Organic Vapor Sampling Group 1 (OVSG-1)
Carbon Disulfide-Extracted Analytes Collected on Coconut Charcoal Sorbent Tubes

---

Method number: 5000

Version number: 1.0

Validated analytes:

Analyte	CAS No.	Analyte	CAS No.
Benzene	71-43-2	Octane	111-65-9
n-Butyl acetate	123-86-4	Pentane	109-66-0
sec-Butyl acetate	105-46-4	*n*-Propyl acetate	109-60-4
tert-Butyl acetate	540-88-5	Perchloroethylene (Tetrachloroethylene)	127-18-4
Cyclohexane	110-82-7		
Ethyl acetate	141-78-6	Toluene	108-88-3
Ethyl benzene	100-41-4	Trichloroethylene	79-01-6
n-Hexane	110-54-3	Trimethyl benzene	25551-13-7
Heptane (*n*-Heptane)	142-82-5	Xylenes (*o*-, *m*-, *p*-isomers)	1330-20-7
Isobutyl acetate	110-19-0		
Nonane	111-84-2		

Procedure: Collect samples by drawing workplace air containing specified organic vapors through an Anasorb coconut shell charcoal (CSC) sorbent tube. Extract samples with carbon disulfide (CS_2) and analyze by gas chromatography (GC) using a flame ionization detector (FID). The analytes listed above are compatible with the sorbent, extraction solvent, and analytical parameters of Method 5000, and may be sampled separately or together.

Recommended sampling time and sampling rate:
*240 min at 50 mL/min (12 L)
*exceptions:
n-propyl acetate 200 min at 50 mL/min (10 L)
cyclohexane 190 min at 50 mL/min (9.5 L)
ethyl acetate 120 min at 50 mL/min (6 L)
n-hexane 98 min at 50 mL/min (4.9 L)
heptane (*n*-heptane), octane, and nonane 80 min at 50 mL/min (4 L)
pentane 45 min at 50 mL/min (2.25 L)

Special requirements: Ship samples for ethyl acetate cold and analyze within 6 days of collection. Refrigerated storage is required for samples containing ethyl acetate and recommended for other analytes. Re-cap extracted samples for pentane, trichloroethylene, and ethyl acetate after initial analysis if further analysis is to be completed.

Validation status: Data found in the respective method appendices have been subjected to the established validation procedures of the OSHA Method Development Team. The method is considered to be fully validated for all analytes so designated.

February 2021

Daren Pearce

Method Development Team
Industrial Hygiene Chemistry Division
OSHA Salt Lake Technical Center
Sandy UT 84070-6406

1 Introduction

For assistance with accessibility problems in using figures and illustrations presented in this method, please contact the Salt Lake Technical Center (SLTC) at (801) 233-4900. This procedure was designed and tested for internal use by OSHA personnel. Mention of any company name or commercial product does not constitute endorsement by OSHA.

This method harmonizes the sampling, sample preparation and analysis of nonpolar and semi-polar analytes collected on Anasorb CSC, sorbent tubes that are extracted with carbon disulfide (CS_2). Validation data for each analyte are described in the relevant appendices.

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

A 6-mm x 70-mm glass sampling tube packed with two sections of 20/40 mesh Anasorb CSC sorbent is required for sampling. The front section contains 100 mg and the back section contains 50 mg. The sections are held in place with glass wool and separated with foam plugs. Commercially available tubes were purchased from SKC Inc. (catalog no. 226-01) 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 A (catalog no. 222-3-1), 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 target analyte. If sampling for multiple target analytes, sample no longer than the shortest duration specified for each of those analytes.

2.2 Reagents

None Required

2.3 Technique

Immediately before sampling, break off the ends of the flame-sealed tube to provide an opening approximately half the internal diameter of the tube. Place tube into a sampling tube holder to minimize the hazard to the worker from the broken ends of the tube. All tubes submitted for analysis (including field blanks) should be from the same lot.

Attach the tube holder (with the adsorbent tube) to the sampling pump so that the adsorbent tube is in an approximately vertical position with the inlet facing down 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 sampling tube.

Sample at 50 mL/min for 240 min (12 L) for all analytes except as specified under "recommended sampling time and sampling rate" on page 1 of this method and as explained in the respective method appendices.

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. Always refrigerate samples for ethyl acetate and ship these cold. Analyze samples for ethyl acetate within 6 days of collection.

3 Analytical Procedure

3.1 Apparatus

- Mechanical vial shaker
- One liter amber glass solvent dispenser capable of dispensing 1.00 mL
- Syringe (25-μL)
- Class A volumetric flasks (1, 2, 5 and 500-mL)
- Amber glass vials with polytetrafluoroethylene (PTFE)-lined crimp caps (2 -mL)
- Mechanical micropipette (adjustable 10 to 100-μL)
- GC instrument with FID

3.2 Reagents

- Benzene (≥99%, analytical grade)
- *n*-Butyl acetate (≥99%, analytical grade)
- *sec*-Butyl acetate (≥99%, analytical grade)
- *tert*-Butyl acetate (≥99%, analytical grade)
- Cyclohexane (≥99%, analytical grade)
- Ethyl acetate (≥99%, analytical grade)
- Ethyl benzene (≥99%, analytical grade)
- *n*-Hexane (≥99%, analytical grade)
- Heptane (*n*-heptane) (≥99%, analytical grade)
- Isobutyl acetate (≥99%, analytical grade)
- Nonane (≥99%, analytical grade)
- Octane (≥99%, analytical grade)
- Pentane (≥99%, analytical grade)
- *n*-Propyl acetate (≥99%, analytical grade)
- Perchloroethylene or Tetrachloroethylene (≥99%, analytical grade)
- Toluene (≥99%, analytical grade)
- Trichloroethylene (≥99%, analytical grade)
- Trimethyl benzene
  - Trimethyl benzene (1,3,5 isomer) [CAS No. 108-67-8] (≥99%, analytical grade)
  - Trimethyl benzene (1,2,4 isomer) [CAS No. 95-63-6] (≥99%, analytical grade)
  - Trimethyl benzene (1,2,3 isomer) [CAS No. 526-73-8] (≥90%, technical grade or better, ensure no significant contamination with other trimethyl benzene isomers)
- Xylenes (*o*-, *m*-, *p*-isomers)
  - Xylene (*o* isomer) [CAS No. 95-47-6] (≥99%, analytical grade)
  - Xylene (*m* isomer) [CAS No. 108-38-3] (≥99%, analytical grade)
  - Xylene (*p* isomer) [CAS No. 106-42-3] (≥99%, analytical grade)
- Carbon disulfide (CS_2) (reagent grade or better, use low-benzene or ensure background is acceptable)
- *n*-Hexylbenzene (> 99%, analytical grade)

3.3 Reagent Preparation

Extraction solvent (CS_2 with 0.25 μL/mL *n*-hexylbenzene as an internal standard (ISTD)): To a 500-mL volumetric flask add approximately 450 mL of CS_2 and exactly 125 μL of *n*-hexylbenzene, then add CS_2 to the mark. Immediately mix the solution and transfer to an amber glass solvent dispenser.

3.4 Standard Preparation

Prepare calibration standards by injecting microliter amounts of the neat chemical into various 2-mL volumetric flasks containing approximately 1 mL of the extraction solvent. Fill to the mark with extraction solvent, mix, and transfer to 2-mL amber glass autosampler vials. Multiple analytes in one calibration standard can substantially dilute the final concentration of the ISTD when it is pre-mixed with the extraction solvent. To minimize this effect on the calibration, correct the ISTD concentration for each standard when calibrating. Acetates should be made as a separate group of standards as *sec*-butyl acetate co-elutes with toluene. For analysis of xylenes (*o*-, *m*-, *p*-isomers), calibrate with xylene (*m* isomer) and xylene (*o* isomer) due to xylene (*p* isomer) co-eluting with xylene (*m* isomer). 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 a sample tube. Transfer the respective 100-mg and 50-mg Anasorb CSC sections into separate 2-mL vials. Discard glass tube, foam, and glass wool plug.

Add 1.00 mL of extraction solvent to each vial and immediately seal with PTFE-lined caps.

Extract the samples by shaking for 30 min.

3.6 Analysis

Analyze samples using a GC-FID instrument and the analytical parameters described below. Use an ISTD calibration method. For each analyte, construct an ordinary least-squares linear regression curve by plotting ISTD-corrected response of standard injections versus micrograms of analyte per sample. A weighted linear least-squares curve using a x^{-1} or x^{-2} weight can be used to minimize the influence of heteroscedasticity and improve accuracy at the lower end of the regression curve. Confirm the presence of analytes when an OSHA Permissible Exposure Limit (PEL) value has been exceeded, as described in Section 3.8. See Figures 1 and 2 below for an example of chromatograms obtained from standards containing analyte mass concentrations equivalent to sampling for the recommended time with each analyte at its respective OSHA 8-hour time weighted average PEL or other suitable target value.

GC parameters

column: Agilent J&W DB-624 capillary column, 20-m × 0.18-mm i.d., d_f = 1.0-µm , or equivalent

inlet liner: Restek Topaz 4.0-mm ID Low Pressure Drop Precision Inlet Liner w/wool (Catalog no. 23309, or equivalent)

carrier: hydrogen, constant pressure (18 psi)

septum purge: hydrogen, 3.0 mL/min

injection: 1.0 µL, split injection, 150:1 ratio

inlet temperature: 250 °C

oven temperature program: 40 °C (hold 2.25 min), ramp to 90 °C at 7 °C/min (hold 0 min), ramp to 225 °C at 25 °C/min (hold 0.2 min)

run time: 14.99 min

retention times:

1.24 min - pentane
1.65 min - CS$_2$
2.25 min - *n*-hexane
3.00 min - ethyl acetate
3.46 min - cyclohexane
3.82 min - benzene
4.22 min – heptane (*n*-heptane)
4.64 min - trichloroethylene
4.91 min - *tert*-butyl acetate
5.36 min - *n*-propyl acetate
6.51 min - toluene
6.51 min - *sec*-butyl acetate
6.88 min - octane
6.95 min - isobutyl acetate
7.39 min - perchloroethylene (tetrachloroethylene)
8.08 min - *n*-butyl acetate
9.16 min - ethyl benzene
9.39 min - xylene (*m* isomer)
9.39 min - xylene (*p* isomer)
9.64 min - nonane
10.02 min - xylene (o isomer)
11.26 min - trimethyl benzene (1,3,5 isomer)
11.63 min - trimethyl benzene (1,2,4 isomer)
12.03 min - trimethyl benzene (1,2,3 isomer)
14.10 min - ISTD

Note: Analytes that co-elute are usually not found together in workplace atmospheres. If needed they can be resolved by using an alternate column or verification with gas chromatography-mass spectrometry (GC-MS).

<u>FID parameters</u>

detector temperature: 250 °C

hydrogen flow: 30 mL/min

air flow: 400 mL/min

nitrogen make up flow: 25 mL/min

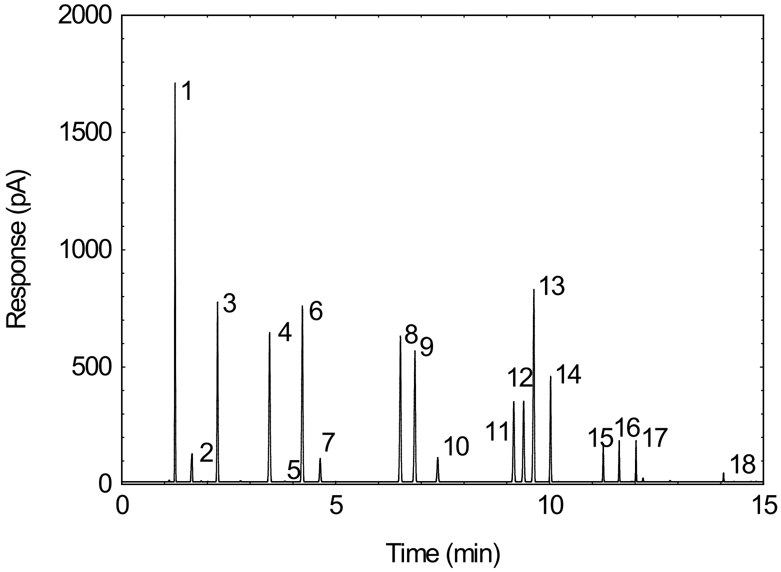

Figure 1. Example chromatogram for analytes excluding acetate compounds. Peak labels: (1) pentane, (2) CS$_2$, (3) *n*-hexane, (4) cyclohexane, (5) benzene, (6) heptane (*n*-heptane), (7) trichloroethylene, (8) toluene, (9) octane, (10) perchloroethylene (tetrachloroethylene), (11) ethyl benzene, (12) xylene (*m* and *p* isomers), (13) nonane, (14) xylene (*o* isomer), (15) trimethyl benzene (1,3,5 isomer), (16) trimethyl benzene (1,2,4 isomer), (17) trimethyl benzene (1,2,3 isomer), (18) ISTD.

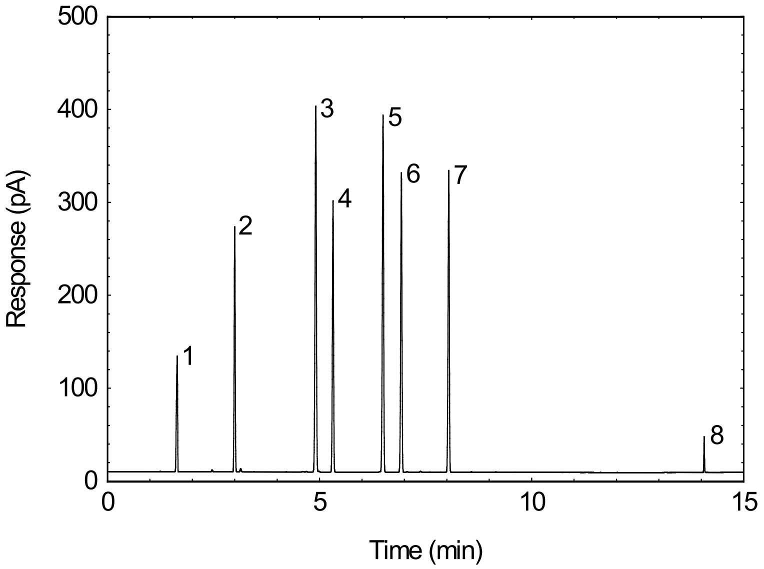

Figure 2. Example chromatogram for acetate compounds. Peak labels: (1) CS_2, (2) ethyl acetate, (3) *tert*-butyl acetate, (4) *n*-propyl acetate, (5) *sec*-butyl acetate, (6) isobutyl acetate, (7) *n*-butyl acetate, (8) ISTD.

3.7 Calculations

Calculate the micrograms recovered per sample (m) for each analyte. 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/m^3) using Equation 1, where V is the volume of air sampled (L), and E_E is the extraction efficiency expressed in decimal format.

$$C = \frac{m}{VE_E} \qquad \text{Equation 1}$$

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/m^3) 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).

$$C_{ppm} = \frac{CV_M}{M} \qquad \text{Equation 2}$$

Values for E_E obtained during validation studies, and M are listed in Table 1 along with the OSHA Integrated Management Information System (IMIS) numbers for each analyte.

Table 1. Molar mass, extraction efficiencies, and OSHA Integrated Management Information System (IMIS) numbers for Method 5000 analytes.

analyte	M (g/mol)	E_E	IMIS
benzene	78.11	0.971	0320
n-butyl acetate	116.16	0.980	0440
sec-butyl acetate	116.16	0.987	0441
tert-butyl acetate	116.16	0.990	0442
cyclohexane	84.16	1.033	0810
ethyl acetate	88.11	0.964	1040
ethyl benzene	106.17	1.004	1080
n-hexane	86.18	1.006	1380
heptane (*n*-heptane)	100.21	1.014	1371
isobutyl acetate	116.16	1.014	1534
nonane	128.25	1.020	N807
octane	114.23	1.015	1957
pentane	72.15	1.010	1990
n-propyl acetate	102.13	0.975	2180
perchloroethylene (tetrachloroethylene)	165.83	0.987	2020
toluene	92.14	0.986	2460
trichloroethylene	131.39	1.005	2490
trimethyl benzene	120.19		2505
trimethyl benzene (1,3,5 isomer)		0.990	
trimethyl benzene (1,2,4 isomer)		0.970	
trimethyl benzene (1,2,3 isomer)		0.930	
xylenes (*o*-, *m*-, *p*- isomers)	106.16		2590
xylene (*o* isomer)		0.949	
xylene (*m* isomer)		0.995	
xylene (*p* isomer)		0.982	

3.8 Qualitative Analysis

When necessary, the identity of an analyte peak can be confirmed by GC-MS using the analytical parameters described below. Confirm the presence of an analyte by matching the retention time and fragmentation pattern of a standard at a similar concentration. See Figures 3 and 4 below for example total ion current (TIC) chromatograms obtained from a standard containing analyte concentrations equivalent to sampling for the recommended time for each analyte at its respective OSHA 8-hour time weighted average PEL value or other suitable target value.

GC parameters

column:	Agilent J&W DB-624 capillary column, 20-m × 0.18-mm i.d., d_f = 1.0-µm , or equivalent
inlet liner:	Restek Topaz 4.0-mm ID Low Pressure Drop Precision Inlet Liner w/wool (Catalog no. 23309, or equivalent)
carrier:	helium, constant flow 1.0 mL/min
septum purge:	helium, 3.0 mL/min
injection:	1.0 µL, split injection, 150:1 ratio
inlet temperature	250 °C
oven temperature program:	40 °C (hold 3.0 min), ramp to 90 °C at 6 °C/min (hold 0 min), ramp to 225 °C at 25 °C/min (hold 0.27 min)
run time:	17 min

retention times:

1.63 min - pentane
2.27 min - CS_2
2.96 min - *n*-hexane
3.96 min - ethyl acetate
4.55 min - cyclohexane
5.00 min - benzene
5.53 min - heptane (*n*-heptane)
6.02 min - trichloroethylene
6.35 min - *tert*-butyl acetate
6.83 min - *n*-propyl acetate
8.24 min - *sec*-butyl acetate - toluene
8.27 min - toluene
8.67 min - octane
8.73 min - isobutyl acetate
9.29 min - perchloroethylene (tetrachloroethylene)
10.02 min - *n*-butyl acetate
11.31 min - ethyl benzene
11.56 min - xylene (*m* isomer)
11.56 min - xylene (*p* isomer)
11.79 min - nonane
12.19 min - xylene (*o* isomer)
13.38 min - trimethyl benzene (1,3,5 isomer)
13.74 min - trimethyl benzene (1,2,4 isomer)
14.10 min - trimethyl benzene (1,2,3 isomer)
16.00 min - ISTD

<u>mass spectrometer parameters</u>

mode: 70 eV electron ionization

acquisition mode: scan, *m/z* 25 – 400

solvent delay: 0.2 min

timed events: 2.2 – 2.6 min MS off

EMV mode: gain factor (5)

temperatures: 250 °C (source), 150 °C (quadrupole assembly), 300 °C (transfer line)

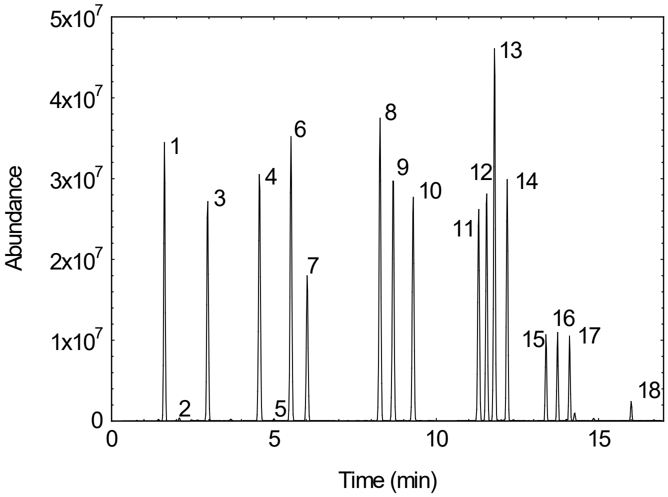

Figure 3. Example TIC GC-MS chromatogram for analytes excluding acetate compounds. Peak labels: (1) pentane, (2) CS_2, (3) *n*-hexane, (4) cyclohexane, (5) benzene, (6) heptane (*n*-heptane), (7) trichloroethylene, (8) toluene, (9) octane, (10) perchloroethylene (tetrachloroethylene), (11) ethyl benzene, (12) xylene (*m* and *p* isomers), (13) nonane, (14) xylene (*o* isomer), (15) trimethyl benzene (1,3,5 isomer), (16) trimethyl benzene (1,2,4 isomer), (17) trimethyl benzene (1,2,3 isomer), (18) ISTD.

