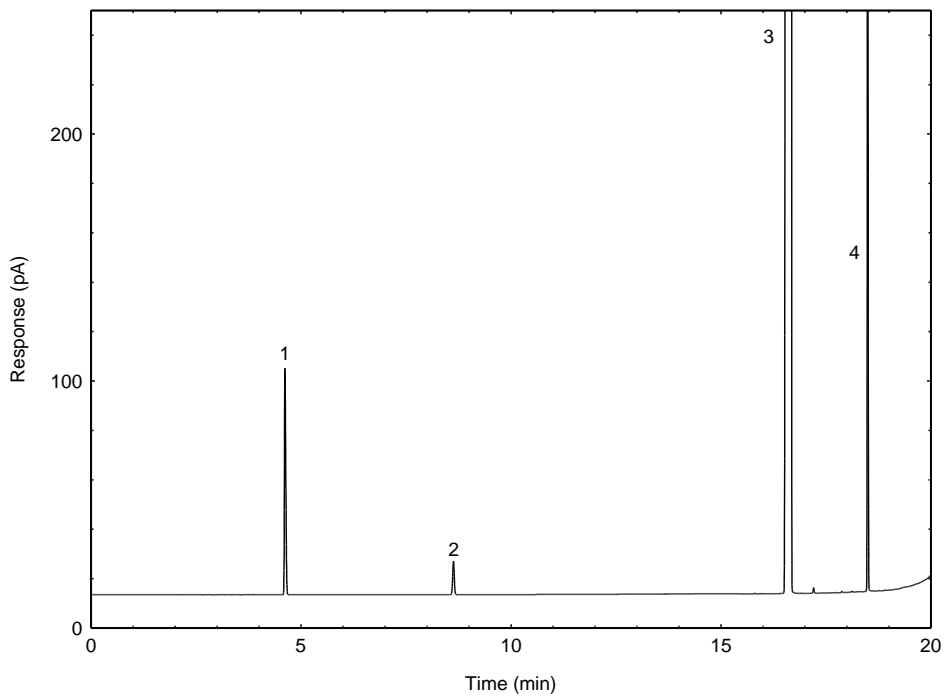
Figure 1. Example chromatogram. Peak labels: (1) CS_2, (2) methylene chloride, (3) DMF, (4) ISTD.
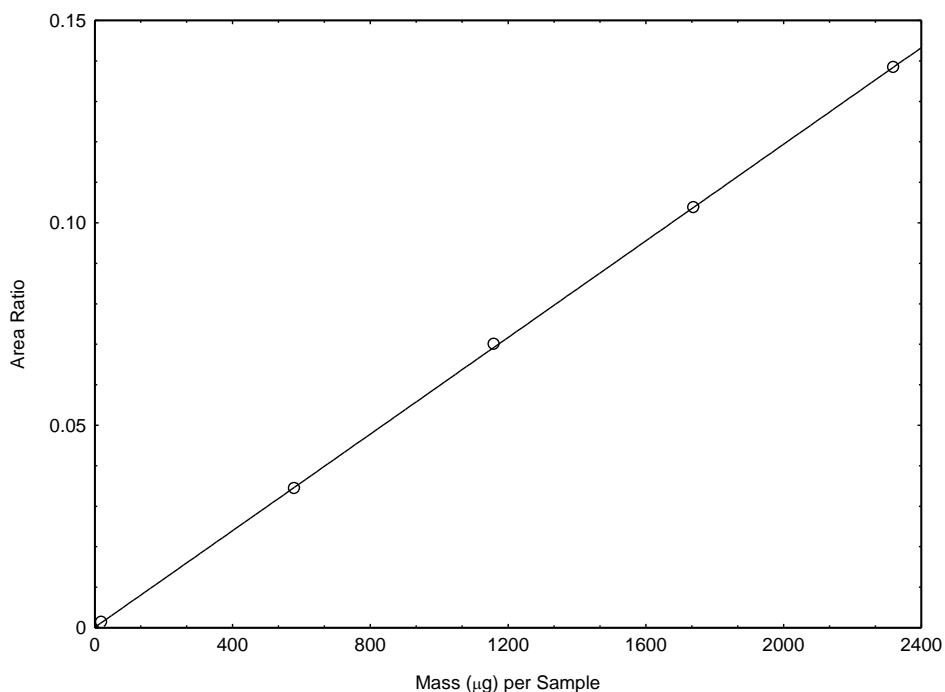
Figure 2. Example calibration curve for methylene chloride ($y = 5.97 \times 10^{-5}x + 1.00 \times 10^{-4}, w_i = x^{-1}$).

3.7 Calculations

Calculate the micrograms recovered per sample (m). The back sorbent section is analyzed primarily to determine the extent of sampler saturation. If any analyte is found on the back section, it is added to the amount found on the front section. If more than 20% of the total amount is found on the back section, report that the sampler may have been saturated on the Form OSHA-91B. Correct m for each sample by subtracting the mass of analyte (if any) found on the sample blank. The analyte air concentration (C) is calculated in mass per volume units (mg/m³) using Equation 1, where V is the volume of air sampled (L), and R_A is the analytical recovery expressed in decimal format.

$$C = \frac{m}{VR_A} \tag{1}$$

The air concentration (C_{ppm}) in terms of parts of analyte vapor per million parts of air (ppm) is obtained using Equation 2, where C is the air concentration with mass per volume units (mg/m³) calculated using Equation 1, V_M is the molar volume of an ideal gas or vapor at 25 °C and 760 Torr (24.46 L/mol), and M is the analyte molar mass (g/mol).

$$C_{ppm} = \frac{CV_M}{M} \tag{2}$$

The value for R_A, obtained during validation, and M are listed in Table 1 along with the OSHA Integrated Management Information System (IMIS) number.