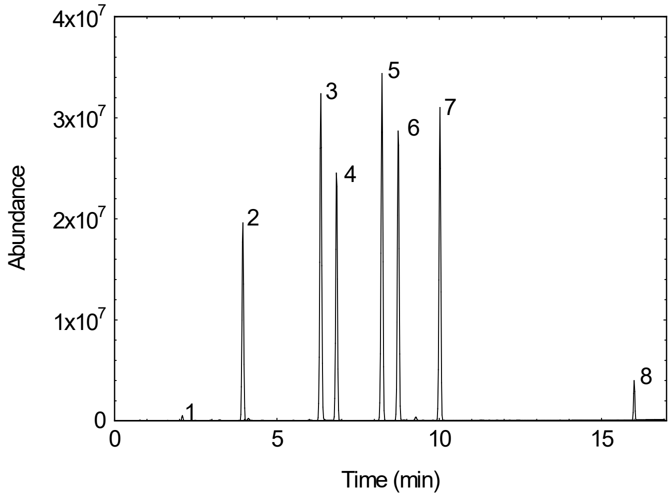

Figure 4. Example TIC GC-MS chromatogram for acetate compounds. Peak labels: (1) CS_2, (2) ethyl acetate, (3) *tert*-butyl acetate, (4) *n*-propyl acetate, (5) *sec*-butyl acetate, (6) isobutyl acetate, (7) *n*-butyl acetate, (8) ISTD.

DEPARTMENT OF LABOR • UNITED STATES OF AMERICA

OSHA 5000, Appendix A
Cyclohexane

Version:	1.0
OSHA PEL:	300 ppm (1050 mg/m^3) 8-Hour TWA, General Industry, Construction, Shipyard
ACGIH TLV:	100 ppm (350 mg/m^3) 8-Hour TWA
Recommended sampling time and sampling rate:	190 min at 50 mL/min (9.5 L)
Reliable quantitation limit:	0.043 ppm (0.15 mg/m^3)
Standard error of estimate:	5.6%
Status:	Fully validated. Method 5000 has been subjected to the established validation procedures of the Method Development Team for sampling and analysis of cyclohexane.

March 2018 (OSHA 1022)	Daren Pearce
February 2021 (OSHA 5000)	Daren Pearce

1 Introduction

1.1 Previous Methods used by OSHA for Sampling and Analysis of Cyclohexane

The specific analyte described in this appendix is cyclohexane, CAS No. 110-82-7. The methodologies described in this appendix for cyclohexane are based on OSHA Method 1022.[1] That method requires the collection of samples using charcoal sorbent tubes, extraction using carbon disulfide containing 1% *N,N*-dimethylformamide, and analysis by gas chromatography using a flame ionization detector. Prior to the use of OSHA Method 1022, OSHA routinely collected and analyzed samples for cyclohexane using NIOSH Method 1500.[2] OSHA Method 1022 made changes to the extraction solvent and analytical column stationary phase compared to NIOSH Method 1500.

1.2 Changes to the Previously-Used Method

This appendix represents an update of OSHA Method 1022[1], which was fully validated at the time it was published based on the validation guidelines in effect at that time. Compared to the previous method used this method includes a new extraction solvent. Data presented from the previously used method are identified by the statement "Pre-existing data from OSHA Method 1022[1] are presented in this section". The change was made to allow the standardized collection and analysis of cyclohexane with other analytes found in Organic Vapor Sampling Group 1, described in OSHA Method 5000.

---

[1] Pearce, D. Cyclohexane (OSHA Method 1022), 2018. Occupational Safety and Health Administration Web site. https://www.osha.gov/dts/sltc/methods/validated/1022/1022.pdf (accessed October 2018).

[2] Pendegrass, S.; May, L. Hydrocarbons, BP 36 ºC-216 ºC (NIOSH Method 1500, Issue 3), 2003. Center for Disease Control, The National Institute for Occupational Safety and Health (NIOSH) Web site. http://www.cdc.gov/niosh/docs/2003-154/pdfs/1500.pdf (accessed October 2018).

1.3 Validation Parameters

The procedures used to develop the method validation data are described in Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis.[3] Air concentrations listed in ppm are referenced to 25 °C and 760 Torr. The target concentration for method evaluation was the OSHA 8-hour time-weighted average (TWA) permissible exposure limit (PEL) for cyclohexane.

2 Detection and Quantification

2.1 Detection Limit of the Analytical Procedure (DLAP)

Pre-existing data from OSHA Method 1022[1] are presented in this section.

The DLAP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLAP $S_{y/x}$) divided by the slope of the line produced from analyses of ten analytical standards prepared with equally spaced increments of analyte mass. The standards were prepared in such a way that the highest standard concentration would produce a peak approximately 10 times the response of a reagent blank at or near the chromatographic retention time of the analyte. The standards and a reagent blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLAP $S_{y/x}$ and slope values for DLAP determination. Results obtained for these analyses are listed in Table A-1, and plotted in Figure A-1.

Table A-1. DLAP data for cyclohexane.

concentration (µg/mL)	mass on column (pg)	area counts (µV·s)
0.00	0.00	0.00
0.934	6.23	0.138
1.87	12.5	0.273
2.80	18.7	0.430
3.73	24.9	0.510
4.67	31.1	0.608
5.60	37.3	0.754
6.54	43.6	0.870
7.47	49.8	0.958
8.40	56.0	1.07
9.34	62.3	1.22

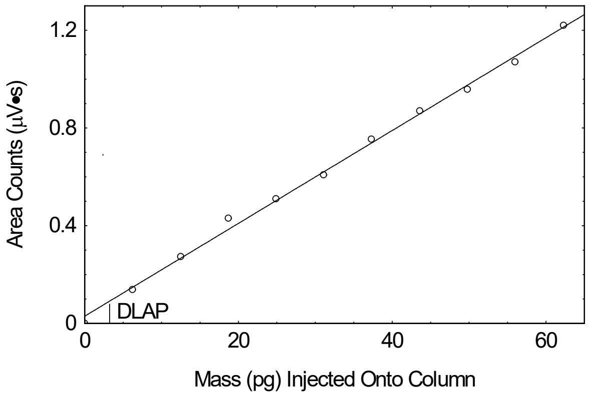

Figure A-1. Plot of data used to determine the DLAP for cyclohexane ($y = 0.0190x + 0.0296$, DLAP $S_{y/x}$ = 0.0225, DLAP = 3.55 pg).

2.2 Detection Limit of the Overall Procedure (DLOP) and Reliable Quantitation Limit (RQL)

Pre-existing data from OSHA Method 1022[1] are presented in this section.

The DLOP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLOP $S_{y/x}$) divided by the slope of the line produced from analyses of ten samples prepared from sorbent tubes spiked with equally spaced increments of analyte mass. 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 RQL is expressed as an air concentration that will provide sufficient analyte mass per sample that produces a response greater than 10× DLOP $S_{y/x}$ divided by the slope of the line described above. The spiked samplers and a sample blank were analyzed with the recommended analytical

---

[3] Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration Web site. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed December 2018).

parameters described in OSHA Method 5000. The resulting data provided the DLOP $S_{y/x}$ and slope values for DLOP and RQL determinations. Results obtained from these analyses are listed in Table A-2, and plotted in Figure A-2.

Table A-2. DLOP and RQL data for cyclohexane.

mass per sample (µg/sample)	area counts (µV·s)
0.00	0.00
0.934	0.107
1.87	0.295
2.80	0.401
3.73	0.502
4.67	0.635
5.60	0.774
6.54	0.907
7.47	1.02
8.40	1.12
9.34	1.26

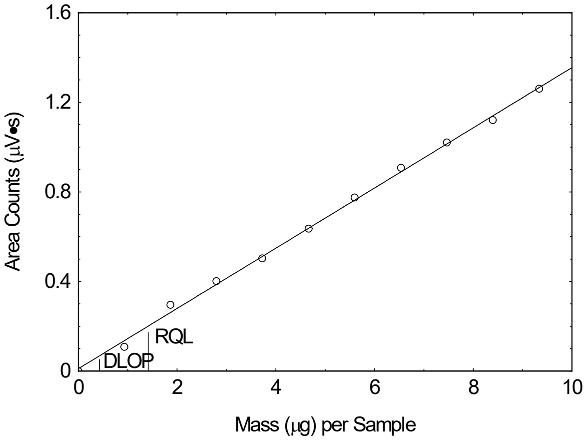

Figure A-2. Plot of data used to determine the DLOP and RQL for cyclohexane ($y = 0.134x + 0.0105$, DLOP $S_{y/x}$ = 0.0189, DLOP = 0.423 µg/sample, RQL = 1.41 µg/sample or 0.0430 ppm).

3 Analytical Precision Across the Calibration Range

Pre-existing data from OSHA Method 1022[1] are presented in this section.

Fifteen analytical standards over a range of 0.02 to 2 times the analyte concentration in solvent that would be obtained from sampling for the recommended time at the target concentration were analyzed with the recommended analytical parameters described in OSHA Method 5000. A weighted least-squares linear regression curve was created by plotting the analyte mass per sample versus the corresponding ratio of analyte peak area to internal standard (ISTD) peak area. The resulting data provided the standard error of estimate (Calibration $S_{y/x}$) value across the calibration range, which provides an indication of the imprecision attributable to the instrumental analysis of the target analyte. Results from these analyses are listed in Table A-3, and plotted in Figure A-3.

Table A-3. Analytical precision data for cyclohexane.

× target	0.02×	0.5×	1.0×	1.5×	2.0×
concn (µg/sample)	217.9	4863	9726	14,395	19,453
area ratio	0.9344	21.12	42.49	62.53	85.68
	0.9309	21.21	42.45	62.11	85.36
	0.9364	21.16	42.29	61.90	84.84

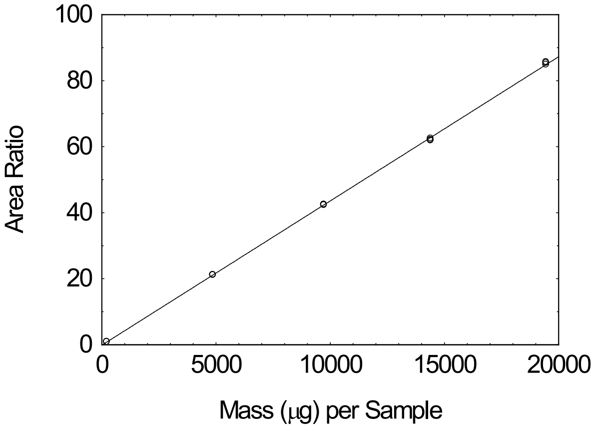

Figure A-3. Plot of data used to determine the precision of the analytical method for cyclohexane ($y = 0.00436x$ - 0.0153, $w_i = 1/x^2$, Calibration $S_{y/x}$ = 0.0000265).

4 Sampler Storage Stability

Pre-existing data from OSHA Method 1022[1] are presented in this section.

Storage stability test samples for cyclohexane were prepared by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13. Sampling from this system followed the recommended sampling parameters published in OSHA Method 5000. The nominal concentration of cyclohexane for both ambient and refrigerated storage testing was the target concentration (respective calculated concentrations of 305 ppm and 304 ppm). The respective relative humidities and temperatures of the air sampled were 69.2% at 25.2 °C and 69.2% at 25.2 °C for both tests. For each test, eighteen samples were prepared, and three of these were analyzed on the same day that samples were created. The remaining fifteen refrigerated storage test samples were stored at reduced temperature (4 °C), while the remaining fifteen ambient storage test samples were kept in a closed drawer at ambient temperature (about 22 °C). For each storage condition, three samples were selected and analyzed from those remaining at 3-4 day intervals. The results of these analyses (uncorrected for extraction efficiency) are provided in Table A-4, and plotted in Figures A-4 through A-5. Some migration of cyclohexane from the front to the rear sorbent tube section was observed on day 17 for the ambient storage test. Analyte migration was not observed with the refrigerated test samples.

The recovery of cyclohexane calculated from the regression line generated for the 17-day ambient storage test was 100.1%.

Table A-4. Sampler storage stability data for cyclohexane.

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	101.6	102.6	101.2	105.3	100.9	101.7
3	105.2	101.1	100.4	100.4	100.3	101.7
7	103.8	101.3	102.7	101.4	101.7	102.0
10	105.7	101.5	102.0	102.3	103.5	102.0
14	101.7	101.6	93.9	103.0	101.9	101.9
17	97.5	100.6	100.8	101.7	101.5	101.6

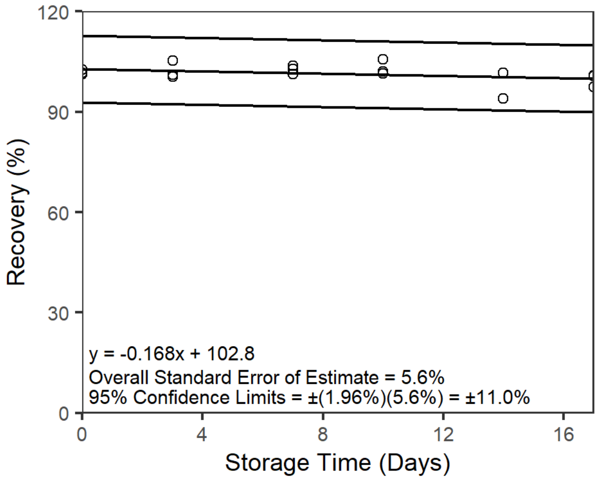

Figure A-4. Plot of ambient storage stability data for cyclohexane.

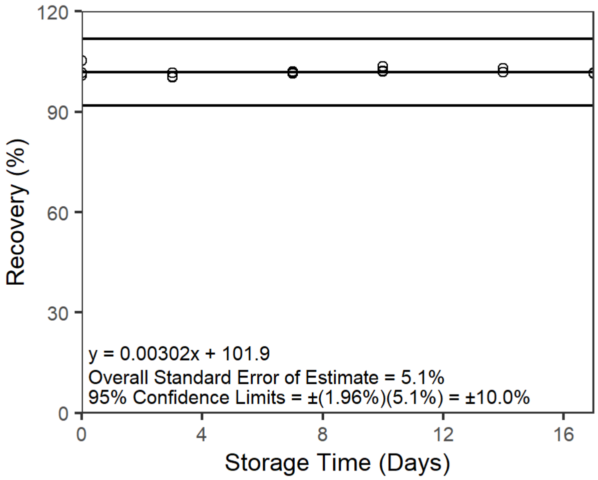

Figure A-5. Plot of refrigerated storage stability data for cyclohexane.

5 Precision of the Overall Procedure

Pre-existing data from OSHA Method 1022[1] are presented in this section.

The overall standard error of estimate obtained from the ambient storage test analyses described in Section 4 and sampling pump variability were used to determine the precision of the overall procedure, where all aspects of sampling and analysis (sampling, sorbent tube handling and solvent extraction, and instrumental analysis) are considered. This value was obtained by taking the square root of the squared ambient storage stability standard error of estimate (Storage $S_{y/x}^2$) added to the squared sampling pump variability value (V_{SP}^2). The resulting precision of the overall procedure at the 95% confidence level for the ambient 17-day storage test (at the target concentration) for cyclohexane was determined to be ±11.0% based on the observed ambient Storage $S_{y/x}$ value of 5.6% and V_{SP} value of 5.0%.

6 Recovery and Stability of Prepared Samples

Quantitative extraction 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 OSHA Method 5000. 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.

A value for extraction efficiency (E_E) was determined by liquid-spiking four replicate sorbent tubes across a range of analyte mass values that would be obtained from sampling at 0.1 to 2 times the target concentration value for 190 min. Four sorbent tubes were also spiked in this fashion at the target concentration after drawing humid air (73.3% relative humidity at 24.8 °C) through these tubes at 50 mL/min for 4 hours. All of the samples described above were analyzed the following day after being kept overnight at ambient temperature. The E_E value at the RQL was 107.8%, while that of the working range samples (excluding the samples through which humid air had been drawn) was 103.3%. The data are shown in Table A-5. Pre-loading sorbent tubes with moisture ("wet" designation in the table) did not have an unacceptable effect on E_E.

Table A-5. Extraction efficiency data for cyclohexane.

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.1	992.1	107.1	108.1	106.4	107.6	107.3
0.25	2451	104.9	103.9	104.1	105.4	104.6
0.5	4980	102.8	102.8	102.4	103.3	102.8
1.0	9726	101.5	100.6	100.2	101.6	101.0
1.5	14,784	101.4	101.2	102.4	103.4	102.1
2.0	19,453	101.1	102.1	101.7	101.9	101.7
RQL	1.56	104.5	124.3	90.0	112.4	107.8
1.0 (wet)	9726	100.2	99.8	101.3	102.5	100.9

The stability of sample extracts prepared according to OSHA Method 5000 was examined by retaining the sample solvent extracts for the target concentration samples described immediately above. Two of the four vials were immediately recapped with new septa following the initial analyses, and again following each re-analysis event. The other two vials retained the original punctured septa throughout. All four 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 septum (whether new or previously used) was punctured four times for each injection. The resulting data are shown in Table A-6.

Table A-6. Extracted sample stability data for cyclohexane.

time (days)	punctured septa replaced recovery (%) 1	punctured septa replaced recovery (%) 2	punctured septa retained recovery (%) 1	punctured septa retained recovery (%) 2
0	100.7	100.3	101.3	101.4
1	99.5	101.7	101.6	101.8
2	101.8	104.0	100.7	101.5
3	97.4	99.9	97.4	99.9

7 Sampler Capacity

Pre-existing data from OSHA Method 1022[1] are presented in this section.

The sampling capacity of the front section of a sorbent tube was tested by sampling a dynamically generated controlled test atmosphere using the system described in Section 13, containing cyclohexane nominally at two times the target concentration (calculated to be 613 ppm). The relative humidity and temperature of the air sampled were 72.9% and 23.5 °C, and the sampling flow rate was 50 mL/min. A sorbent tube testing system was made by placing a complete sorbent tube in series behind another tube, which contained only the front sorbent section. The rear tube was changed and analyzed at 150, 195, 210, 225, 240, and 300 min. Data from three sorbent tube testing systems, shown in Table A-7, were used to determine a recommended sampling volume of 9.5 liters for cyclohexane, as 80% of the volume needed to produce 5% breakthrough. This volume corresponds to a 190 min sampling period, which is the maximum recommended sampling time as described in OSHA 5000. Results are plotted in Figure A-6.