Table 1. Molar mass, analytical recovery, and OSHA Integrated Management Information System (IMIS) number for methylene chloride.

analyte	M (g/mol)	R_A	IMIS
methylene chloride	84.93	1.013	1730

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3.8   Qualitative Analysis

When necessary, the identity of the analyte peak can be confirmed by gas chromatography-mass spectrometry (GC-MS) using the analytical parameters described below. Confirm the presence of methylene chloride by matching the retention time and fragmentation pattern of a standard at a similar concentration. See Figure 3 below for an example total ion current (TIC) chromatogram obtained from a standard containing a methylene chloride mass concentration equivalent to sampling for the recommended time at the OSHA 8-hour TWA. See Figure 4 below for the mass spectrum obtained.

GC parameter

column:	Agilent J&W DB-WAX capillary column, 60-m × 0.32-mm i.d., d_f = 0.5-µm (Catalog no. 123-7063, or equivalent)
inlet liner:	Restek Topaz 4.0-mm ID Precision Inlet Liner w/wool (Catalog no. 23305, or equivalent)
carrier:	helium, constant flow 1.6 mL/min
septum purge:	helium, 3.0 mL/min
injection:	1.0 µL, split injection, 50:1 ratio
inlet temperature:	235 °C
oven temperature program:	40 °C (hold 4.15 min), ramp to 70 °C at 4.7 °C/min (hold 0 min), ramp to 205 °C at 13 °C/min (hold 0 min), ramp to 240 °C at 35 °C/min (hold 0 min)
run time:	21.9 min
retention times:	9.00 min - methylene chloride 20.44 min - ISTD

mass spectrometer parameters

mode:	70 eV electron ionization
acquisition mode:	scan, *m/z* 20 - 150
solvent delay:	6 min
timed events:	17.8 - 19.20 min MS off
EMV mode:	gain factor (1)
temperatures:	250 °C (source), 200 °C (quadrupole assembly), 250 °C (transfer line)

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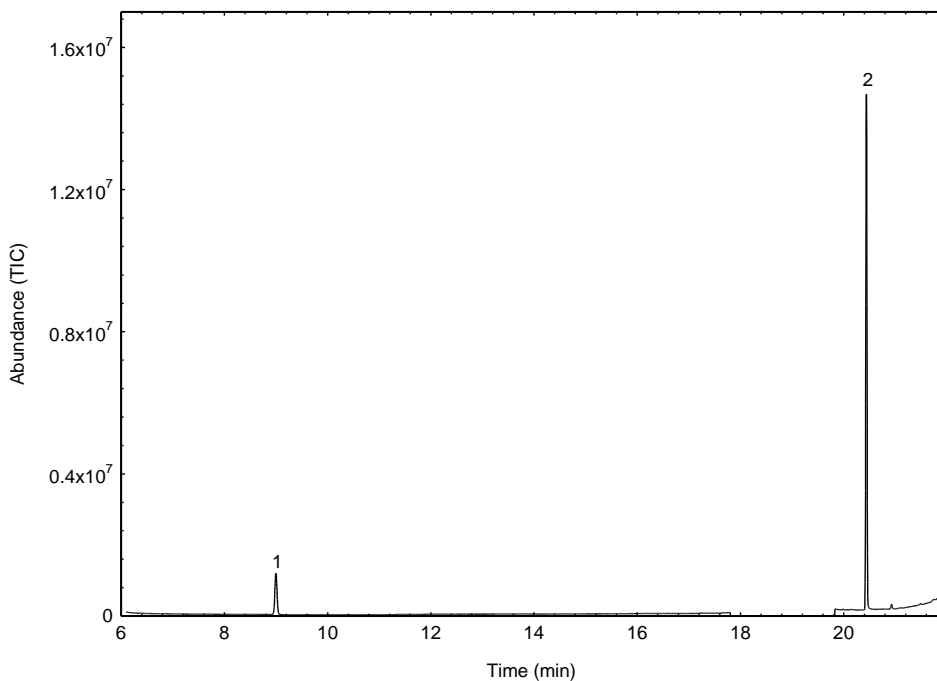Administration

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Figure 3. Example TIC GC-MS chromatogram. Peak labels: (1) methylene chloride, (2) ISTD.

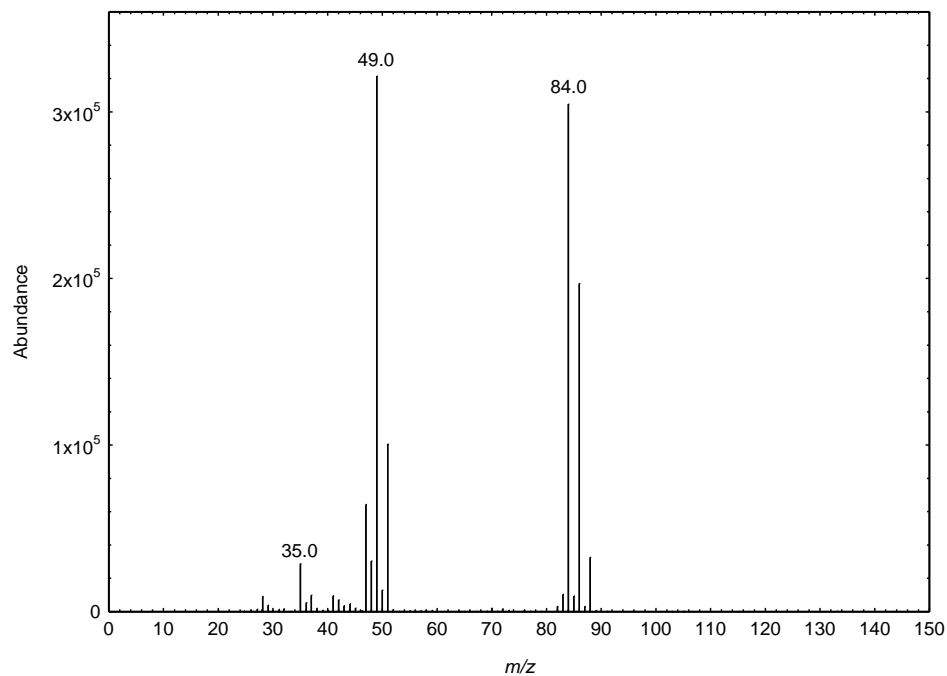**Figure 4.** Mass spectrum of methylene chloride.

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4   Method Validation

The procedures used to develop the method validation data are described in OSHA Technical Center's Guideline 1 *Sampling and Analytical Methods*.[2] Air concentrations listed in ppm are referenced to 25 °C and 760 Torr. The target concentration (T_C) for method evaluation was the OSHA 8-hour TWA PEL and the 15-minute STEL for methylene chloride. The target mass (T_M) is the equivalent analyte mass per sample collected on a sampler at the T_C using the recommended sampling time and sampling rate.

Dynamically generated controlled test atmospheres were created in a walk-in hood. House air was regulated using a flow-temperature-humidity control system. A measured flow of liquid methylene chloride was introduced with a syringe pump through a short length of uncoated fused silica capillary into a heated zone near the air flow entrance of the test atmosphere generator, where it was evaporated into a measured flow of dilution air from the flow-temperature-humidity control system. The resulting methylene chloride vapor and dilution air flowed into a mixing chamber, and then into a sampling chamber. Sampling was completed using sampling ports on the sampling chamber. Temperature and humidity measurements were obtained near the exit of the sampling chamber.

4.1   Limit of Detection (LOD), Limit of Quantitation (LOQ), and Reporting Limit (RL)

The LOD is the analyte mass introduced onto the chromatographic column that produces a response greater than 3.3× the standard error of estimate ($S_{y/x}$) divided by the slope of the line produced from analyses of three spiked samples at five evenly spaced levels, for a total of fifteen spiked media samples. Sorbent tubes were spiked in such a way that the highest mass loading produced a peak approximately 10 times greater than that of a sample blank at or near the chromatographic retention time of the analyte. The LOQ is expressed as an air concentration that will provide sufficient analyte mass per sample that produces a response greater than 10 × $S_{y/x}$ divided by the slope of the line described above. The spiked samplers and three sample blanks were analyzed with the recommended analytical parameters. The resulting data provided the $S_{y/x}$ and the slope values for LOD and LOQ determinations. Results obtained from these analyses are listed in Table 2, and plotted in Figure 5.

Table 2. LOD and LOQ data for methylene chloride.

mass per sample (μg/sample)	area ratio
0.00	0.00
0.00	0.00
0.00	0.00
4.24	4.67×10^{-4}
4.24	2.95×10^{-4}
4.24	4.18×10^{-4}
8.49	6.19×10^{-4}
8.49	5.72×10^{-4}
8.49	6.77×10^{-4}
12.7	9.44×10^{-4}
12.7	8.61×10^{-4}
12.7	8.36×10^{-4}
17.0	1.09×10^{-3}
17.0	1.15×10^{-3}
17.0	1.13×10^{-3}
21.2	1.42×10^{-3}
21.2	1.47×10^{-3}
21.2	1.40×10^{-3}