Table A-7. Sampler capacity data for cyclohexane.

sample no.	air vol (L)	sampling time (min)	cumulative downstream concn (mg/m^3)	break-through (%)
1	7.05	150	0.00	0.00
	9.17	195	2.64	0.13
	9.87	210	11.3	0.54
	10.6	225	29.9	1.4
	11.3	240	65.6	3.1
	14.1	300	436	20.7
2	7.60	150	0.00	0.00
	9.88	195	0.847	0.04
	10.6	210	12.0	0.57
	11.4	225	51.6	2.4
	12.2	240	132	6.3
	15.2	300	560	26.6
3	7.39	150	0.00	0.00
	9.56	195	0.00	0.00
	10.3	210	2.60	0.12
	11.1	225	20.7	0.98
	11.8	240	78.5	3.7
	14.8	300	498	23.6

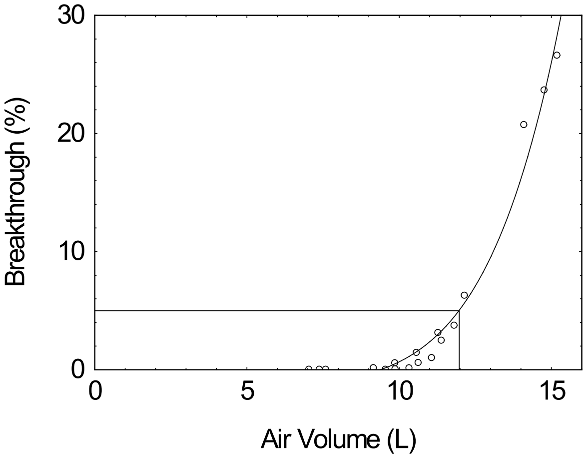

Figure A-6. Plot of data used to determine sampler capacity for cyclohexane. The 5% breakthrough volume shown is based on the curve in the figure, which is fit to the data provided in Table A-7.

8 Low Humidity

Pre-existing data from OSHA Method 1022[1] are presented in this section.

The effect of low humidity was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing cyclohexane nominally at two times the target concentration (calculated to be 611 ppm). The relative humidity and temperature of the air sampled were 17.3% and 25.5 °C, and the sampling flow rate was 50 mL/min. Samples were collected on three sorbent tubes for 190 min. After immediate analyses, results as a percentage of expected recovery were 95.8%, 98.5%, and 101.6%.

9 Chemical Interference

Pre-existing data from OSHA Method 1022[1] are presented in this section.

The effect of potential chemical sampling interference was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing cyclohexane nominally at the target concentration (calculated to be 305 ppm). The relative humidity and temperature of the air sampled were 70.5% and 25.2 °C, and the sampling flow rate was 50 mL/min. Toluene was present as a potential interferent, nominally at its permissible exposure limit (calculated to be 198 ppm). Samples were collected on three sorbent tubes for 240 min. After immediate analysis, results for cyclohexane as a percentage of expected recovery were 103.2%, 101.4%, and 101.1%.

10 Analytical Method Reproducibility

Pre-existing data from OSHA Method 1022[1] are presented in this section.

Samples were prepared by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing cyclohexane nominally at the target concentration (calculated to be 305 ppm). The relative humidity and temperature of the air sampled were 67.6% and 25.0 °C, and the sampling flow rate was 50 mL/min. Samples were collected on six sorbent tubes for 190 min. The resulting samples were submitted to the OSHA Salt Lake Technical Center for analysis using the procedures described in OSHA Method 1022 after storage for 19 days at 4 °C. The analytical results corrected for E_E are provided in Table A-8. No sample result for cyclohexane fell outside the permissible bounds set by the precision of the overall procedure determined in Section 5 of this appendix.

Table A-8. Reproducibility data for cyclohexane.

sampled (ppm)	recovered (ppm)	recovery (%)	deviation (%)
305	314	103.0	+3.0
305	305	100.0	+0.0
305	329	107.9	+7.9
305	310	101.6	+1.6
305	300	98.4	-1.6
305	309	101.3	+1.3

11 Effect of Sampling a Low Concentration

Pre-existing data from OSHA Method 1022[1] are presented in this section.

The effect of sampling a low concentration of cyclohexane vapor was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing cyclohexane nominally at one-tenth the target concentration (calculated to be 30.7 ppm). The relative humidity and temperature were 69.0% and 25.3 °C, and the sampling flow rate was 50 mL/min. Samples were collected on three sorbent tubes for 240 min. After immediate analysis, results for cyclohexane as a percentage of expected recovery were 108.8%, 103.6%, and 111.5%.

12 Estimation of Uncertainty

While systematic biases such as analyte storage loss are examined, and limits are placed on these, an estimation of uncertainty that encompasses both potential random and systematic error was not completed. Instead, the overall standard error of estimate was calculated from the random error inherent to the points about the regression line produced by the ambient storage test described in Section 5, as prescribed by the OSHA validation guidelines in use at the time OSHA Method 1022 was originally validated. See Section 5 of this appendix for details.

13 Controlled Test Atmosphere Procedure

Dynamically generated controlled test atmospheres were created in a walk-in hood. House air was regulated using a Miller Nelson Model 401 flow-temperature-humidity control system. A measured flow of liquid cyclohexane was introduced with an ISCO model 100DM syringe pump through a short length of 0.53 mm internal diameter 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 cyclohexane vapor and dilution air flowed into a mixing chamber (76 cm length x 15 cm diameter), and then into a sampling chamber (56 cm length x 9.5 cm diameter). Sampling was completed from sampling ports present on the sampling chamber. Temperature and humidity measurements were obtained near the exit of the sampling chamber using a Vaisala HUMICAP Model HM70 hand-held humidity and temperature meter.

OSHA 5000, Appendix B
Trimethyl Benzene

Version:	1.0
OSHA PEL:	25 ppm (120 mg/m^3) 8-Hour TWA, Construction, Shipyard
ACGIH TLV:	25 ppm (123 mg/m^3) 8-Hour TWA
Recommended sampling time and sampling rate:	240 min at 50 mL/min (12 L)
Reliable quantitation limit:	0.11 ppm (0.54 mg/m^3, trimethyl benzene (1,2,3 isomer)), 0.096 ppm (0.47 mg/m^3, trimethyl benzene (1,2,4 isomer)), 0.072 ppm (0.35 mg/m^3, trimethyl benzene (1,3,5 isomer))
Standard error of estimate:	5.8% trimethyl benzene (1,2,3 isomer), 5.7% trimethyl benzene (1,2,4 isomer), 5.7% trimethyl benzene (1,3,5 isomer)
Status:	Fully validated. Method 5000 has been subjected to the established validation procedures of the Method Development Team for sampling and analysis of trimethyl benzene.

June 2016 (OSHA 1020)	Daren Pearce
February 2021 (OSHA 5000)	Meghan McCormick, Daren Pearce

1 Introduction

1.1 Previous Methods used by OSHA for Sampling and Analysis of Trimethyl Benzene

The specific analyte described in this appendix is trimethyl benzene, CAS No. 25551-13-7, the concentration of which is determined by considering the combined concentrations of trimethyl benzene (1,2,3 isomer), CAS No. 526-73-8, trimethyl benzene (1,2,4 isomer), CAS No. 95-63-6, and trimethyl benzene (1,3,5 isomer), CAS No. 108-67-8. The methodologies described in this appendix for trimethyl benzene are based on OSHA Method 1020.[1] That method requires the collection of samples using charcoal sorbent tubes, extraction using carbon disulfide containing 1% *N,N*-dimethylformamide, and analysis by gas chromatography using a flame ionization detector. Prior to the use of OSHA Method 1020, OSHA routinely sampled for trimethyl benzene on charcoal sorbent tubes using OSHA Method PV2091.[2] OSHA Method 1020 recorded data to provide a fully validated method compared to OSHA Method PV2091 and included changes to the sample collection flow rate, collection time, extraction solvent, and analytical parameters.

1.2 Changes to the Previously-Used Method

This appendix represents an update of OSHA Method 1020[1], which was fully validated at the time it was published based on the validation guidelines in effect at that time. Compared to the previous method used this method includes new extraction solvent and flame ionization detector temperature. Data presented from the previously used method are identified by the statement “Pre-existing data from OSHA Method 1020[1] are presented in this section”. The changes were made to allow the standardized collection and analysis of trimethyl benzene with other analytes found in Organic Vapor Sampling Group 1, described in OSHA Method 5000.

---

[1] Pearce, D. Trimethylbenzenes (mixed isomers) (OSHA Method 1020), 2016. United States Department of Labor, Occupational Safety & Health Administration Web site. https://www.osha.gov/dts/sltc/methods/validated/1020/1020.pdf (accessed October 2018).

[2] Gasser, F. Trimethylbenzenes (OSHA Method PV2091), 1987. United States Department of Labor, Occupational Safety & Health Administration Web site. http://www.osha.gov/dts/sltc/methods/partial/pv2091/pv2091.html (accessed January 2016).

1.3 Validation Parameters

The procedures used to develop the method validation data are described in Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis.[3] Air concentrations listed in ppm are referenced to 25 °C and 760 Torr. The target concentration for method evaluation was the OSHA 8-hour time-weighted average (TWA) permissible exposure limit (PEL) for trimethyl benzene.

2 Detection and Quantification

2.1 Detection Limit of the Analytical Procedure (DLAP)

Pre-existing data from OSHA Method 1020[1] are presented in this section.

The DLAP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLAP $S_{y/x}$) divided by the slope of the line produced from analyses of ten analytical standards prepared with equally spaced increments of analyte mass. The standards were prepared in such a way that the highest standard concentration would produce a peak approximately 10 times the response of a reagent blank at or near the chromatographic retention time of the analyte. The standards and a reagent blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLAP $S_{y/x}$ and slope values for DLAP determination. Results obtained for these analyses are listed below in Tables B-1 through B-3, and are plotted in Figures B-1 through B-3.

Table B-1. DLAP data for trimethyl benzene (1,2,3 isomer).

concentration (µg/mL)	mass on column (pg)	area counts (µV·s)
0.00	0.00	0.00
0.894	5.96	14.8
2.01	13.4	26.6
3.13	20.9	30.9
4.25	28.3	39.5
5.36	35.7	48.9
6.48	43.2	51.8
7.60	50.7	65.7
8.72	58.1	66.8
9.83	65.5	77.4
11.0	73.3	97.3

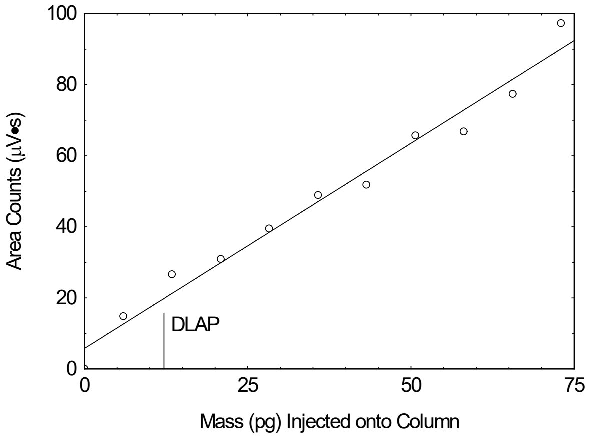

Figure B-1. Plot of data used to determine the DLAP for trimethyl benzene (1,2,3 isomer) ($y = 1.15x + 5.80$, DLAP $S_{y/x}$ = 4.59, DLAP = 11.9 pg).

---

[3] Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration Web site. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed December 2018).

Table B-2. DLAP data for trimethyl benzene (1,2,4 isomer).

concentration (µg/mL)	mass on column (pg)	area counts (µV·s)
0.00	0.00	19.9
0.864	5.76	20.7
1.94	12.9	24.1
3.02	20.1	36.0
4.10	27.3	41.5
5.18	34.5	52.3
6.26	41.7	57.9
7.34	48.9	69.7
8.42	56.1	71.4
9.50	63.3	90.8
10.6	70.7	102

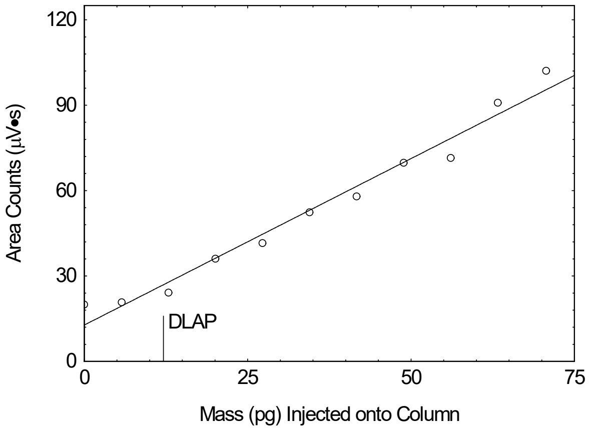

Figure B-2. Plot of data used to determine the DLAP for trimethyl benzene (1,2,4 isomer) ($y = 1.17x + 12.8$, DLAP $S_{y/x}$ = 4.69, DLAP = 12.0 pg).

Table B-3. DLAP data for trimethyl benzene (1,3,5 isomer).

concentration (µg/mL)	mass on column (pg)	area counts (µV·s)
0.00	0.00	0.00
0.864	5.76	10.9
1.94	12.9	25.8
3.02	20.1	33.2
4.10	27.3	37.5
5.18	34.5	46.7
6.26	41.7	71.6
7.34	48.9	65.6
8.42	56.1	73.2
9.50	63.3	85.6
10.6	70.7	92.6

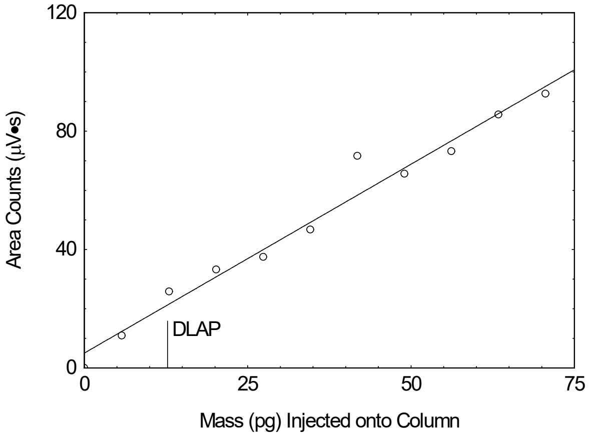

Figure B-3. Plot of data used to determine the DLAP for trimethyl benzene (1,3,5 isomer) ($y = 1.28x + 5.12$, DLAP $S_{y/x}$ = 5.42, DLAP = 12.7 pg).

2.2 Detection Limit of the Overall Procedure (DLOP) and Reliable Quantitation Limit (RQL)

Pre-existing data from OSHA Method 1020[1] are presented in this section.

The DLOP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLOP $S_{y/x}$) divided by the slope of the line produced from analyses of ten samples prepared from sorbent tubes spiked with equally spaced increments of analyte mass. 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 RQL is expressed as an air concentration that will provide sufficient analyte mass per sample that produces a response greater than 10× DLOP $S_{y/x}$ divided by the slope of the line described above. The spiked samplers and a sample blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLOP $S_{y/x}$ and slope values for DLOP and RQL determinations. Results obtained from these analyses are listed below in Tables B-4 through B-6, and plotted in Figures B-4 through B-6.

Table B-4. DLOP and RQL data for trimethyl benzene (1,2,3 isomer).

mass per sample (µg/sample)	area counts (µV·s)
0.00	0.00
0.966	11.9
2.17	21.5
3.38	37.2
4.59	45.1
5.79	50.6
7.00	68.4
8.21	69.7
9.41	72.2
10.6	82.6
11.8	96.6

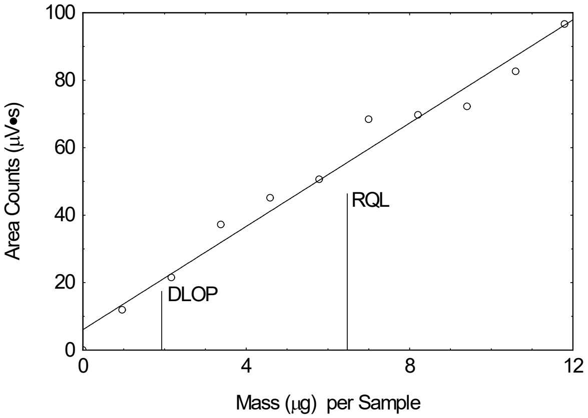

Figure B-4. Plot of data used to determine the DLOP and RQL for trimethyl benzene (1,2,3 isomer) ($y = 7.65x + 6.06$, DLOP $S_{y/x}$ = 4.91, DLOP = 1.93 µg/sample, RQL = 6.42 µg/sample or 0.109 ppm).

Table B-5. DLOP and RQL data for trimethyl benzene (1,2,4 isomer).

mass per sample (µg/sample)	area counts (µV·s)
0.00	0.00
1.03	16.4
2.32	31.4
3.61	34.3
4.89	47.7
6.18	65.7
7.47	70.4
8.76	76.3
10.0	84.6
11.3	96.7
12.6	109

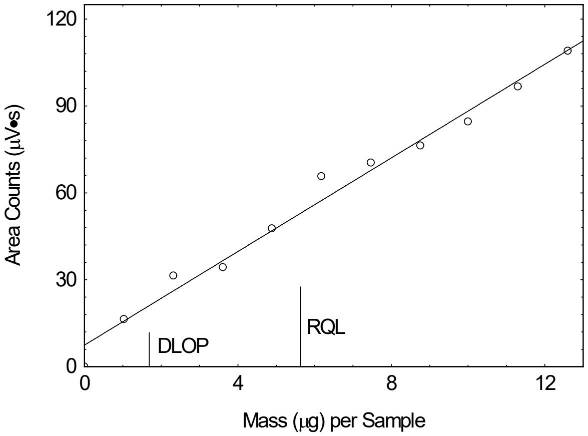

Figure B-5. Plot of data used to determine the DLOP and RQL for trimethyl benzene (1,2,4 isomer) ($y = 8.08x + 7.43$, DLOP $S_{y/x}$ = 4.55, DLOP = 1.69 µg/sample, RQL = 5.63 µg/sample or 0.0955 ppm).

Table B-6. DLOP and RQL data for trimethyl benzene (1,3,5 isomer).

mass per sample (µg/sample)	area counts (µV·s)
0.00	0.00
1.02	13.9
2.29	27.7
3.56	32.4
4.83	47.5
6.10	55.8
7.37	69.1
8.64	77.0
9.91	95.6
11.2	101
12.4	105

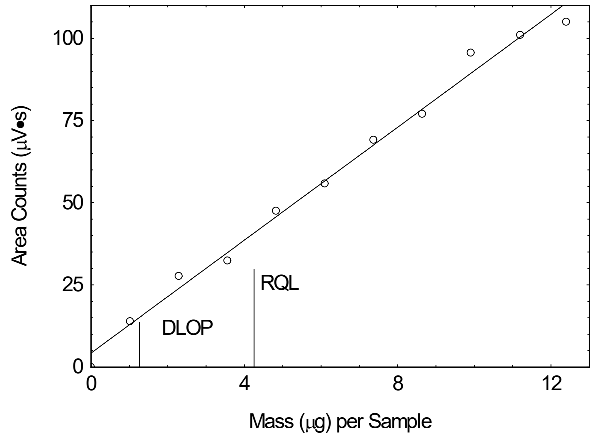

Figure B-6. Plot of data used to determine the DLOP and RQL for trimethyl benzene (1,3,5 isomer) ($y = 8.59x + 4.27$, DLOP $S_{y/x}$ = 3.65, DLOP = 1.27 µg/sample, RQL = 4.25 µg/sample or 0.0721 ppm).

3 Analytical Precision Across the Calibration Range

Pre-existing data from OSHA Method 1020[1] are presented in this section.

Fifteen analytical standards over a range of 0.1 to 2 times the analyte concentration in solvent that would be obtained from sampling for the recommended time at the target concentration were analyzed with the recommended analytical parameters described in OSHA Method 5000. An ordinary least-squares linear regression curve was created by plotting the analyte mass per sample versus the corresponding ratio of analyte peak area to internal standard (ISTD) peak area. The resulting data provided the standard error of estimate (Calibration $S_{y/x}$) value across the calibration range, which provides an indication of the imprecision attributable to the instrumental analysis of the target analyte. Results obtained from these analyses are listed in Tables B-7 through B-9, and plotted in Figures B-7 through B-9.

Table B-7. Analytical precision data for trimethyl benzene (1,2,3 isomer).