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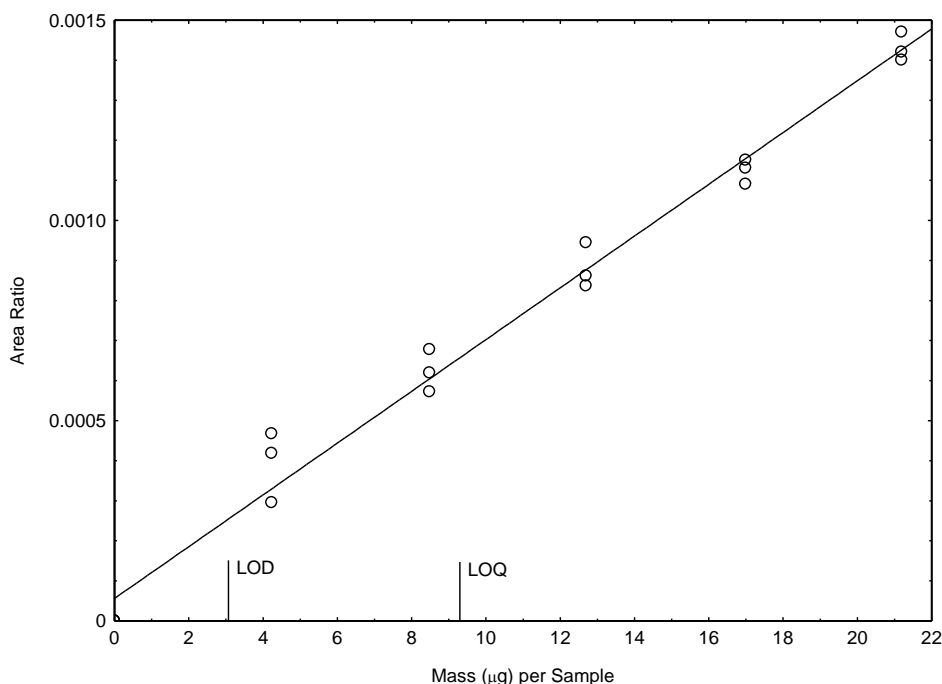
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Figure 5. Plot of data used to determine the LOD and LOQ for methylene chloride ($y = 6.46 \times 10^{-5}x + 5.62 \times 10^{-5}$, $S_{y/x} = 6.00 \times 10^{-5}$, LOD = 3.06 µg/sample, LOQ = 9.29 µg/sample or 0.223 ppm at the 8-hour TWA and 3.57 ppm at the 15-minute STEL).

The RL is expressed as an air concentration at the equivalent mass per sample at the lowest analytical calibration standard providing the recovery is within ±25%. Six replicate sorbent tubes were liquid-spiked with 20.15 µg of methylene chloride. After one hour of storge at ambient temperature the samples were analyzed using the analytical calibration procedure described in Section 4.2. After analysis, results for methylene chloride as a percentage of expected recovery were 113.3%, 99.4%, 102.8%, 110.4%, 112.7%, 103.9%. The mean percentage of expected recovery was 107.1%. The reporting limits are 0.484 ppm at the 8-hour TWA and 7.74 ppm at the 15-minute STEL

4.2 Analytical Calibration

Thirty analytical standards over a range of 0.02 to 2.2 times the 8-hour TWA T_M were analyzed with the recommended analytical parameters. Graphical and statistical examination of these data indicate the appropriate regression model and fitting technique were weighted-least-squares linear regression with a x^{-1} weighting factor. Results from these analyses are listed in Table 3 and plotted with the selected regression model and fitting technique in Figure 6. Five standards prepared over this range are used for analytical calibration as described in Section 3.4 and shown in Figure 2.

Table 3. Analytical calibration data for methylene chloride.

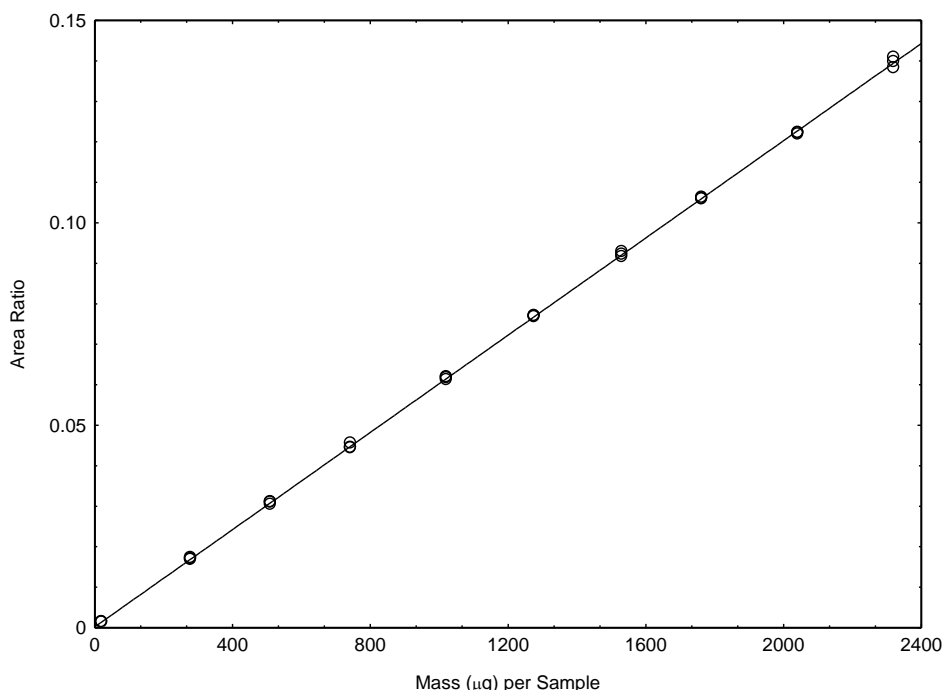| × 8-hour TWA T_M (µg/sample)	0.02× (20.15)	0.3× (278.4)	0.5× (510.5)	0.7× (742.5)	1.0× (1021)	1.2× (1276)	1.5× (1531)	1.7× (1763)	2.0× (2042)	2.2× (2320)
	0.1425	1.729	3.112	4.559	6.197	7.697	9.225	10.63	12.19	14.09
area ratio (×10⁻²)	0.1338	1.687	3.042	4.442	6.173	7.707	9.163	10.60	12.22	13.83
	0.1468	1.701	3.096	4.454	6.125	7.677	9.288	10.59	12.23	13.98

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Figure 6. Plot of data used to determine the analytical calibration procedure for methylene chloride ($y = 6.00 \times 10^{-4}x + 2.11 \times 10^{-4}, w_i = x^{-1}$).

4.3   Post Sampling Storage

The 8-hour TWA post sampling storage stability test samples for methylene chloride were prepared by sampling a dynamically generated controlled test atmosphere, using the system described in Section 4. Sampling from this system followed the recommended sampling parameters. The nominal concentration of methylene chloride for ambient storage 8-hour TWA testing was the target concentration (calculated to be 25.6 ppm). The relative humidity and temperature of the air sampled were 78% and 23 °C. Eighteen samples were prepared and three of these were analyzed on the day that samples were created. The remaining fifteen samples were stored on a bench-top at ambient temperature (about 22°C). Three samples were selected and analyzed from those remaining at 3 to 4-day intervals. The results of these analyses (uncorrected for analytical recovery) are provided in Table 4. The regression line equation determined from these results was $y = 0.0960x + 104.3$.

The change in recovery (Δ_{ss_TWA}) of methylene chloride calculated from the regression line generated for the 17-day post sampling storage test was 1.6%.

Table 4. Ambient post sampling storage stability data for methylene chloride (8-hour TWA).

time (days)	sample 1 (%)	sample 2 (%)	sample 3 (%)
0	109.4	103.0	102.0
3	100.4	108.1	105.2
6	106.1	100.3	107.1
9	103.0	105.3	105.1
13	105.4	106.1	106.9
17	106.5	102.8	108.8

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The 15-minute STEL post sampling storage stability test samples for methylene chloride were prepared by sampling a dynamically generated controlled test atmosphere, using the system described in Section 4. Sampling from this system followed the recommended sampling parameters. The nominal concentration of methylene chloride for ambient storage 15-min STEL testing was the target concentration (calculated to be 126 ppm). The relative humidity and temperature of the air sampled were 79% and 22 °C for this test. Eighteen samples were prepared and three of these were analyzed on the day that samples were created. The remaining fifteen samples were stored on a bench-top at ambient temperature (about 22 °C). Three samples were selected and analyzed from those remaining at 3 to 4-day intervals. The results of these analyses (uncorrected for analytical recovery) are provided in Table 5. The regression line equation determined from these results was $y = -0.00454x + 96.1$.

The change in recovery (Δ_{ss_STEL}) of methylene chloride calculated from the regression line generated for the 18-day post sampling storage test was 0.082%.

Table 5. Ambient post sampling storage stability data for methylene chloride (15-minute STEL).

time (days)	sample 1 (%)	sample 2 (%)	sample 3 (%)
0	96.1	95.3	95.7
4	96.7	96.0	97.8
7	96.1	97.9	95.4
11	94.5	95.3	95.4
14	96.2	96.4	96.1
18	96.5	96.0	96.2

4.4   Method Precision and Bias

The 8-hour TWA method precision and bias was determined by sampling dynamically generated controlled test atmospheres using the system described in Section 4. Six samples were collected at each of five levels across a concentration range of 0.1 to 2 times the 8-Hour TWA T_C at 50 mL/min for 240 min. Samples collected at each level were analyzed immediately after collection and independently from the other levels, including use of freshly prepared calibration standards. The results of these analyses are provided in Table 6, along with the concentration, temperature, and relative humidity of each test atmosphere. The percent coefficient of variation of the means of the five levels tested (CV_{m_TWA}) was 2.5%, and the pooled coefficient of variation of each of the five levels tested (CV_{pl_TWA}) was 1.6%. The resulting 8-hour TWA method precision (u_{mp_PEL}) for methylene chloride was determined to be 2.9%. The mean recovery of the thirty samples was 95.1%, resulting in a method bias (B_{mp_TWA}) of 4.9% and a coefficient of variation (CV_{mb_TWA}) of 2.7%.

Table 6. Method precision data for methylene chloride (8-hour TWA).

concn (ppm)	temp (°C)	RH (%)	sample 1 (%)	sample 2 (%)	sample 3 (%)	sample 4 (%)	sample 5 (%)	sample 6 (%)	mean (%)
2.56	22	80	91.1	93.9	89.4	93.0	94.1	95.3	92.8
12.8	23	77	90.4	92.0	92.5	92.6	92.8	93.9	92.4
25.4	22	80	95.9	95.7	97.8	98.1	99.6	98.6	97.6
37.8	22	81	93.9	97.4	96.8	96.6	97.4	97.3	96.6
50.5	22	81	96.0	96.0	96.4	96.1	94.6	98.6	96.3

The 15-minute STEL method precision and bias was determined by sampling dynamically generated controlled test atmospheres using the system described in Section 4. Six samples were collected at each of four levels across a concentration range of 0.5 to 2 times the 15-minute STEL T_C at 50 mL/min for 15 min. Samples collected at each level were analyzed immediately after collection and independently from the other levels, including use of freshly prepared calibration standards. The results of these analyses are provided in Table 7, along with the concentration, temperature,

and relative humidity of each test atmosphere. The percent coefficient of variation of the means of the five levels tested (CV_{m_STEL}) was 2.4%, and the pooled coefficient of variation of each of the five levels tested (CV_{pl_STEL}) was 1.0%. The resulting 15-minute STEL method precision (u_{mp_STEL}) for methylene chloride was determined to be 2.6%. The mean recovery of the twenty-four samples was 95.4%, resulting in a method bias (B_{mp_STEL}) of 4.6% and a coefficient of variation (CV_{mb_STEL}) of 2.3%.