× target	0.1×	0.5×	1.0×	1.5×	2.0×
concn (µg/sample)	160.9	670.5	1341	2012	2682
area ratio	0.4107	1.871	3.717	5.397	7.284
	0.4109	1.863	3.714	5.417	7.300
	0.4105	1.871	3.723	5.398	7.352

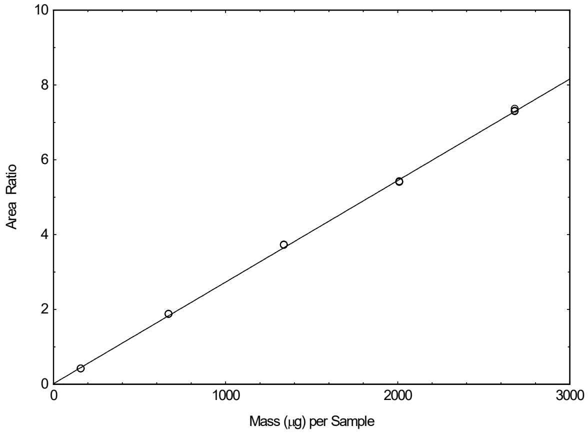

Figure B-7. Plot of data used to determine the precision of the analytical method for trimethyl benzene (1,2,3 isomer, $y = 0.00271x + 0.0149$, Calibration $S_{y/x}$ = 0.0554).

Table B-8. Analytical precision data for trimethyl benzene (1,2,4 isomer).

× target	0.1×	0.5×	1.0×	1.5×	2.0×
concn (µg/sample)	171.7	715.4	1431	2146	2862
area ratio	0.4391	2.005	3.982	5.786	7.800
	0.4398	1.994	3.979	5.803	7.819
	0.4381	2.002	3.985	5.780	7.876

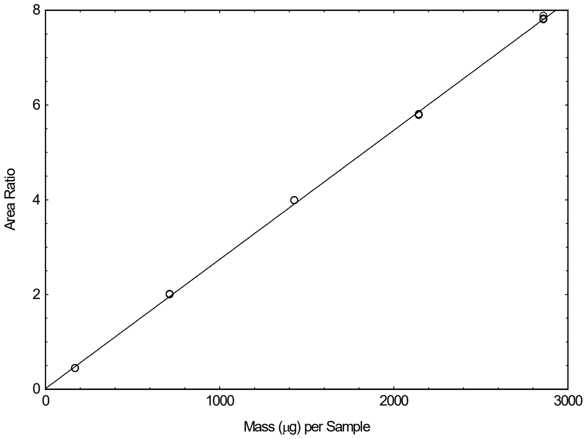

Figure B-8. Plot of data used to determine the precision of the analytical method for trimethyl benzene (1,2,4 isomer, $y = 0.00273x + 0.150$, Calibration $S_{y/x}$ = 0.0580).

Table B-9. Analytical precision data for trimethyl benzene (1,3,5 isomer).

× target	0.1×	0.5×	1.0×	1.5×	2.0×
concn (µg/sample)	169.3	705.6	1411	2117	2822
area ratio	0.4358	1.988	3.952	5.743	7.745
	0.4368	1.982	3.952	5.756	7.765
	0.4345	1.989	3.965	5.744	7.814

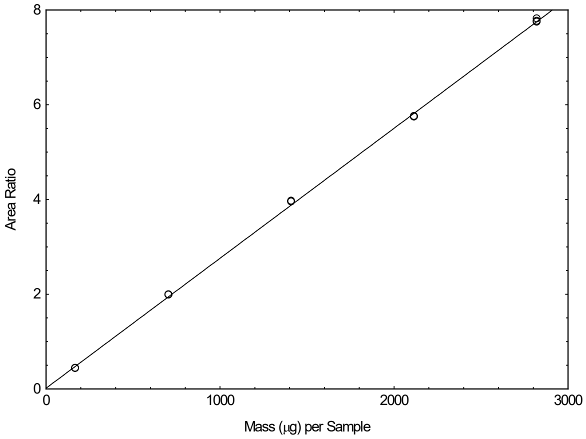

Figure B-9. Plot of data used to determine the precision of the analytical method for trimethyl benzene (1,3,5 isomer, $y = 0.00274x + 0.0156$, Calibration $S_{y/x}$ = 0.0589).

4 Sampler Storage Stability

Pre-existing data from OSHA Method 1020[1] are presented in this section.

Storage stability test samples for trimethyl benzene were prepared by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13. Sampling from this system followed the recommended sampling parameters published in OSHA Method 1020. The nominal concentration of trimethyl benzene (1,2,3-isomer), trimethyl benzene (1,2,4-isomer), and trimethyl benzene (1,3,5-isomer) for both ambient and refrigerated storage testing was the target concentration (respective calculated concentrations of 23.7, 25.3, 25.0 ppm and 23.8, 25.4, 25.1 ppm). The respective relative humidities and temperatures for ambient and refrigerated storage testing were 65.8% at 24.7 °C and 64.7% at 26.1 °C. For each test, eighteen samples were prepared, and three of these were analyzed on the same day that samples were created. The remaining fifteen refrigerated storage test samples were stored at reduced temperature (4 °C), while the remaining fifteen ambient storage test samples were kept in a closed drawer at ambient temperature (about 22 °C). For each storage condition, three samples were selected and analyzed from those remaining at 3-4 day intervals. The results of these analyses (uncorrected for extraction efficiency) are provided in Tables B-10 through B-12, and in Figures B-10 through B-15.

The recoveries of trimethyl benzene (1,2,3 isomer), trimethyl benzene (1,2,4 isomer), and trimethyl benzene (1,3,5 isomer) calculated from the regression line generated for the 19-day ambient storage test were respectively 89.7%, 93.7% and 97.7%.

Table B-10. Sampler storage stability data for trimethyl benzene (1,2,3 isomer).

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	88.4	92.6	92.1	90.3	94.6	92.2
3	94.1	91.8	89.1	96.4	94.6	93.2
7	95.6	92.6	93.8			
8				95.2	93.6	91.0
10	93.1	92.6	87.5	91.0	91.0	90.7
14				86.4	84.9	87.4
15	95.0	91.6	91.7			
18	84.7	85.7	88.6			
19				87.9	91.2	87.5

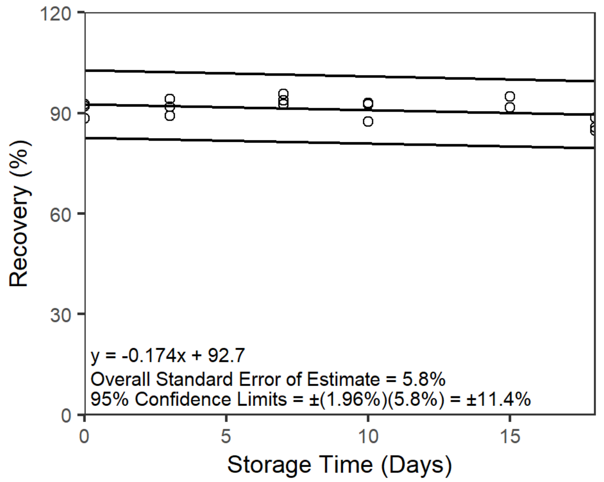

Figure B-10. Plot of ambient storage stability data for trimethyl benzene (1,2,3 isomer).

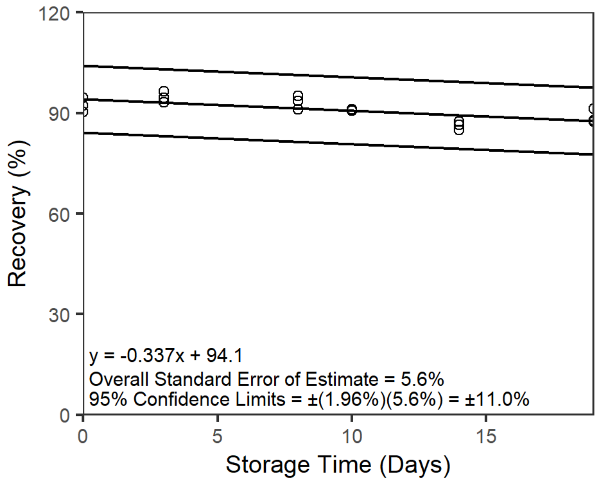

Figure B-11. Plot of refrigerated storage stability data for trimethyl benzene (1,2,3 isomer).

Table B-11. Sampler storage stability data for trimethyl benzene (1,2,4 isomer).

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	91.8	96.0	95.4	93.6	98.0	95.6
3	97.5	95.3	92.3	99.7	98.1	96.4
7	99.0	96.3	97.2			
8				98.7	97.3	94.6
10	96.5	96.0	92.3	94.9	95.1	94.6
14				91.6	89.8	92.4
15	98.5	95.1	95.2			
18	89.0	89.8	92.7			
19				92.6	95.2	91.2

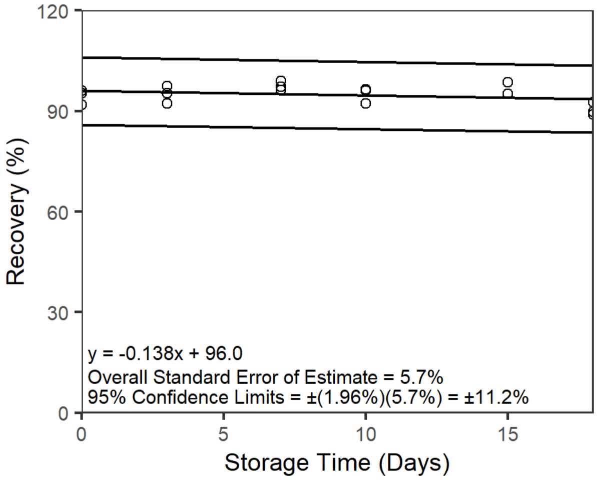

Figure B-12. Plot of ambient storage stability data for trimethyl benzene (1,2,4 isomer).

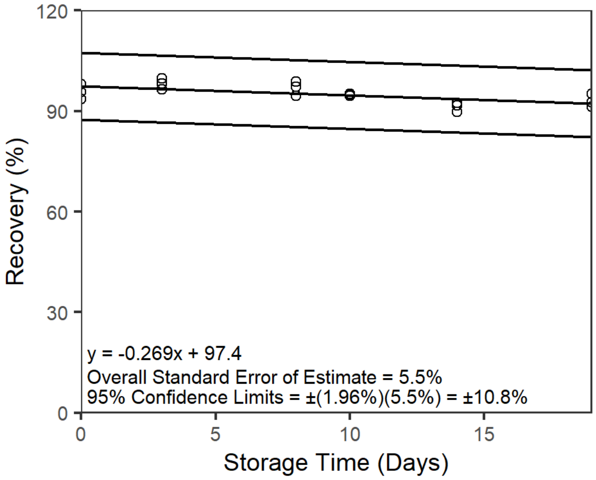

Figure B-13. Plot of refrigerated storage stability data for trimethyl benzene (1,2,4 isomer).

Table B-12. Sampler storage stability data trimethyl benzene (1,3,5 isomer).

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	94.9	99.1	98.2	96.5	100.9	98.5
3	97.5	95.3	92.3	102.9	101.0	99.4
7	102.0	99.6	100.2			
8				101.8	100.3	97.6
10	99.6	99.0	97.9	98.3	98.4	98.0
14				97.1	95.3	97.3
15	101.9	98.0	98.4			
18	93.8	94.3	97.0			
19				97.4	98.7	94.7

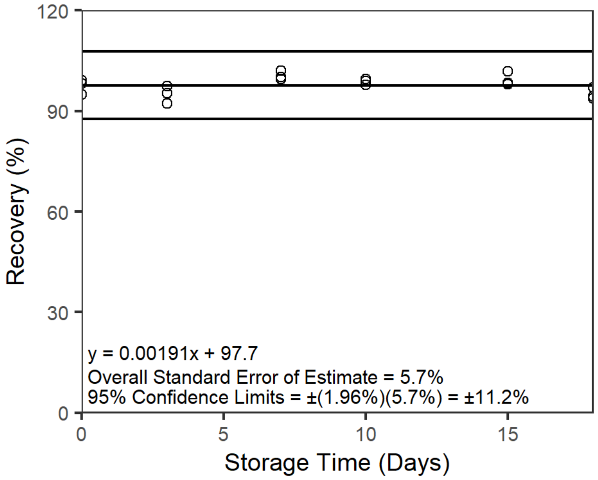

Figure B-14. Plot of ambient storage stability data for trimethyl benzene (1,3,5 isomer).

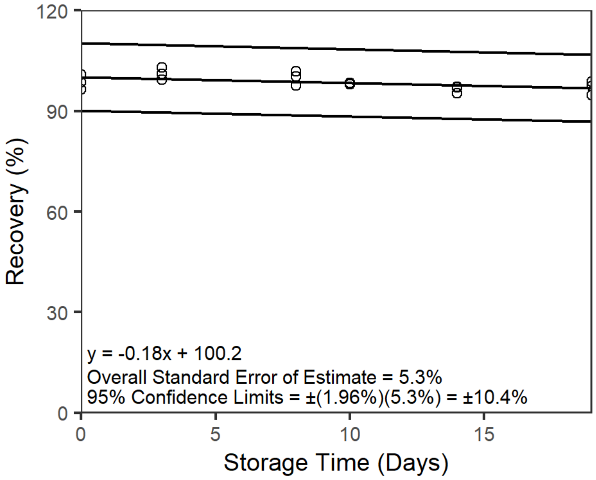

Figure B-15. Plot of refrigerated storage stability data for trimethyl benzene (1,3,5 isomer).

5 Precision of the Overall Procedure

Pre-existing data from OSHA Method 1020[1] are presented in this section.

The overall standard error of estimate obtained from the ambient storage test analyses described in Section 4 and sampling pump variability were used to determine the precision of the overall procedure, where all aspects of sampling and analysis (sampling, sorbent tube handling and solvent extraction, and instrumental analysis) are considered. This value was obtained by taking the square root of the squared ambient storage stability standard error of estimate (Storage $S_{y/x}^2$) added to the squared sampling pump variability value (V_{SP}^2). The resulting precision of the overall procedure at the 95% confidence level for the ambient 19-day storage test (at the target concentration) for trimethyl benzene (1,2,3 isomer), trimethyl benzene (1,2,4 isomer), and trimethyl benzene (1,3,5 isomer) were determined to be ±11.4, ±11.2, and ±11.2% based on the observed ambient Storage $S_{y/x}$ values of 5.8%, 5.7%, and 5.7% and V_{SP} value of 5.0%.

6 Recovery and Stability of Prepared Samples

Quantitative extraction is affected by the extraction solvent, the ISTD, the sampling medium, and the technique used to extract samples. The data presented demonstrate the validity for extraction solvent, ISTD, sampling medium, and extraction technique described in OSHA Method 5000. 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.

Values for extraction efficiency (E_E) of 1,2,3-trimethyl benzene, 1,2,4-trimethyl benzene, and 1,3,5-trimethyl benzene were determined by liquid-spiking four replicate sorbent tubes across a range of analyte mass values that would be obtained from sampling at 0.1 to 2 times the target concentration value for 240 min. Four sorbent tubes were also spiked in this fashion at the target concentration after drawing humid air (62.3% relative humidity at 26.4 °C) through these tubes at 50 mL/min for 4 hours. All of the samples described above were analyzed the following day after being kept overnight at ambient temperature. The E_E values at the RQL were 96.5% for trimethyl benzene (1,2,3 isomer), 92.4% for trimethyl benzene (1,2,4 isomer), and 95.9% for trimethyl benzene (1,3,5 isomer), while those of the working range samples (excluding the samples through which humid air had been drawn) were 93.0% for trimethyl benzene (1,2,3 isomer), 97.0% for trimethyl benzene (1,2,4 isomer), and 99.0% for trimethyl benzene (1,3,5 isomer). The data are shown in Tables B-13 through B-15. Pre-loading sorbent tubes with moisture ("wet" designation in the table) did not have an unacceptable effect on E_E.

Table B-13. Extraction efficiency data for trimethyl benzene (1,2,3 isomer).

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.1	95.30	91.8	92.6	92.5	90.0	91.7
0.25	363.4	90.1	93.0	94.9	91.0	92.3
0.5	710.4	92.5	92.1	91.9	91.5	92.0
1.0	1272	94.6	94.6	94.4	94.1	94.4
1.5	1976	92.8	93.9	93.5	93.1	93.3
2.0	2667	94.1	94.4	93.8	93.5	94.0
RQL	5.91	96.5	94.8	103.4	91.2	96.5
1.0 (wet)	1302	85.0	89.5	92.3	94.2	90.2

Table B-14. Extraction efficiency data for trimethyl benzene (1,2,4 isomer).

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.1	141.1	94.5	95.0	95.9	96.6	95.5
0.25	369.2	97.0	96.1	95.1	97.3	96.4
0.5	732.0	97.9	97.4	97.5	97.2	97.5
1.0	1389	98.5	97.4	97.0	97.9	97.7
1.5	2220	97.3	97.6	98.6	97.0	97.6
2.0	2916	96.6	97.8	97.1	97.3	97.2
RQL	6.40	93.4	92.9	89.6	93.8	92.4
1.0 (wet)	1395	86.3	93.6	96.4	97.1	93.4

Table B-15. Extraction efficiency data for trimethyl benzene (1,3,5 isomer).

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.1	151.8	98.7	98.4	97.5	99.6	98.6
0.25	349.0	99.5	98.3	100.0	98.2	99.0
0.5	718.1	98.9	99.1	95.2	99.1	98.1
1.0	1396	99.8	99.2	99.3	99.9	99.6
1.5	2125	99.0	99.8	100.1	99.7	99.7
2.0	2921	98.0	99.1	99.2	99.6	99.0
RQL	6.41	95.2	96.1	96.0	96.1	95.9
1.0 (wet)	1355	98.4	98.6	97.3	99.1	98.4

The stability of sample extracts prepared according to OSHA Method 5000 was examined by retaining the samples solvent extracts for the target concentration samples described immediately above. Two of the four vials were immediately recapped with new septa following the initial analyses, and again following each re-analysis event. The other two vials retained the original punctured septa throughout. All four vials were re-analyzed at 24, 28, and 72 hours after the initial analyses, with all the vials remaining in the autosampler tray kept at 22 °C. Freshly prepared standards were used for each analysis event, and each septum (whether new or previously used) was punctured four times for each injection. The resulting data are shown in Tables B-16 through B-18.

Table B-16. Extracted sample stability data for trimethyl benzene (1,2,3 isomer).

	punctured septa replaced recovery (%)		punctured septa retained recovery (%)	
time (days)	1	2	1	2
0	103.6	106.7	106.4	106.7
1	101.8	105.3	104.4	104.2
2	100.0	102.7	101.5	101.6
3	100.5	103.2	101.7	101.6

Table B-17. Extracted sample stability data for trimethyl benzene (1,2,4 isomer).

	punctured septa replaced recovery (%)		punctured septa retained recovery (%)	
time (days)	1	2	1	2
0	102.3	105.3	105.2	105.3
1	101.4	104.7	104.2	103.4
2	99.2	101.8	101.2	101.6
3	99.7	102.3	101.6	101.0

Table B-18. Extracted sample stability data for trimethyl benzene (1,3,5 isomer).

	punctured septa replaced recovery (%)		punctured septa retained recovery (%)	
time (days)	1	2	1	2
0	102.7	105.9	105.8	105.7
1	102.2	105.6	105.4	104.3
2	100.0	102.5	102.4	101.9
3	100.3	103.1	102.9	102.1

7 Sampler Capacity

Pre-existing data from OSHA Method 1020[1] are presented in this section.