Table 7. Method precision data for methylene chloride (15-minute STEL).

concn (ppm)	temp (°C)	RH (%)	sample 1 (%)	sample 2 (%)	sample 3 (%)	sample 4 (%)	sample 5 (%)	sample 6 (%)	mean (%)
62.4	23	78	98.0	98.3	97.8	97.6	98.1	99.1	98.2
125	23	80	95.3	96.3	95.0	95.9	92.7	93.5	94.8
188	22	81	95.0	95.0	97.0	97.0	96.1	95.7	96.0
248	22	80	91.5	92.4	93.4	93.2	92.7	92.4	92.6

4.5 Analytical Recovery and Stability of Prepared Samples

Analytical recovery is affected by the extraction solvent, the ISTD, the sampling medium, and the technique used to extract samples. The data presented demonstrate validity for the extraction solvent, ISTD, sampling medium, and extraction technique described in this method. If other combinations of these are to be used, testing must be completed to satisfy the requirements found in current OSHA sampling and analysis method validation guidelines. Acceptable testing results must be documented.

The 8-hour TWA analytical recovery (R_A) was determined by liquid-spiking six replicate sorbent tubes across a range of analyte mass values that would be obtained from sampling at 0.1 to 2 times the 8-Hour TWA T_C for 240 min. Samples were analyzed following one hour of storage at ambient temperature. The R_A was 101.3%. The percent coefficient of variation of the thirty spiked samples ($CV_{R_{A\_TWA}}$) was 0.71%. The data are shown in Table 8.

Table 8. Analytical recovery data for methylene chloride (8-hour TWA).

× 8-hour TWA T_M	µg per sample	sample 1 (%)	sample 2 (%)	sample 3 (%)	sample 4 (%)	sample 5 (%)	sample 6 (%)	mean (%)
0.1×	141.0	101.0	100.5	101.1	102.0	100.3	102.7	101.3
0.5×	510.5	100.7	99.9	100.3	101.0	101.0	101.7	100.8
1.0×	1044	100.6	101.6	101.3	101.0	101.2	100.5	101.0
1.5×	1578	100.3	102.3	102.0	101.2	101.0	101.7	101.4
2.0×	2088	102.1	102.6	101.2	102.0	101.9	101.1	101.8

The 15-minute STEL analytical recovery (R_A) was determined by liquid-spiking six replicate sorbent tubes across a range of analyte mass values that would be obtained from sampling at 0.5 to 2 times the 15-min STEL T_C for 15 min. Samples were analyzed following one hour of storage at ambient temperature. The R_A was 101.2%. The percent coefficient of variation of the thirty spiked samples ($CV_{R_{A\_STEL}}$) was 1.1%. The data are shown in Table 9.

Table 9. Analytical recovery data for methylene chloride (15-minute STEL).

× 15-minute STEL T_M	µg per sample	sample 1 (%)	sample 2 (%)	sample 3 (%)	sample 4 (%)	sample 5 (%)	sample 6 (%)	mean (%)
0.5×	160.4	100.4	100.5	99.6	102.0	101.8	101.5	101.0
1.0×	320.9	103.3	102.1	103.4	100.1	102.0	100.6	101.9
1.5×	481.3	99.6	102.4	101.6	101.7	101.2	101.4	101.3
2.0×	656.3	100.9	99.9	100.8	100.7	101.4	99.1	100.5

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The 8-hour TWA stability of sample extracts was examined by retaining the six sample solvent extracts for the 1 times 8-hour TWA T_M samples described immediately above. All six vials were re-analyzed at 24, 48, and 72 hours after the initial analyses, with all vials remaining in the autosampler tray kept at 22 °C. Freshly prepared standards were used for each analysis event, and each sample septum was punctured four times for each injection. The results of these analyses are provided in Table 10. The regression line equation determined from these results was $y = -0.0600x + 100.9$.

The change in recovery (Δ_{ps_TWA}) of methylene chloride calculated from the regression line generated for the 3-day storage test was 0.18%.

Table 10. Stability of prepared sample data for methylene chloride (8-hour TWA).

day	sample 1 (%)	sample 2 (%)	sample 3 (%)	sample 4 (%)	sample 5 (%)	sample 6 (%)
0	100.6	101.6	101.3	101.0	101.2	100.5
1	100.5	101.5	100.9	100.6	101.0	100.8
2	99.7	100.1	100.0	99.8	100.4	100.2
3	100.3	101.0	101.2	101.7	101.7	100.8

The 15-min STEL stability of sample extracts was examined by retaining the six sample solvent extracts for the 1 times 15-min STEL T_M samples described immediately above. All six vials were re-analyzed at 24, 48, and 72 hours after the initial analyses, with all vials remaining in the autosampler tray kept at 22 °C. Freshly prepared standards were used for each analysis event, and each sample septum was punctured four times for each injection. The results of these analyses are provided in Table 11. The regression line equation determined from these results was $y = -1.23x + 101.9$.

The change in recovery (Δ_{ps_STEL}) of methylene chloride calculated from the regression line generated for the 3-day storage test was 3.7%.

Table 11. Stability of prepared sample data for methylene chloride (15-minute STEL).

day	sample 1 (%)	sample 2 (%)	sample 3 (%)	sample 4 (%)	sample 5 (%)	sample 6 (%)
0	103.3	102.1	103.4	100.1	102.0	100.6
1	101.4	102.6	103.4	100.8	102.6	99.5
2	95.9	97.6	98.8	97.9	97.1	97.0
3	98.1	100.1	99.3	99.5	99.9	98.6

4.6   Sampler Capacity

The sampling capacity of a single 400 mg sorbent tube was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 4, containing methylene chloride nominally at two times the 8-hour TWA T_C (calculated to be 50.8 ppm). The relative humidity and temperature of the air sampled were 78% and 22 °C, and the sampling flow rate was 50 mL/min. A sorbent tube testing system was made by placing two sampling tubes in series. The rear 400-mg sorbent tube was removed and analyzed at 300 min. No breakthrough in any of three replicate samples was observed after sampling for 300 minutes (corresponding to 15 liters). Data from three sorbent tube testing systems were used to determine a recommended sampling volume of 12 liters for methylene chloride. This volume corresponds to a 240 min sampling period which is the maximum recommended sampling time regardless of breakthrough.

4.7   Effect of Humidity

The 8-hour TWA effect of humidity was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 4, containing methylene chloride nominally at two times the target concentration (calculated to be 51.7 ppm). The relative humidity and temperature of the air sampled were 20% and 22 °C, and the sampling flow rate was 50 mL/min. Samples were collected on six sorbent tubes for 240 min. After immediate analysis, results for methylene chloride as a percentage of expected recovery using dry air were 94.8%, 96.0%, 95.6%, 95.1%, 95.9%, 97.3%. The mean percentage of expected recovery was 95.8%. The effect of humidity (Δ_{h_TWA}), calculated as the absolute difference between the mean low humidity recovery and the mean humid recovery taken from the 50.5 ppm method precision test described in Section 4.4, was 0.50%.

The 15-minute STEL effect of humidity was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 4, containing methylene chloride nominally at two times the target concentration (calculated to be 248 ppm). The relative humidity and temperature of the air sampled were 21% and 22 °C, and the sampling flow rate was 50 mL/min. Samples were collected on six sorbent tubes for 15 min. After immediate analysis, results for methylene chloride as a percentage of expected recovery using dry air were 89.5%, 89.9%, 89.7%, 88.9%, 89.9%, 89.9%. The mean percentage of expected recovery was 89.6%. The effect of humidity (Δ_{h_STEL}), calculated as the absolute difference between the mean low humidity recovery and the mean humid recovery taken from the 248 ppm method precision test described in Section 4.4, was 3.0%.

4.8   Sampling and Analytical Interferents

Isopropyl alcohol, with a retention time of 8.69 min using the GC-FID parameters described in Section 3.6, can cause a positive interference for methylene chloride. Confirm the presence of methylene chloride when the OSHA Action Level, PEL, or STEL value has been exceeded as described in Section 3.8.

4.9   Analytical Reproducibility

Eight-hour TWA analytical reproducibility samples were prepared by sampling a dynamically generated controlled test atmosphere, using the system described in Section 4, containing methylene chloride nominally at the target concentration (calculated to be 25.4 ppm). The relative humidity and temperature of the air sampled were 77% and 23 °C, and the sampling flow rate was 50 mL/min. Samples were collected on six sorbent tubes for 240 min. The resulting samples were submitted to the OSHA Technical Center for analysis using the procedures described in OSHA Method 1025 after storage for 19 days at -2 °C. The analytical results corrected for R_A are provided in Table 12. No sample result for methylene chloride fell outside the permissible bounds set by the expanded uncertainty determined in Section 4.10.

Table 12. Reproducibility data for methylene chloride (8-hour TWA).

sampled (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
994.1	1005	101.1	+1.1
996.5	1024	102.8	+2.8
983.9	1019	103.6	+3.6
1036	1069	103.2	+3.2
1039	921.4	88.7	-11.3
1030	909.3	88.3	-11.7

Fifteen-minute STEL analytical reproducibility samples were prepared by sampling a dynamically generated controlled test atmosphere, using the system described in Section 4, containing methylene chloride nominally at the target concentration (calculated to be 126.4 ppm). The relative humidity and temperature of the air sampled were 80% and 22 °C, and the sampling flow rate was 50 mL/min. Samples were collected on six sorbent tubes for 15 min. The resulting

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samples were submitted to the OSHA Technical Center for analysis using the procedures described in OSHA Method 1025 after storage for 19 days at -2 °C. The analytical results corrected for R_A are provided in Table 13. No sample result for methylene chloride fell outside the permissible bounds set by the expanded uncertainty determined in Section 4.10.