The sampling capacity of the front section of a sorbent tube was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing each trimethyl benzene isomer nominally at two times the target concentration (calculated to be 41.5 ppm for trimethyl benzene (1,2,3 isomer), 49.9 ppm for trimethyl benzene (1,2,4 isomer), and 49.2 ppm for trimethyl benzene (1,3,5 isomer)). The relative humidity and temperature of the air sampled were 64.6% and 27.5 °C, and the sampling flow rate was 50 mL/min. A sorbent tube testing system was made by placing a complete sorbent tube in series behind another tube, which contained only the front sorbent section. The rear tube was changed and analyzed at 375, 452, and 600 min. Breakthrough was not observed after sampling for 600 min (corresponding to 30 liters). Data from three sorbent tube testing systems were used to determine a recommended sampling volume of 12 liters for trimethyl lbenzene as described in OSHA Method 5000. This volume corresponds to a 240 min sampling period, which is the maximum recommended sampling time regardless of breakthrough.

8 Low Humidity

Pre-existing data from OSHA Method 1020[1] are presented in this section.

The effect of low humidity was tested by sampling a dynamically generated controlled test atmosphere, using the system in Section 13, containing trimethyl benzene nominally at two times the target concentration (calculated to be 47.6 ppm for trimethyl benzene (1,2,3 isomer), 50.9 ppm for trimethyl benzene (1,2,4 isomer), and 50.1 ppm for trimethyl benzene (1,3,5 isomer)). The relative humidity and temperature of the air sampled were 16.5% relative humidity and 26.3 °C, and the sampling flow rate was 50 mL/min. Samples were collected on three sorbent tubes for 240 min. After immediate analysis, results as a percentage of expected recovery were 101.6%, 102.9%, and 100.4% for trimethyl benzene (1,2,3 isomer), 100.3%, 101.5%, and 98.9% for trimethyl benzene (1,2,4 isomer), and 100.8%, 101.9%, and 102.7% for trimethyl benzene (1,3,5 isomer).

9 Chemical Interference

Pre-existing data from OSHA Method 1020[1] are presented in this section.

The effect of potential chemical sampling interference was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing trimethyl benzene nominally at the target concentration (calculated to be 23.7 ppm for trimethyl benzene (1,2,3 isomer), 25.3 ppm for trimethyl benzene (1,2,4 isomer), and 25.0 ppm for trimethyl benzene (1,3,5 isomer)). The relative humidity and temperature of the air sampled were 62.5% and 26.4 °C, and the sampling flow rate was 50 mL/min. Toluene was present as a potential interferent, nominally at its permissible exposure limit (calculated to be 276.3 ppm). Samples were collected on three sorbent tubes for 240 min. After immediate analysis, results as a percentage of expected recovery were 99.3%, 101.2%, and 99.0% for trimethyl benzene (1,2,3 isomer), 98.7%, 100.5%, and 98.4% for trimethyl benzene (1,2,4 isomer), and 98.9%, 100.7%, and 98.8% for trimethyl benzene (1,3,5 isomer).

10 Analytical Method Reproducibility

Pre-existing data from OSHA Method 1020[1] are presented in this section.

Samples were prepared by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing trimethyl benzene nominally at the target concentration (calculated to be 23.9 ppm for trimethyl benzene (1,2,3 isomer), 25.5 ppm for trimethyl benzene (1,2,4 isomer), and 25.2 ppm for trimethyl benzene (1,3,5 isomer)). The relative humidity and temperature of the air sampled were 64.3% and 25.8 °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 Salt Lake Technical Center for analysis using the procedures described in OSHA Method 1020 after storage for 5 days at 4 °C. The analytical results corrected for E_E are provided in Tables B-21 through B-23. No sample result for trimethyl benzene fell outside the permissible bounds set by the precision of the overall procedure determined in Section 5 of this appendix.

Table B-21. Reproducibility data for trimethyl benzene (1,2,3 isomer).

sampled (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
1421.6	1400.6	98.5	-1.5
1439.1	1372.3	95.4	-4.6
1482.3	1440.9	97.2	-2.8
1442.9	1395.2	96.7	-3.3
1461.8	1414.3	96.8	-3.2
1423.0	1373.1	96.5	-3.5

Table B-22. Reproducibility data for trimethyl benzene (1,2,4 isomer).

sampled (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
1516.8	1615.5	106.5	+6.5
1535.5	1585.8	103.3	+3.3
1581.6	1664.3	105.2	+5.2
1539.5	1616.0	105.0	+5.0
1559.7	1628.7	104.4	+4.4
1518.3	1583.6	104.3	+4.3

Table B-23. Reproducibility data for trimethyl benzene (1,3,5 isomer).

sampled (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
1496.0	1570.0	104.9	+4.9
1514.4	1545.1	102.0	+2.0
1559.9	1621.1	103.9	+3.9
1518.5	1577.0	103.9	+3.9
1538.4	1580.5	102.7	+2.7
1497.5	1538.7	102.8	+2.8

11 Effect of Sampling a Low Concentration

Pre-existing data from OSHA Method 1020[1] are presented in this section.

The effect of sampling a low concentration of trimethyl benzene vapor was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing trimethyl benzene nominally at one-tenth the target concentration (calculated to be 2.36 ppm for trimethyl benzene (1,2,3 isomer), 2.52 ppm for trimethyl benzene (1,2,4 isomer), and 2.48 ppm for trimethyl benzene (1,3,5 isomer)). The relative humidity and temperature of the air sampled were 60.8% and 26.2 °C, and the sampling flow rate was 50 mL/min. Samples were collected on three sorbent tubes for 240 min. After immediate analysis, results for trimethyl benzene as a percentage of expected recovery were 101.4%, 99.4%, 98.4% for trimethyl benzene (1,2,3 isomer); 101.8%, 98.4%, and 98.6% for trimethyl benzene (1,2,4 isomer); and 101.8%, 100.0%, and 100.1% for trimethyl benzene (1,3,5 isomer).

12 Estimation of Uncertainty

While systematic biases such as analyte storage loss are examined, and limits are placed on these, an estimation of uncertainty that encompasses both potential random and systematic error was not completed. Instead, the overall standard error of estimate was calculated from the random error inherent to the points about the regression line produced by the ambient storage test described in Section 5, as prescribed by the OSHA validation guidelines in use at the time OSHA Method 1020 was originally validated. See Section 5 of this appendix for details.

13 Controlled Test Atmosphere Procedure

Dynamically generated controlled test atmospheres were created in a walk-in hood. House air was regulated using a Miller Nelson Model 401 flow-temperature-humidity control system. A measured flow of liquid trimethyl benzene was introduced with an ISCO model 100DM syringe pump through a short length of 0.53 mm internal diameter 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 trimethyl benzene vapor and dilution air flowed into a mixing chamber (76 cm length x 15 cm diameter), and then into a sampling chamber (56 cm length x 9.5 cm diameter). Sampling was completed from sampling ports present on the sampling chamber. Temperature and humidity measurements were obtained near the exit of the sampling chamber using a Vaisala HUMICAP Model HM70 hand-held humidity and temperature meter.

OSHA 5000, Appendix C
Pentane

Version:	1.0
OSHA PEL:	1000 ppm (2950 mg/m^3) 8-Hour TWA, General Industry 500 ppm (1500 mg/m^3) 8-Hour TWA, Construction, Shipyard
ACGIH TLV:	1000 ppm (2950 mg/m^3) 8- Hour TWA
Recommended sampling time and sampling rate:	45 min at 50 mL/min (2.25 L)
Reliable quantitation limit:	0.40 ppm (1.2 mg/m^3)
Standard error of estimate:	5.7%
Status:	Fully validated. Method 5000 has been subjected to the established validation procedures of the Method Development Team for sampling and analysis of pentane.

February 2021 Daren Pearce

1 Introduction

1.1 Previous Methods used by OSHA for Sampling and Analysis of Pentane

The specific analyte described in this appendix is pentane, CAS No. 110-82-7. The methodologies described in this appendix for pentane replace OSHA Method 7 Organic Vapors[1], which simply described a modification of NIOSH Method 1500.[2] That method requires the collection of samples using charcoal sorbent tubes, extraction using carbon disulfide containing 1% *N*,*N*-dimethylformamide, and analysis by gas chromatography using a flame ionization detector.

1.2 Changes to the Previously-Used Method

This appendix represents a new method to replace OSHA Method 7, Organic Vapors[1] for sampling and analysis of pentane. Compared to the previous method used this method includes new analytical parameters, a new internal standard (ISTD), and a new sample collection flow rate and collection time. The data found in all subsequent sections of this appendix are new. The changes were made to allow the standardized collection and analysis of pentane with other analytes found in Organic Vapor Sampling Group 1, described in OSHA Method 5000.

1.3 Validation Parameters

The procedures used to develop the method validation data are described in Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis.[3] Air concentrations listed in ppm are referenced to 25 °C and 760 Torr.

---

[1] OSHA Method 7 Organic Vapors. United States Department of Labor, Occupational Safety & Health Administration Web site. https://www.osha.gov/dts/sltc/methods/archive/org007/org007.pdf (accessed March 2019).

[2] Pendegrass, S.; May, L. Hydrocarbons, BP 36 ºC-216 ºC (NIOSH Method 1500, Issue 3), 2003. Center for Disease Control, The National Institute for Occupational Safety and Health (NIOSH) Web site. http://www.cdc.gov/niosh/docs/2003-154/pdfs/1500.pdf (accessed October 2018).

[3] Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration Web site. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed December 2018).

The target concentration for method evaluation was the OSHA 8-hour time-weighted average (TWA) permissible exposure limit (PEL) for pentane.

2 Detection and Quantification

2.1 Detection Limit of the Analytical Procedure (DLAP)

The DLAP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLAP $S_{y/x}$) divided by the slope of the line produced from analyses of ten analytical standards prepared with equally spaced increments of analyte mass. The standards were prepared in such a way that the highest standard concentration would produce a peak approximately 10 times the response of a reagent blank at or near the chromatographic retention time of the analyte. The standards and a reagent blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLAP $S_{y/x}$ and slope for the DLAP determination. Results obtained for these analyses are listed in Table C-1, and plotted in Figure C-1.

Table C-1. DLAP data for pentane.

concentration (µg/mL)	mass on column (pg)	area counts (µV·s)
0.00	0.00	0.00
0.501	3.34	0.102
1.00	6.67	0.150
1.50	10.0	0.230
2.00	13.3	0.281
2.50	16.7	0.347
3.00	20.0	0.404
3.51	23.4	0.448
4.01	26.7	0.523
4.51	30.1	0.646
5.01	33.4	0.682

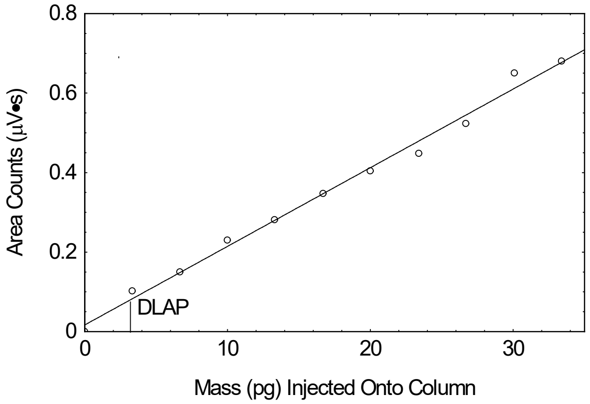

Figure C-1. Plot of data used to determine the DLAP for pentane ($y = 0.0198x + 0.0168$, DLAP $S_{y/x}$ = 0.0200, DLAP = 3.03 pg).

2.2 Detection Limit of the Overall Procedure (DLOP) and Reliable Quantitation Limit (RQL)

The DLOP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLOP $S_{y/x}$) divided by the slope of the line produced from analyses of ten samples prepared from sorbent tubes spiked with equally spaced increments of analyte mass. 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 RQL is expressed as an air concentration that will provide sufficient analyte mass per sample that produces a response greater than 10× DLOP $S_{y/x}$ divided by the slope of the line described above. The spiked samplers and a sample blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLOP $S_{y/x}$ and slope values for DLOP and RQL determinations. Results obtained from these analyses are listed in Table C-2, and plotted in Figure C-2.

Table C-2. DLOP and RQL data for pentane.

mass per sample (µg/sample)	area counts (µV·s)
0.00	0.00
0.626	0.196
1.25	0.231
1.88	0.287
2.50	0.336
3.13	0.442
3.76	0.524
4.38	0.596
5.01	0.657
5.63	0.721
6.26	0.834

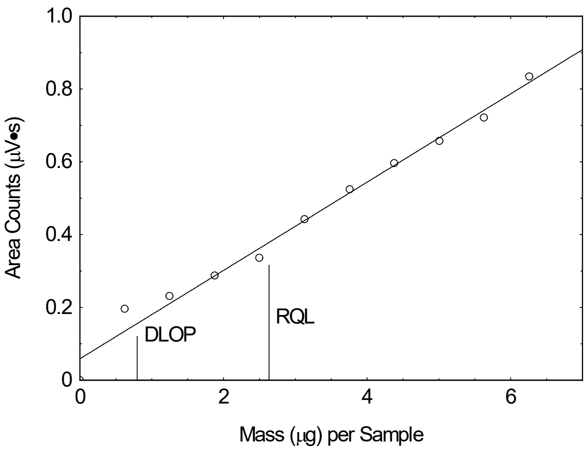

Figure C-2. Plot of data used to determine the DLOP and RQL for pentane ($y = 0.121x + 0.0588$, DLOP $S_{y/x}$ = 0.0320, DLOP = 0.793 µg/sample, RQL = 2.64 µg/sample or 0.398 ppm).

3 Analytical Precision Across the Calibration Range

Fifteen analytical standards over a range of 0.1 to 2 times the analyte concentration in solvent that would be obtained from sampling for the recommended time at the target concentration were analyzed with the analytical recommended analytical parameters described in OSHA Method 5000. An ordinary least-squares linear regression curve was created by plotting the analyte mass per sample versus the corresponding ratio of analyte peak area to internal standard (ISTD) peak area. The resulting data provided the standard error of estimate (Calibration $S_{y/x}$) value across the calibration range, which provides an indication of the imprecision attributable to the instrumental analysis of the target analyte. Results from these analyses are listed in Table C-3, and plotted in Figure C-3.

Table C-3. Analytical precision data for pentane.

× target	0.1×	0.5×	1.0×	1.5×	2.0×
concn (µg/sample)	626	3130	6260	9390	12,520
area ratio	1.672	8.519	17.25	25.71	33.93
	1.747	8.832	17.67	26.09	33.60
	1.775	8.752	17.16	25.67	34.26

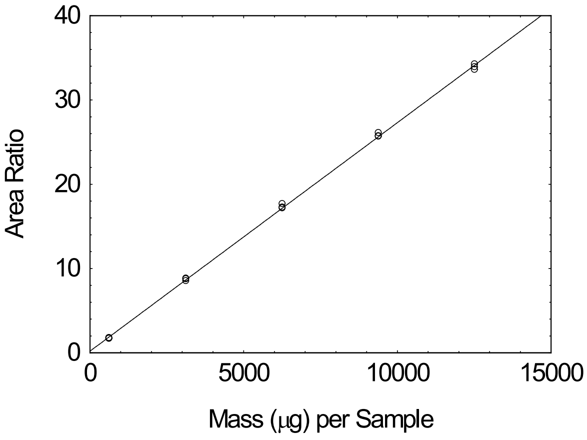

Figure C-3. Plot of data used to determine the precision of the analytical method for pentane ($y = 0.00271x + 0.194$, Calibration $S_{y/x}$ = 0.270).

4 Sampler Storage Stability

Storage stability test samples for pentane were prepared by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13. Sampling from this system followed the recommended sampling parameters published in OSHA Method 5000. The nominal concentration of pentane for ambient and refrigerated storage testing was the target concentration (respective calculated concentrations of 1028 ppm and 1029 ppm). The respective relative humidity and temperature were 81.6% and 21.6 °C and 81.9% and 21.8 °C for both tests. For each test, eighteen samples were prepared and three of these were analyzed on the same day that samples were created. The remaining fifteen refrigerated storage test samples were stored at reduced temperature (4 °C), while the remaining fifteen ambient storage test samples were stored in a closed drawer at ambient temperature (about 22 °C). For each storage condition, three samples were selected and analyzed from those remaining at 3-4 day intervals. The results of these analyses (uncorrected for extraction efficiency) are provided in Table C-4 and plotted in Figures C-4 through C-5. Some migration of pentane (up to 3%) from the front to the rear sorbent tube section was observed on day 19 for the ambient storage test. Analyte migration was not observed on the refrigerated test samples.

The recovery of pentane calculated from the regression line generated for the 19-day ambient storage test was 98.3%.

Table C-4. Sampler storage stability data for pentane.

Time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	96.1	96.7	98.9	103.6	100.5	105.5
5	88.4	92.9	95.4	98.3	96.1	99.1
8	99.3	100.3	100.3	100.9	100.4	102.3
12	97.5	97.3	97.5	94.1	96.1	100.1
15	99.1	99.1	97.4	97.7	99.1	96.2
19	97.2	98.2	97.6	97.8	98.7	97.8

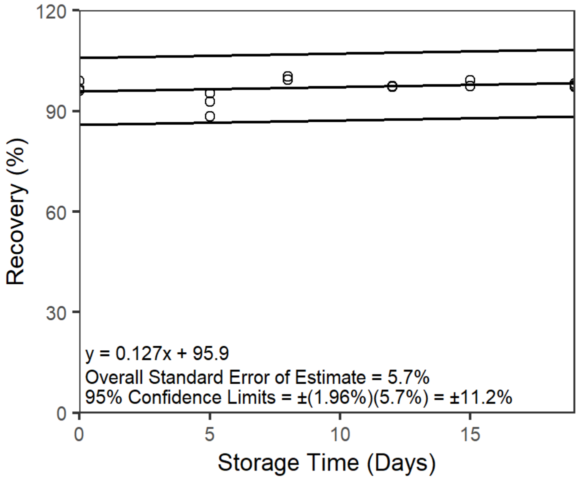

Figure C-4. Plot of ambient storage stability data for pentane.

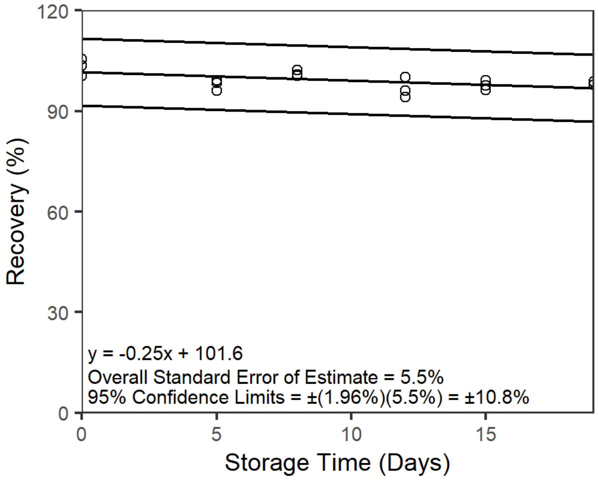

Figure C-5. Plot of refrigerated storage stability data for pentane.

5 Precision of the Overall Procedure

The overall standard error of estimate obtained from the ambient storage test analyses described in Section 4 and sampling pump variability were used to determine the precision of the overall procedure, where all aspects of sampling and analysis (sampling, sorbent tube handling and solvent extraction, and instrumental analysis) are considered. This value was obtained by taking the square root of the squared ambient storage stability standard error of estimate (Storage $S_{y/x}^2$) added to the squared sampling pump variability value (V_{SP}^2). The resulting precision of the overall procedure at the 95% confidence level for the ambient 19-day storage test (at the target concentration) for pentane was determined to be ±11.2% based on the observed ambient Storage $S_{y/x}$ value of 5.7% and V_{SP} value of 5.0%.

6 Recovery and Stability of Prepared Samples

Quantitative extraction 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 OSHA Method 5000. 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.

A value for extraction efficiency (E_E) was determined by liquid-spiking four replicate sorbent tubes across a range of analyte mass values that would be obtained from sampling at 0.05 to 2 times the target concentration value for 45 min. Four sorbent tubes were also spiked in this fashion at the target concentration after drawing humid air (80.2% relative humidity at 21.8 °C) through these tubes at 50 mL/min for 45 min. All of the samples described above were analyzed the following day after being kept overnight at ambient temperature. The E_E value at the RQL was 109.9%, while that of the working range samples (excluding the samples through which humid air had been drawn) was 101.0%. The data are shown in Table C-5. Pre-loading sorbent tubes with moisture ("wet" designation in the table) did not have an unacceptable effect on E_E.

Table C-5. Extraction efficiency data for pentane.

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.05	338.0	97.7	101.2	99.6	101.4	100.0
0.25	1690	102.0	101.7	100.6	101.4	101.4
0.5	3443	101.6	101.2	100.9	99.06	100.7
1.0	6573	102.1	96.79	100.2	101.6	100.2
1.5	10,016	101.1	102.4	102.4	102.9	102.1
2.0	13,146	102.0	102.6	100.6	100.5	101.7
RQL	1.56	101.7	120.0	112.3	105.4	109.9
1.0 (wet)	6573	106.7	104.3	104.2	105.7	105.2

The stability of extracted samples extracts prepared according to OSHA Method 5000 was examined by retaining the sample solvent extracts for the target concentration samples described immediately above. Two of the four vials were immediately recapped with new septa following the initial analyses, and again following each re-analysis event. The other two vials retained the original punctured septa throughout. All four vials were re-analyzed at 24, 48, and 72 hours after the initial analyses, with all vials remaining in an autosampler tray kept at 22 °C. Freshly prepared standards were used for each analysis event and each septum (whether new or previously used) was punctured four times for each injection. Re-cap all vials after analysis due to the loss of analyte in the punctured septa test. The resulting data are shown in Table C-6.

Table C-6. Extracted sample stability data for pentane.

	punctured septa replaced recovery (%)		punctured septa retained recovery (%)	
time (days)	1	2	1	2
0	94.8	100.9	100.8	101.1
1	97.7	102.3	103.2	103.2
2	93.5	97.8	93.7	95.3
3	91.6	97.9	85.5	89.9

7 Sampler Capacity

The sampling capacity of the front section of a sorbent tube was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing pentane nominally at two times the target concentration (calculated to be 1959 ppm). The relative humidity and temperature of the air sampled were 78.0% and 22 °C, and the sampling flow rate was 50 mL/min. A sorbent tube testing system was made by placing a complete sorbent tube in series behind another tube, which contained only the front sorbent section. The rear tube was changed and analyzed at 30, 40, 45, 50, 55, and 60 min. Data from three sorbent tube testing systems, shown in Table C-7, were used to determine a recommended sampling volume of 2.28 liters for pentane, as 80% of the volume needed to produce 5% breakthrough. This volume corresponds to a 45 min sampling period, which is the maximum recommended sampling time as described in OSHA Method 5000. Results are plotted in Figure C-6.

Table C-7. Sampler capacity data for pentane.

sample no.	air vol (L)	sampling time (min)	cumulative downstream concn (mg/m^3)	break-through (%)
1	1.57	30	0.00	0.00
	2.09	40	0.00	0.00
	2.35	45	0.00	0.00
	2.61	50	26.1	0.40
	2.87	55	231	4.0
	3.14	60	1093	18.9
2	1.48	30	0.00	0.00
	1.97	40	0.00	0.00
	2.21	45	0.00	0.00
	2.46	50	0.00	0.00
	2.71	55	41.7	0.700
	2.95	60	716	12.4
3	1.53	30	0.00	0.00
	2.05	40	0.00	0.00
	2.30	45	0.00	0.00
	2.56	50	7.0	0.10
	2.81	55	132	2.3
	3.07	60	919	15.9

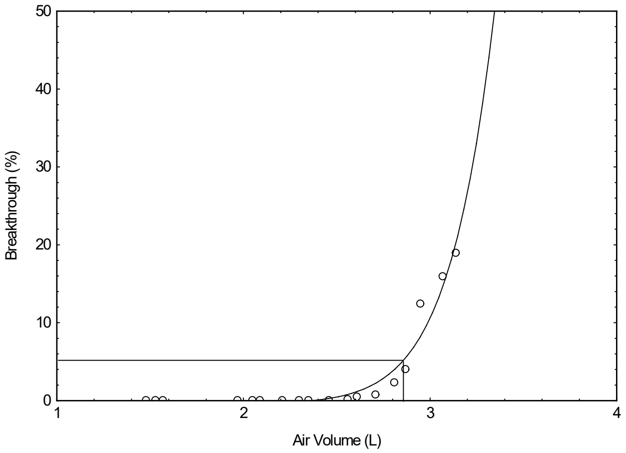

Figure C-6. Plot of data used to determine sampler capacity for pentane. The 5% breakthrough volume shown is based on the curve in the figure, which is fit to the data provided in Table C-7.

8 Low Humidity

The effect of low humidity was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing pentane nominally at two times the target concentration (calculated to be 2102 ppm). The relative humidity and temperature of the air sampled were 2.91% and 19.5 °C, and the sampling flow rate was 50 mL/min. Samples were collected on three sorbent tubes for 45 min. After immediate analysis, results as a percentage of expected recovery were 94.9%, 98.3%, and 102.2%.

9 Chemical Interference

The effect of potential chemical sampling interference was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing pentane nominally at two times the target concentration (calculated to be 2080 ppm). The relative humidity and temperature of the air sampled were 78.7% and

22.9 °C, and the sampling flow rate was 50 mL/min. Cyclohexane was present as a potential interferent, nominally at its permissible exposure limit (calculated to be 317 ppm). Samples were collected on three sorbent tubes for 45 min. After immediate analysis, results for pentane as a percentage of expected recovery were 102.4%, 101.9%, and 104.8%.

10 Analytical Method Reproducibility

Samples were prepared by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing pentane nominally at the target concentration (calculated to be 1045 ppm). The relative humidity and temperature of the air sampled were 67.6% and 22.5 °C, and the sampling flow rate was 50 mL/min. Samples were collected on six sorbent tubes for 45 min. The resulting samples were submitted to the OSHA Salt Lake Technical Center for analysis using the procedures described in OSHA Method 5000 after storage for 19 days at 4 °C. The analytical results corrected for E_E are provided in Table C-8. No sample result for pentane fell outside the permissible bounds set by the precision of the overall procedure determined in Section 5 of this appendix.

Table C-8. Reproducibility data for pentane.

sampled (ppm)	recovered (ppm)	recovery (%)	deviation (%)
1045	997.5	95.4	-4.6
1045	983.1	94.1	-5.9
1045	982.7	94.0	-6.0
1045	975.7	93.4	-6.6
1045	949.3	90.8	-9.2
1045	980.1	93.8	-6.2

11 Effect of Sampling a Low Concentration

The effect of sampling a low concentration of pentane vapor was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing pentane nominally at one-tenth the target concentration (calculated to be 99.6 ppm). The relative humidity and temperature of the air sampled were 76.7% and 24.1 °C, and the sampling flow rate was 50 mL/min. Samples were collected on three sorbent tubes for 45 min. After immediate analysis, results for pentane as percentage of expected recovery were 97.5%, 98.7%, and 100.2%.

12 Estimation of Uncertainty

While systematic biases such as analyte storage loss are examined, and limits are placed on these, an estimation of uncertainty that encompasses both potential random and systematic error was not completed. Instead, the overall standard error of estimate was calculated from the random error inherent to the points about the regression line produced by the ambient storage test described in Section 5, as prescribed by the OSHA validation guidelines in use at the time OSHA Method 5000 was originally validated. See Section 5 of this appendix for details.

13 Controlled Test Atmosphere Procedure

Dynamically generated controlled test atmospheres were created in a walk-in hood. House air was regulated using a Miller Nelson Model 401 flow-temperature-humidity control system. A measured flow of liquid pentane was introduced with an ISCO model 100DM syringe pump through a short length of 0.53 mm internal diameter 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 pentane vapor and dilution air flowed into a mixing chamber (76 cm length x 15 cm diameter), and then into a sampling chamber (56 cm length x 9.5 cm diameter). Sampling was completed from sampling ports present on the sampling chamber. Temperature and humidity measurements were obtained near the exit of the sampling chamber using a Vaisala HUMICAP Model HM70 hand-held humidity and temperature meter.

OSHA 5000, Appendix D
Trichloroethylene

Version:	1.0
OSHA PEL:	100 ppm (537 mg/m^3) Z-2 8-Hour TWA, General Industry, Construction, Shipyard; 200 ppm (1074 mg/m^3) Z-2 Ceiling (up to Peak value, no more than 5 minutes in a 2-hour period), General Industry; 300 ppm (1612 mg/m3) Z-2 Peak, General Industry
ACGIH TLV:	10 ppm (54 mg/m^3) 8-Hour TWA; 25 ppm (135 mg/m^3) 15-Minute STEL
Recommended sampling time and sampling rate:	240 min at 50 mL/min (12 L, 8-Hour TWA); 5 min at 50 mL/min (0.25 L, Ceiling); 1 min at 50 mL/min (0.05 L, Peak)
Reliable quantitation limit:	0.052 ppm (0.25 mg/m^3, 8-Hour TWA); 2.2 ppm (12 mg/m^3, Ceiling); 11 ppm (61 mg/m^3, Peak)
Standard error of estimate:	5.1% (8-Hour TWA); 5.0% (Ceiling); 5.1% (Peak)
Status:	Fully validated. Method 5000 has been subjected to the established validation procedures of the Method Development Team for sampling and analysis of trichloroethylene.

May 1999 (OSHA1001)	Daren Pearce
February 2021 (OSHA 5000)	Anna Tang, Daren Pearce

1 Introduction

1.1 Previous Methods used by OSHA for Sampling and Analysis of Trichloroethylene

The specific analyte described in this appendix is trichloroethylene, CAS No. 79-01-6. The methodologies described in this appendix for trichloroethylene are based on OSHA Method 1001.[1] That method requires the collection of samples using charcoal sorbent tubes, extraction using carbon disulfide, and analysis by gas chromatography using a flame ionization detector.

1.2 Changes to the Previously-Used Method

This appendix represents an update of OSHA Method 1001[1], which was fully validated at the time it was published based on the validation guidelines in effect at that time. Compared to the previous method used this method includes new analytical parameters and internal standard (ISTD). Data presented from the previously used method are identified by the statement "Pre-existing data from OSHA Method 1001[1] are presented in this section". The changes were made to allow the standardized collection and analysis of trichloroethylene with other analytes found in Organic Vapor Sampling Group 1, described in OSHA Method 5000.

---

[1] Elskamp. C.J. Tetrachloroethylene Trichloroethylene (OSHA Method 1001), 1999. Occupational Safety and Health Administration Web site. https://www.osha.gov/dts/sltc/methods/mdt/mdt1001/1001.html (accessed October 2018).

1.3 Validation Parameters

The procedures used to develop the method validation data are described in Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis.[2] Air concentrations listed in ppm are referenced to 25 °C and 760 Torr. The target concentration for method evaluation was the OSHA Z-2 8-hour time-weighted average (TWA) permissible exposure limit (PEL) for trichloroethylene.

2 Detection and Quantification

2.1 Detection Limit of the Analytical Procedure (DLAP)

The DLAP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLAP $S_{y/x}$) divided by the slope of the line produced from analyses of ten analytical standards prepared with equally spaced increments of analyte mass. The standards were prepared in such a way that the highest standard concentration would produce a peak approximately 10 times the response of a reagent blank at or near the chromatographic retention time of the analyte. The standards and a reagent blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLAP $S_{y/x}$ and slope values for DLAP determination. Results obtained for these analyses are listed in Table D-1, and plotted in Figure D-1.

Table D-1. DLAP data for trichloroethylene.

concentration (µg/mL)	mass on column (pg)	area counts (µV·s)
0.00	0.00	0.00
1.17	7.80	0.049
2.34	15.6	0.135
3.51	23.4	0.217
4.69	31.3	0.261
5.86	39.1	0.312
7.03	46.9	0.336
8.20	54.7	0.393
9.37	62.5	0.450
10.5	70.0	0.505
11.7	78.0	0.560

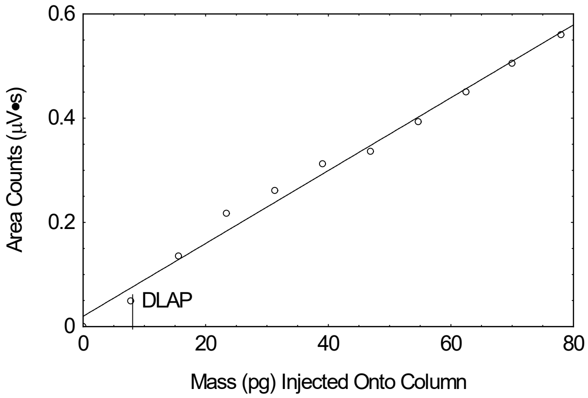

Figure D-1. Plot of data used to determine the DLAP for trichloroethylene ($y = 0.00699x + 0.0197$, DLAP $S_{y/x}$ = 0.0193, DLAP = 8.30 pg).

2.2 Detection Limit of the Overall Procedure (DLOP) and Reliable Quantitation Limit (RQL)

The DLOP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLOP $S_{y/x}$) divided by the slope of the line produced from analyses of ten samples prepared from sorbent tubes spiked with equally spaced increments of analyte mass. 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 RQL is expressed as an air concentration that will provide sufficient analyte mass per sample that produces a response greater than 10× DLOP $S_{y/x}$ divided by the slope of the line described above. The spiked samplers and a sample blank were analyzed with the recommended analytical parameters described in OSHA Method 5000.The resulting data provided the DLOP $S_{y/x}$ and the slope values for DLOP and RQL determinations. Results obtained from these analyses are listed in Table D-2, and plotted in Figure D-2.

---

[2] Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration Web site. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed December 2018).

Table D-2. DLOP and RQL data for trichloroethylene.

mass per sample (µg/sample)	area counts (µV·s)
0.00	0.00
0.974	0.0830
1.95	0.117
2.92	0.225
3.90	0.245
4.87	0.295
5.84	0.362
6.82	0.444
7.79	0.502
8.76	0.565
9.74	0.586

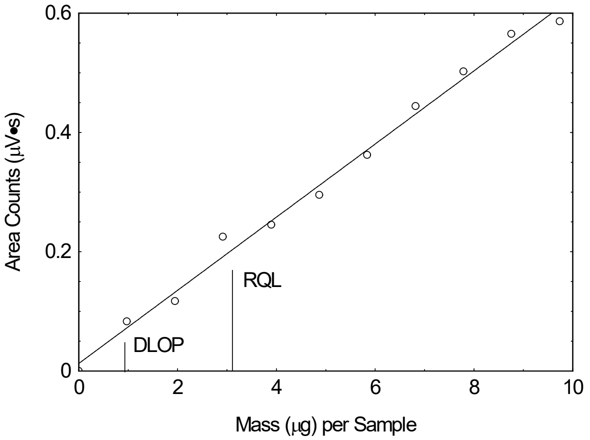

Figure D-2. Plot of data used to determine the DLOP and RQL for trichloroethylene ($y = 0.0613x + 0.0127$, DLOP $S_{y/x}$ = 0.0186, DLOP = 0.910 µg/sample, RQL = 3.03 µg/sample or 0.0515 ppm).

3 Analytical Precision Across the Calibration Range

Fifteen analytical standards over a range of 0.1 to 2 times the analyte concentration in solvent that would be obtained from sampling for the recommended time at the target concentration were analyzed with the recommended analytical parameters described in OSHA Method 5000. An ordinary least-squares linear regression curve was created by plotting the analyte mass per sample versus the corresponding ratio of analyte peak area to internal standard (ISTD) peak area. The resulting data provided the standard error of estimate (Calibration $S_{y/x}$) value across the calibration range, which provides an indication of the imprecision attributable to the instrumental analysis of the target analyte. Results from these analyses are listed below in Table D-3, and plotted in Figure D-3.

Table D-3. Analytical precision data for trichloroethylene.

× target	0.1×	0.5×	1.0×	1.5×	2.0×
concn (µg/sample)	585.7	2928	5857	10,249	14,642
area ratio	0.4954	2.438	4.915	8.704	12.62
	0.5040	2.553	5.118	8.700	12.98
	0.5200	2.600	5.217	9.270	13.32

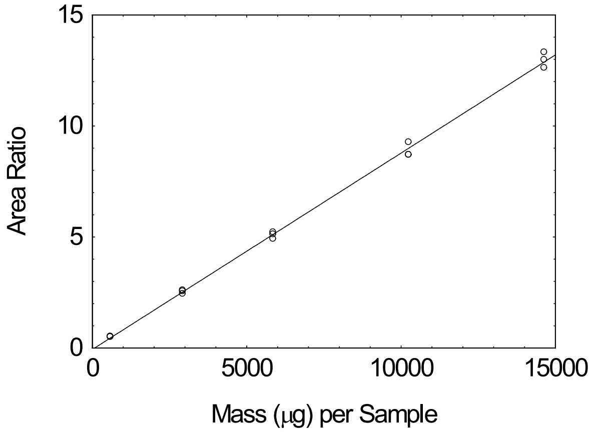

Figure D-3. Plot of data used to determine the precision of the analytical method for trichloroethylene ($y = 0.000884x - 0.0632$, Calibration $S_{y/x}$ = 0.213).

4 Sampler Storage Stability

Pre-existing data from OSHA Method 1001[1] are presented in this section.

Storage stability test samples for trichloroethylene were prepared by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13. Sampling from this system followed the recommended sampling parameters published in OSHA Method 1001. The nominal concentrations of trichloroethylene for both ambient and refrigerated storage testing were the target concentrations (calculated to be 100 ppm for the Z-2 8-hour TWA, 200 ppm for the Z-2 ceiling, and 300 ppm for the Z-2 peak). The relative humidity and temperature of the air sampled were 80% and 22 °C for both tests. For each test, twenty-one samples were prepared and six of these were analyzed on the day that samples were created. The remaining fifteen refrigerated storage test samples were stored at reduced temperature (0 °C), while the remaining fifteen ambient storage test samples were kept in a closed drawer at ambient temperature (20-25 °C). For each storage condition, three samples were selected and analyzed from those remaining at 3-6 day intervals. The results of these analyses (extraction efficiency correction was not specified in OSHA Method 1001[1]) are provided in Tables D-4 through D-6, and plotted in Figures D-4 through D-9.

The recovery of trichloroethylene calculated from the regression line generated for the 17-day Z-2 8-hour TWA ambient storage test was 98.5%.

Table D-4. Sampler storage stability data for trichloroethylene (Z-2 8-hour TWA).

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	99.7	98.6	100.7	99.7	98.6	100.7
0	99.6	100.2	100.2	99.6	100.2	100.2
6	100.9	97.8	99.3	101.6	98.9	100.0
10	98.8	98.6	100.5	98.8	99.4	100.4
13	98.2	99.2	99.0	98.8	99.8	99.8
15	99.0	98.5	98.7	99.2	99.3	98.9
17	99.2	98.4	98.0	98.4	100.4	99.3

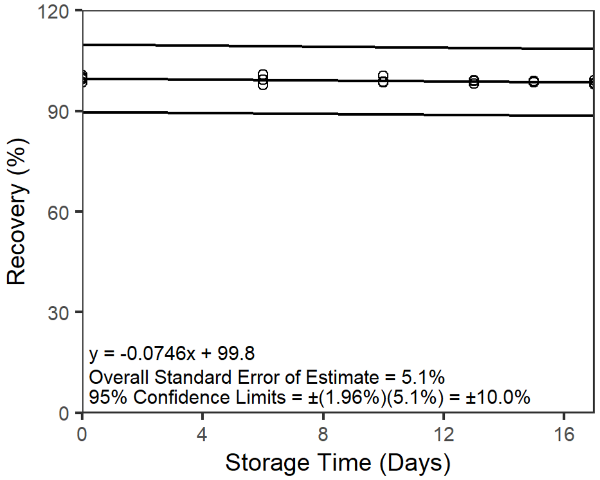

Figure D-4. Plot of Z-2 8-hour TWA ambient storage stability data for trichloroethylene.