Table 13. Reproducibility data for methylene chloride (15-minute STEL).

sampled (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
306.8	313.2	102.1	+2.1
309.5	319.6	103.3	+3.3
305.4	314.6	103.0	+3.0
321.2	329.6	102.6	+2.6
324.1	330.6	102.0	+2.0
318.2	325.5	102.3	+2.3

4.10 Estimation of Uncertainty

Methylene chloride sampling and storage percent relative standard uncertainty components are provided in Table 14 for both 8-hour TWA and 15-minute STEL sampling. The sampling and storage percent relative uncertainty (u_s) was determined to be 3.7% for 8-hour TWA sampling and 4.5% for 15-minute STEL sampling.

Table 14. Sampling and storage uncertainty.

uncertainty component	8-hour TWA (%)	15-min STEL (%)	notes
flow rate measurement (u_{fr})	0.056	0.056	Calculated from replicate flow readings at 50 mL/min
flow rate calibration (u_{fc})	0.58	0.58	$u_{fc} = 1\%/\sqrt{3}$, assumes a maximum flow meter calibration tolerance of ±1% at 50 mL/min
pump flow stability (u_{fs})	3.5	3.5	$u_{fs} = 6\%/\sqrt{3}$, assumes flow rate is maintained to within ±6% at 50 mL/min
sampling time (u_{st})	0.17	2.7	$u_{st} = \left[(B_{st} \times t_{st}^{-1})/\sqrt{6} \right] \times 100\%$, time sampled to nearest minute, where B_{st} = 1 min, and t_{st} = minutes sampled (240 and 15 min)
sampling efficiency (u_{se})	0.00	0.00	Sampler capacity not exceeded at recommended sampling time and rate, see Section 4.6
post sampling storage (u_{ss})	0.92	0.047	$u_{ss} = \Delta_{ss}/\sqrt{3}$, where Δ_{ss_TWA} = 1.6% and Δ_{ss_STEL} = 0.082%, see Section 4.3
sampling and storage uncertainty (u_s)	3.7	4.5	

Methylene chloride analytical percent relative standard uncertainty components are provided in Table 15 for both 8-hour TWA and 15-minute STEL sample analyses. The analytical percent relative uncertainty (u_s) was determined to be 7.8% for 8-hour TWA sampling and 8.0% for 15-minute STEL sampling.

Table 15. Analytical uncertainty.

uncertainty component	8-hour TWA (%)	15-min STEL (%)	notes
calibration standards (u_{cs})	1.2	1.2	Calculated from repeatability tests using the volumetric flasks and syringes specified for use in Section 3.4 and the manufacturer reported purity of methylene chloride of ≥99.8%
analytical recovery (u_{ar})	0.13	0.22	$u_{ar} = CV_{R_A}/\sqrt{n}$, where $CV_{R_A\_TWA} = 0.71\%$, $n_{TWA} = 30$, $CV_{R_A\_STEL} = 1.1\%$ and $n_{STEL} = 24$, see Section 4.5, assumes results are corrected for analytical recovery
stability of prepared samples (u_{ps})	0.10	2.1	$u_{ps} = \Delta_{ps}/\sqrt{3}$, where $\Delta_{ps\_TWA} = 0.18\%$ and $\Delta_{ps\_STEL} = 3.7\%$, see Section 4.5
method precision (u_{mp})	2.9	2.6	$u_{mp} = \sqrt{(CV_m)^2 + (1 - 1/n) \times (CV_{pl})^2}$, where $CV_{m\_TWA} = 2.5$, $CV_{pl\_TWA} = 1.6$, $CV_{m\_STEL} = 2.4$, $CV_{pl\_STEL} = 1.0$, and $n = 6$, see Section 4.4
method bias (u_{mb})	4.2	4.0	$u_{mb} = \sqrt{(B_{mb}/\sqrt{3})^2 + (CV_{mb}/\sqrt{n})^2 + (u_{rc})^2}$, where $B_{mb\_TWA} = 4.9\%$, $CV_{mb\_TWA} = 2.7\%$, $n_{TWA} = 30$, $B_{mb\_STEL} = 4.6\%$, CV_{mb_STEL} is 2.3%, and $n_{STEL} = 24$, see Section 4.4; $u_{rc} = 3\%$, see Reference 3
effect of humidity (u_h)	0.29	1.7	$u_h = \Delta_h/\sqrt{3}$, where $\Delta_{h\_TWA} = 0.50\%$ and $\Delta_{h\_STEL} = 3.0\%$, see Section 4.7
instrument response drift (u_{dr})	5.8	5.8	$u_{dr} = 10\%/\sqrt{3}$, assumes a maximum instrument response drift of ±10%,
analytical uncertainty (u_a)	7.8	8.1	

The combined percent relative standard uncertainty of the sampling and analysis procedure $\left(u = \sqrt{(u_s)^2 + (u_a)^2}\right)$ was determined to be 8.6% for 8-hour TWA samples and 9.3% for 15-min STEL samples. The expanded uncertainty ($U = 2 \times u$) was determined to be 17% for 8-hour TWA samples and 19% for 15-minute STEL samples.

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