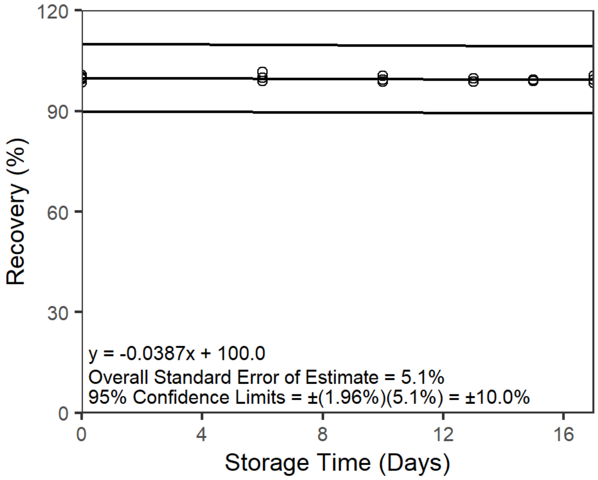

Figure D-5. Plot of Z-2 8-hour TWA refrigerated storage stability data for trichloroethylene.

Table D-5. Sampler storage stability data for trichloroethylene (Z-2 ceiling).

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	99.3	99.8	100.0	99.3	99.8	100.0
0	100.0	99.7	98.5	100.0	99.7	98.5
6	99.6	99.2	100.4	100.3	99.4	99.4
10	98.4	98.9	100.0	99.9	101.2	97.9
13	99.5	98.3	98.4	99.4	98.2	97.4
15	99.8	98.8	98.4	101.2	100.5	100.8
17	99.4	99.0	98.3	98.5	99.0	101.6

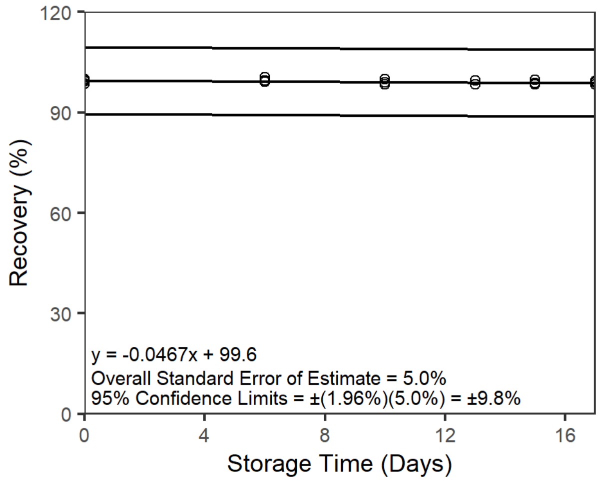

Figure D-6. Plot of Z-2 ceiling ambient storage stability data for trichloroethylene.

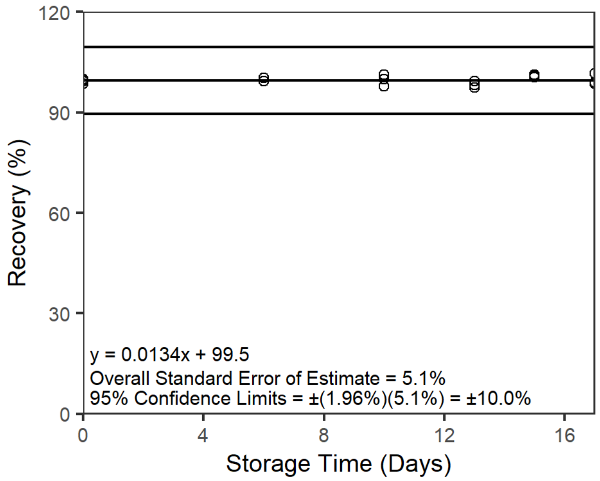

Figure D-7. Plot of Z-2 ceiling frozen storage stability data for trichloroethylene.

Table D-6. Sampler storage stability data for trichloroethylene (Z-2 peak).

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	97.5	97.5	96.6	97.5	97.5	96.6
0	94.7	95.2	95.5	94.7	95.2	95.5
6	97.6	96.3	97.2	98.0	96.8	98.9
10	97.7	98.0	97.4	95.7	97.4	98.1
13	96.3	96.9	95.9	96.8	99.0	96.2
15	97.2	97.5	97.3	98.3	96.9	97.1
17	96.6	96.1	95.5	96.6	95.5	96.2

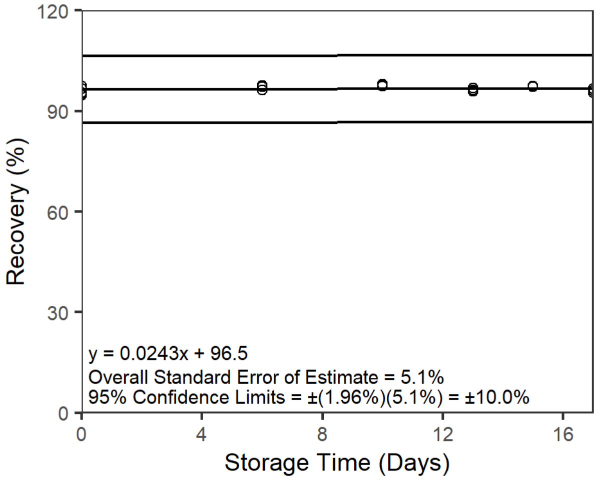

Figure D-8. Plot of Z-2 peak ambient storage stability data for trichloroethylene.

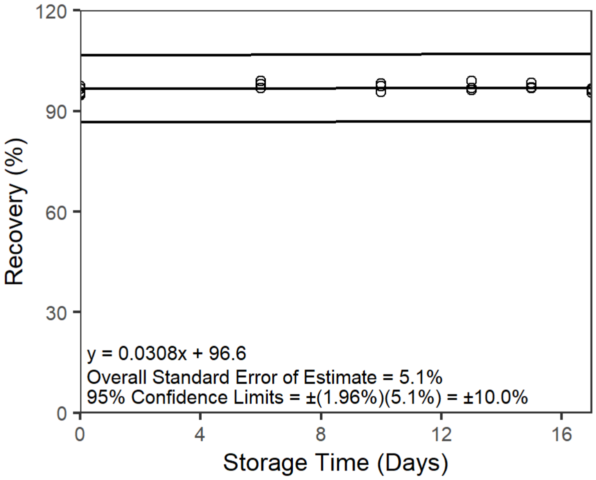

Figure D-9. Plot of Z-2 peak refrigerated storage stability data for trichloroethylene.

5 Precision of the Overall Procedure

Pre-existing data from OSHA Method 1001[1] are presented in this section.

The overall standard error of estimate obtained from the ambient storage test analyses described in Section 4 and sampling pump variability were used to determine the precision of the overall procedure, where all aspects of sampling and analysis (sampling, sorbent tube handling and solvent extraction, and instrumental analysis) are considered. This value was obtained by taking the square root of the squared ambient storage stability standard error of estimate (Storage $S_{y/x}^2$) added to the squared sampling pump variability value (V_{SP}^2). The resulting precision of the overall procedure at the 95% confidence level for the Z-2 8-hour TWA ambient 17-day storage test (at the corresponding target concentration) for trichloroethylene was determined to be ±10.0% based on the observed ambient Storage $S_{y/x}$ value of 5.1% and V_{sp} value of 5.0%. The resulting precision of the overall procedure at the 95% confidence level for the Z-2 ceiling ambient 17-day storage test (at the corresponding target concentration) for trichloroethylene was determined to be ±9.9% based on the observed ambient Storage $S_{y/x}$ value of 5.0% and V_{sp} value of 5.0%. The resulting precision of the overall procedure at the 95% confidence level for the Z-2 peak ambient 17-day storage test (at the corresponding target concentration) for trichloroethylene was determined to be ±10.0% based on the observed ambient Storage $S_{y/x}$ value of 5.1% and V_{SP} value of 5.0%.

6 Recovery and Stability of Prepared Samples

Quantitative extraction is affected by the extraction solvent, the ISTD, the sampling medium, and the technique used to extract samples. The data presented demonstrates validity for the extraction solvent, ISTD, sampling medium, and extraction technique described in OSHA Method 5000. 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.

A value for extraction efficiency (E_E) was determined by liquid-spiking four replicate sorbent tubes across a range of analyte mass values that would be obtained from sampling at 0.1 to 2 times the target concentration value for 240 min. Four sorbent tubes were also spiked in this fashion at the target concentration after drawing humid air (79.4% relative humidity at 22.3 °C) through these tubes at 50 mL/min for 4 hours. All of the samples described above were analyzed the following day after being kept overnight at ambient temperature. The E_E value at the RQL was 111.9%, while that of the working range samples (excluding the samples through which humid air had been drawn) was 100.5%. The data are shown in Table D-7. Pre-loading sorbent tubes with moisture ("wet" designation in table) did not have an unacceptable effect on E_E.

Table D-7. Extraction efficiency data for trichloroethylene.

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.1	585.7	101.6	100.5	102.7	100.0	101.2
0.25	1523	99.4	100.4	100.7	99.8	100.1
0.5	2928	98.8	100.4	101.0	101.2	100.3
1.0	5857	98.8	99.2	99.6	99.9	99.4
1.5	10,249	98.5	99.7	103.3	100.5	100.5
2.0	14,642	98.4	101.8	102.4	103.9	101.6
RQL	2.92	110.9	118.4	106.2	112.0	111.9
1.0 (wet)	5857	98.9	99.0	100.1	101.0	99.7

The stability of sample extracts prepared according to OSHA Method 5000 was examined by retaining the sample solvent extracts for the target concentration samples described immediately above. Two of the four vials were immediately recapped with new septa following the initial analyses, and again following each re-analysis event. The other two vials retained the original punctured septa throughout. All four 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 septum (whether new or previously used) was punctured four times for each injection. Re-cap all vials after analysis due to the loss of analyte in the punctured septa. The resulting data are shown in Table D-8.

Table D-8. Extracted sample stability data for trichloroethylene.

	punctured septa replaced recovery (%)		punctured septa retained recovery (%)	
time (days)	1	2	1	2
0	99.2	100.4	100.1	98.7
1	95.9	96.8	94.6	92.7
2	99.4	100.8	94.9	93.0
3	93.7	95.2	85.3	83.2

7 Sampler Capacity

Pre-existing data from OSHA Method 1001[1] are presented in this section.

The sampling capacity of the front section of a sorbent tube was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing trichloroethylene nominally at two times the target concentration (calculated to be 192.0 ppm). The relative humidity and temperature of the air sampled were 64.5% and 25.8 °C, and the sampling flow rate was 50 mL/min. A sorbent tube testing systems was made by placing a complete sorbent tube in series behind another tube, which contained only the front sorbent section. The rear tube was changed and analyzed at 240, 300, 360, 420, 465, and 495 min. Breakthrough was observed after sampling for 466 min (corresponding to 23.3 liters). Data from three sorbent tube testing systems, shown in Table D-9, were used to determine a recommended sampling volume of 12 liters for trichloroethylene as described in OSHA Method 5000. This volume corresponds to a 240 min sampling period, which is the maximum recommended sampling time regardless of breakthrough. Results are plotted in Figure D-10.

Table D-9. Sampler capacity data for trichloroethylene.

sample no.	air vol (L)	sampling time (min)	cumulative downstream concn (mg/m^3)	break-through (%)
1	6.1	240	0.00	0.00
	13.7	300	0.00	0.00
	16.7	360	0.06	0.01
	19.7	420	5.19	0.50
	22.4	465	44.6	4.3
	24.3	495	119.7	11.6
2	5.8	240	0.00	0.00
	13.1	300	0.00	0.00
	16.0	360	0.00	0.00
	18.9	420	0.56	0.05
	21.4	465	5.86	0.6
	23.2	495	21.4	2.08
3	6.3	240	0.00	0.00
	14.2	300	0.02	0.002
	17.4	360	0.30	0.03
	20.5	420	8.03	0.78
	23.3	465	50.3	4.9
	25.3	495	119.6	11.6

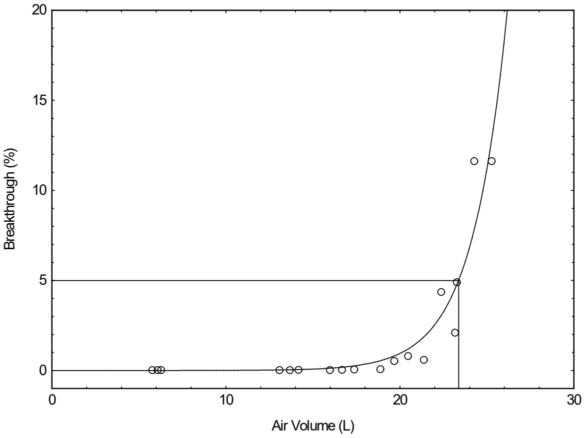

Figure D-10. Plot of data used to determine sampler capacity for trichloroethylene. The 5% breakthrough volume shown is based on the curves in the figure, which are fit to the data provided in Table D-9.

8 Low Humidity

Pre-existing data from OSHA Method 1001[1] are presented in this section.

The effect of low humidity was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing trichloroethylene nominally at two times the target concentration (calculated to be 199 ppm). The relative humidity and temperature of the air sampled were 3% and 26 °C, and the sampling flow rate was 50 mL/min. Samples were collected on three sorbent tubes for 240 min. After immediate analysis, results as a percentage of expected recovery were 98.4%, 98.1%, and 97.9%.

9 Chemical Interference

Pre-existing data from OSHA Method 1001[1] are presented in this section.

The effect of potential chemical sampling interference was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing trichloroethylene nominally at the target concentration (calculated to be 100 ppm). The relative humidity and temperature of the air sampled were 70% and 24 °C, and the sampling flow rate was 50 mL/min. Methylene chloride, isopropyl alcohol, 2-butanone (methyl ethyl ketone), *n*-butyl acetate, dioxane, and *n*-amyl acetate were present as interferents, at known concentrations (calculated to be at 83 ppm, 70 ppm, 71 ppm, 17 ppm, 26 ppm, and 17 ppm respectively). Samples were collected on three sorbent tubes for 240 min. After immediate analysis, results as a percentage of expected recovery were 96.8%, 100.0%, and 100.6%.

10 Analytical Method Reproducibility

Pre-existing data from OSHA Method 1001[1] are presented in this section.

Samples were prepared by repeatedly sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing trichloroethylene nominally at the Z-2 TWA, Z-2 ceiling, and Z-2 peak target concentrations (calculated to be 89 ppm, 184 ppm, and 272 ppm). The relative humidity and temperature of the air sampled were not reported. Samples were collected on six sorbent tubes and the flow rate and time were not reported. The resulting samples were submitted to the OSHA Salt Lake Technical for analysis using the procedures described in OSHA Method 1001 after storage for 22 days at ambient temperature. The analytical results corrected for E_E are provided in Tables D-10 through D-12. No sample result for trichloroethylene fell outside the permissible bounds set by the precision of the overall procedure determined in Section 5 of this appendix.

Table D-10. Reproducibility data for trichloroethylene (Z-2 TWA).

sampled (mg/m^3)	recovered (mg/m^3)	recovery (%)	deviation (%)
479.2	459.1	95.8	-4.2
479.2	457.4	95.5	-4.5
479.2	457.4	95.5	-4.5
479.2	455.4	95.0	-5.0
479.2	445.5	93.0	-7.0
479.2	456.5	95.3	-4.7

Table D-11. Reproducibility data for trichloroethylene (Z-2 ceiling).

sampled (mg/m^3)	recovered (mg/m^3)	recovery (%)	deviation (%)
990.0	1001	101.1	+1.1
990.0	954.2	96.4	-3.6
990.0	965.2	97.5	-2.5
990.0	964.2	97.4	-2.6
990.0	958.4	96.8	-3.2
990.0	951.2	96.1	-3.9

Table D-12. Reproducibility data for trichloroethylene (Z-2 peak).

sampled (mg/m^3)	recovered (mg/m^3)	recovery (%)	deviation (%)
1463	1385	94.7	-5.3
1463	1380	94.3	-5.7
1463	1388	94.9	-5.1
1463	1397	95.5	-4.5
1463	1404	96.0	-4.0
1463	1404	96.0	-4.0

11 Effect of Sampling a Low Concentration

Pre-existing data from OSHA Method 1001[1] are presented in this section.

The effect of sampling a low concentration of trichloroethylene vapor was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing trichloroethylene nominally at one-tenth the target concentration (calculated to be 10.7 ppm). The relative humidity and temperature of the air sampled were 67% and 26 °C, and the sampling flow rate was 50 mL/min. Samples were collected on three sorbent tubes for 240 min. After immediate analysis, results for trichloroethylene as a percentage of expected recovery were 98.5%, 99.3%, and 99.5%.

12 Estimation of Uncertainty

While systematic biases such as analyte storage loss are examined, and limits are placed on these, an estimation of uncertainty that encompasses both potential random and systematic error was not completed. Instead, the overall standard error of estimate was calculated from the random error inherent to the points about the regression line produced by the ambient storage test described in Section 5, as prescribed by the OSHA validation guidelines in use at the time OSHA Method 1001[1] was originally validated. See Section 5 of this appendix for details.

13 Controlled Test Atmosphere Procedure

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 trichloroethylene 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 trichloroethylene 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.

OSHA 5000, Appendix E
Perchloroethylene (Tetrachloroethylene)

Version:	1.0
OSHA PEL:	100 ppm (678 mg/m^3) Z-2 8-Hour TWA, General Industry, Construction, Shipyard; 200 ppm (1356 mg/m^3) Z-2 Ceiling (up to Peak value, no more than 5 minutes in a 3-hour period), General Industry; 300 ppm (2034 mg/m^3) Z-2 Peak, General Industry
ACGIH TLV:	25 ppm (170 mg/m^3) 8-Hour TWA; 100 ppm (685 mg/m^3) 15-Minute STEL
Recommended sampling time and sampling rate:	240 min at 50 mL/min (12 L, 8-Hour TWA); 5 min at 50 mL/min (0.25 L, Ceiling), ≥1 min at 50 mL/min (0.05 L, Peak)
Reliable quantitation limit:	0.071 ppm (0.48 mg/m^3, 8-Hour TWA); 3.4 ppm (23 mg/m^3, Ceiling); 17 ppm (115 mg/m^3, Peak)
Standard error of estimate:	5.1% (8-Hour TWA); 5.0% (Ceiling); 5.2% (Peak)
Status:	Fully validated. Method 5000 has been subjected to the established validation procedures of the Method Development Team for sampling and analysis of perchloroethylene (tetrachloroethylene).

May 1999 (OSHA 1001)	Mary Eide
February 2021 (OSHA 5000)	Anna Tang, Daren Pearce

1 Introduction

1.1 Previous Methods used by OSHA for Sampling and Analysis of Perchloroethylene (Tetrachloroethylene)

The specific analyte described in this appendix is perchloroethylene (tetrachloroethylene), CAS No. 127-18-4. The methodologies described in this appendix for perchloroethylene (tetrachloroethylene) are based on OSHA Method 1001.[1] That method requires the collection of samples using charcoal sorbent tubes, extraction using carbon disulfide, and analysis by gas chromatography using a flame ionization detector.

1.2 Changes to the Previously-Used Method

This appendix represents an update of OSHA Method 1001[1], which was fully validated at the time it was published based on the validation guidelines in effect at that time. Compared to the previous method used this method includes new analytical parameters and internal standard (ISTD). Data presented from the previously used method are identified by the statement "Pre-existing data from OSHA Method 1001[1] are presented in this section". The changes were made to allow the standardized collection and analysis of perchloroethylene (tetrachloroethylene) with other analytes found in Organic Vapor Sampling Group 1, described in OSHA Method 5000.

---

[1] Elskamp, C.J. Tetrachloroethylene Trichloroethylene (OSHA Method 1001), 1999. United States Department of Labor, Occupational Safety and Health Administration Web site. https://www.osha.gov/dts/sltc/methods/mdt/mdt1001/1001.html (accessed October 2018).

1.3 Validation Parameters

The procedures used to develop the method validation data are described in Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis.[2] Air concentrations listed in ppm are referenced to 25 °C and 760 Torr. The target concentration for method evaluation was the OSHA Z-2 8-hour time-weighted average (TWA) permissible exposure limit (PEL) for perchloroethylene (tetrachloroethylene).

2 Detection and Quantification

2.1 Detection Limit of the Analytical Procedure (DLAP)

The DLAP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLAP $S_{y/x}$) divided by the slope of the line produced from analyses of ten analytical standards prepared with equally spaced increments of analyte mass. The standards were prepared in such a way that the highest standard concentration would produce a peak approximately 10 times the response of a reagent blank at or near the chromatographic retention time of the analyte. The standards and a reagent blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLAP $S_{y/x}$ and slope values for DLAP determination. Results obtained for these analyses are listed in Table E-1, and plotted in Figure E-1.

Table E-1. DLAP data for perchloroethylene (tetrachloroethylene).

concentration (µg/mL)	mass on column (pg)	area counts (µV·s)
0.00	0.00	0.00
0.974	6.49	0.127
1.95	13.0	0.142
2.92	19.5	0.158
3.90	26.0	0.194
4.87	32.5	0.253
5.84	38.9	0.266
6.82	45.5	0.323
7.79	51.9	0.318
8.76	58.4	0.372
9.74	64.9	0.385

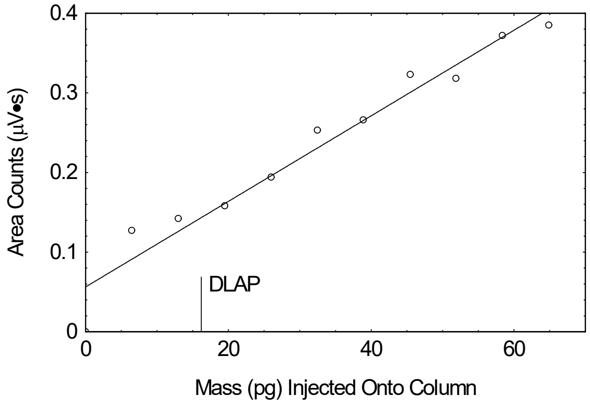

Figure E-1. Plot of data used to determine the DLAP for perchloroethylene (tetrachloroethylene) ($y = 0.00537x + 0.0563$, DLAP $S_{y/x}$ = 0.0267, DLAP = 14.9 pg).

2.2 Detection Limit of the Overall Procedure (DLOP) and Reliable Quantitation Limit (RQL)

The DLOP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLOP $S_{y/x}$) divided by the slope of the line produced from analyses of ten samples prepared from sorbent tubes spiked with equally spaced increments of analyte mass. 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 RQL is expressed as an air concentration that will provide sufficient analyte mass per sample that produces a response greater than 10× DLOP $S_{y/x}$ divided by the slope of the line described above. The spiked samplers and a sample blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLOP $S_{y/x}$ and the slope values for DLOP and RQL determinations. Results obtained from these analyses are listed in Table E-2, and plotted in Figure E-2.

---

[2] Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration Web site. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed December 2018).

Table E-2. DLOP and RQL data for perchloroethylene (tetrachloroethylene).

mass per sample (µg/sample)	area counts (µV·s)
0.00	0.00
0.974	0.0400
1.95	0.133
2.92	0.178
3.90	0.231
4.87	0.233
5.84	0.262
6.82	0.333
7.79	0.396
8.76	0.379
9.74	0.463

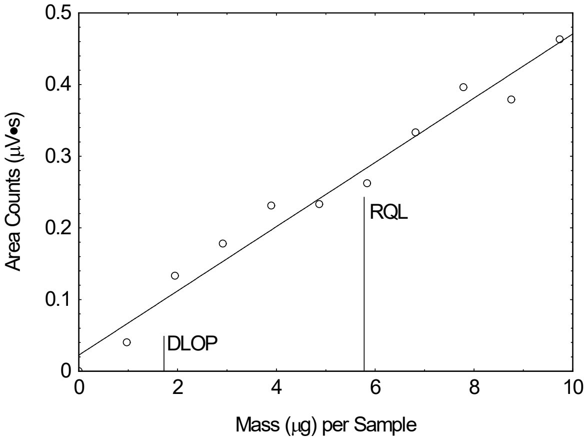

Figure E-2. Plot of data used to determine the DLOP and RQL for perchloroethylene (tetrachloroethylene) ($y = 0.0448x + 0.0224$, DLOP $S_{y/x}$ = 0.0257, DLOP = 1.72 µg/sample, RQL = 5.74 µg/sample or 0.071 ppm).

3 Analytical Precision Across the Calibration Range

Fifteen analytical standards over a range of 0.1 to 2 times the analyte concentration in solvent that would be obtained from sampling for the recommended time at the target concentration were analyzed with the recommended analytical parameters described in OSHA Method 5000. An ordinary least squares linear regression curve was created by plotting the analyte mass per sample versus the corresponding ratio of analyte peak area to internal standard (ISTD) peak area. The resulting data provided the standard error of estimate (Calibration $S_{y/x}$) value across the calibration range, which provides an indication of the imprecision attributable to the instrumental analysis of the target analyte. Results from these analyses are listed in Table E-3, and plotted in Figure E-3.

Table E-3. Analytical precision data for perchloroethylene (tetrachloroethylene).

× target	0.1×	0.5×	1.0×	1.5×	2.0×
concn (µg/sample)	779.0	4869	8115	11,361	16,230
area ratio	0.6159	3.824	6.399	9.071	13.23
	0.6142	3.796	6.356	9.148	13.28
	0.6408	3.997	6.602	9.433	13.55

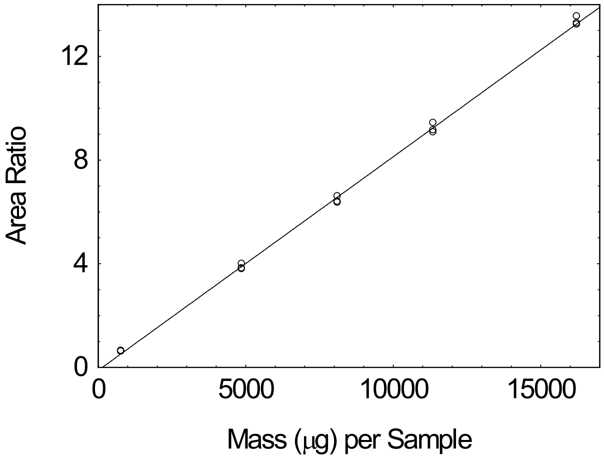

Figure E-3. Plot of data used to determine the precision of the analytical method for perchloroethylene (tetrachloroethylene) ($y = 0.000824x - 0.114$, Calibration $S_{y/x}$ = 0.150).

4 Sampler Storage Stability

Pre-existing data from OSHA Method 1001[1] are presented in this section.

Storage stability test samples for perchloroethylene (tetrachloroethylene) were prepared by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13. Sampling from this system followed the recommended sampling parameters published in OHSA Method 1001. The nominal concentration of perchloroethylene (tetrachloroethylene) for both ambient and refrigerated storage testing was the target concentration (calculated to be 100 ppm for eight the Z-2 8-hour TWA, 200 ppm for the Z-2 ceiling, and 300 ppm for the Z-2 peak). The relative humidity and temperature of the air sampled were 80% and 22 °C for both tests. For each test, twenty-one samples were prepared, and six of these were analyzed on the day that samples were created. The remaining fifteen refrigerated storage test samples were stored at reduced temperature (0 °C), while the remaining fifteen ambient storage test samples were kept in a closed drawer at ambient temperature (20-25 °C). For each storage condition, three samples were selected and analyzed from those remaining at 2-6 day intervals. The results for these analyses (extraction efficiency correction was not specified in OSHA Method 1001[1]) are provided below in Tables E-4 through E-6, and plotted in Figures E-4 through E-9.

The recovery of perchloroethylene (tetrachloroethylene) calculated from the regression line generated for the 17-day TWA ambient storage test was 99.1%.

Table E-4. Sampler storage stability data for perchloroethylene (tetrachloroethylene) (Z-2 8-hour TWA).

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	100.6	102.0	99.9	98.7	98.2	100.5
0	102.8	100.4	101.3	99.6	99.9	99.6
6	101.7	98.7	100.0	101.8	99.4	100.4
10	99.4	99.3	100.8	99.4	99.8	100.9
13	99.3	100.0	99.8	99.3	100.5	100.2
15	99.6	99.0	99.3	99.6	99.6	99.3
17	100.0	99.3	98.7	99.0	100.7	99.8

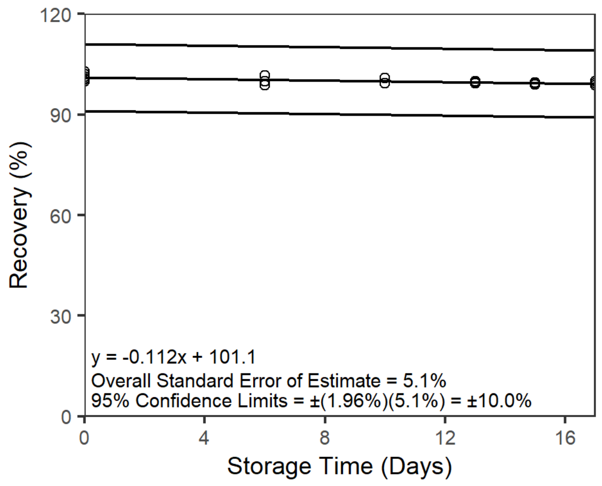

Figure E-4. Plot of Z-2 8-hour TWA ambient storage stability data for perchloroethylene (tetrachloroethylene).

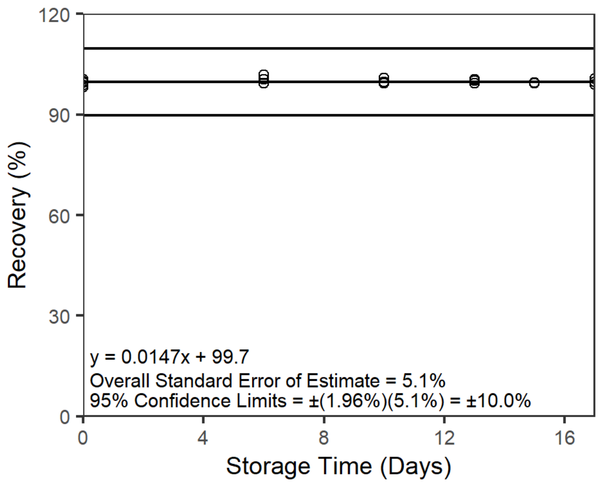

Figure E-5. Plot of Z-2 8-hour TWA refrigerated storage stability data for perchloroethylene (tetrachloroethylene).

Table E-5. Sampler storage stability data for perchloroethylene (tetrachloroethylene) (Z-2 ceiling).

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	101.8	100.0	101.2	101.8	100.0	101.2
0	100.9	101.1	99.7	100.9	101.1	99.7
6	101.0	100.1	101.7	101.8	100.7	95.1
10	99.8	100.1	100.2	100.9	102.3	99.3
13	100.6	99.5	100.0	101.1	99.4	99.1
15	101.0	99.4	98.8	102.4	100.5	102.2
17	100.9	100.6	99.9	99.8	100.1	103.1

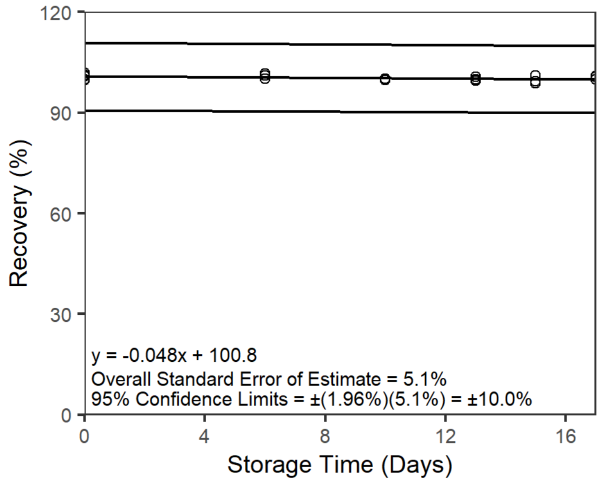

Figure E-6. Plot of Z-2 ceiling ambient storage stability data for perchloroethylene (tetrachloroethylene).

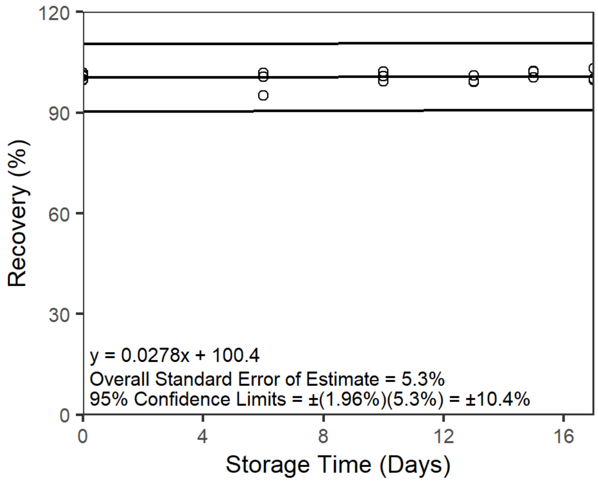

Figure E-7. Plot of Z-2 ceiling refrigerated storage stability data for perchloroethylene (tetrachloroethylene).

Table E-6. Sampler storage stability data for perchloroethylene (tetrachloroethylene) (Z-2 peak).

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	99.6	98.6	96.9	99.6	98.6	96.9
0	96.5	96.9	97.1	96.5	96.9	97.1
6	97.4	96.4	96.7	97.6	96.0	96.8
10	97.2	97.6	97.3	95.9	97.0	97.7
13	95.2	95.4	94.3	95.3	97.8	96.3
15	99.1	100.0	96.2	100.1	99.2	99.1
17	97.5	98.7	97.4	98.5	97.5	95.7

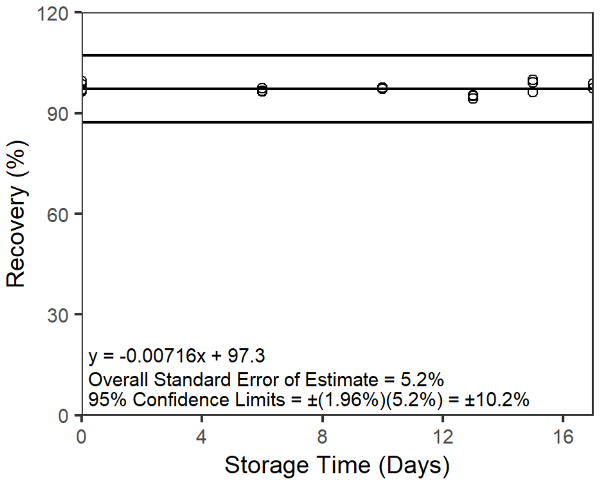

Figure E-8. Plot of Z-2 peak ambient storage stability data for perchloroethylene (tetrachloroethylene).

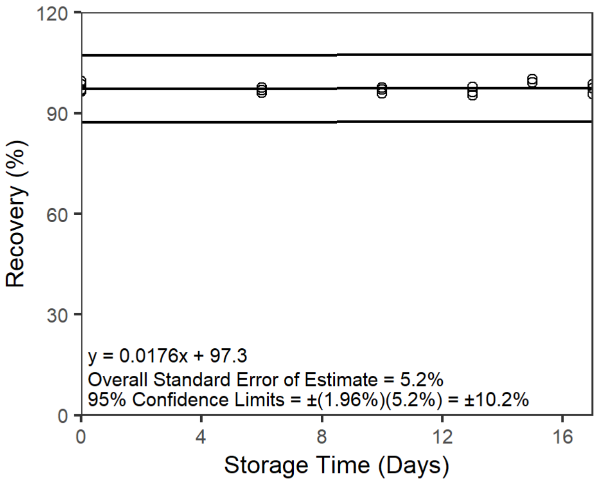

Figure E-9. Plot of Z-2 peak refrigerated storage stability data for perchloroethylene (tetrachloroethylene).

5 Precision of the Overall Procedure

Pre-existing data from OSHA Method 1001[1] are presented in this section.

The overall standard error of estimate obtained from the ambient storage test analyses described in Section 4 and sampling pump variability were used to determine the precision of the overall procedure, where all aspects of sampling and analysis (sampling, sorbent tube handling and solvent extraction, and instrumental analysis) are considered. This value was obtained by taking the square root of the squared ambient storage stability standard error of estimate (Storage $S_{y/x}^2$) added to the squared sampling pump variability value (V_{SP}^2). The resulting precision of the overall procedure at the 95% confidence level for the Z-2 8-hour TWA ambient 17-day storage test (at the corresponding target concentration) for perchloroethylene (tetrachloroethylene) was determined to be ±10.0% based on the observed ambient Storage $S_{y/x}$ value of 5.1% and V_{SP} value of 5.0%. The resulting precision of the overall procedure at the 95% confidence level for the Z-2 ceiling ambient 17-day storage test (at the corresponding target concentration) for perchloroethylene (tetrachloroethylene) was determined to be ±10.0% based on the observed ambient Storage $S_{y/x}$ value of 5.1% and V_{SP} value of 5.0%. The resulting precision of the overall procedure at the 95% confidence level for the Z-2 peak ambient 17-day storage test (at the corresponding target concentration) for perchloroethylene (tetrachloroethylene) was determined to be ±10.2% based on the observed ambient Storage $S_{y/x}$ value of 5.2% and V_{SP} value of 5.0%.

6 Recovery and Stability of Prepared Samples

Quantitative extraction 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 OSHA Method 5000. 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.

A value for extraction efficiency (E_E) was determined by liquid-spiking four replicate sorbent tubes across a range of analyte mass values that would be obtained from sampling at 0.1 to 2 times the target concentration value for 240 min. Four sorbent tubes were also spiked in this fashion at the target concentration after drawing humid air (77.5% relative humidity at 23.7 °C) through these tubes at 50 mL/min for 4 hours. All of the samples described above were analyzed the following day after being kept overnight at ambient temperature. The E_E value at the RQL was 91.2%, while that of the working range samples (excluding the samples through which humid air had been drawn) was 98.7%. The data are shown in Table E-7. Pre-loading sorbent tubes with moisture (“wet designation in the table) did not have an unacceptable effect on E_E.

Table E-7. Extraction efficiency data for perchloroethylene (tetrachloroethylene).

level		sample number				
× target Concn	µg per sample	1	2	3	4	mean
0.1	779.0	94.3	98.6	99.8	99.4	98.0
0.25	1948	98.9	98.9	99.6	97.8	98.8
0.5	4869	96.4	99.4	100.0	97.0	98.2
1.0	8115	98.6	104.4	102.8	101.3	101.8
1.5	11,361	97.2	99.6	97.2	94.7	97.2
2.0	16,230	97.3	97.9	99.1	99.2	98.4
RQL	5.84	88.3	95.0	87.7	93.7	91.2
1.0 (wet)	8115	99.5	101.1	101.7	102.1	101.1

The stability of sample extracts prepared according to OSHA Method 5000 was examined by retaining the sample solvent extracts for the target concentration samples described immediately above. Two of the four vials were immediately recapped with new septa following the initial analyses, and again following each re-analysis event. The other two vials retained the original punctured septa throughout. All four 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 septum (whether new or previously used) was punctured four times for each injection. The resulting data are shown in Table E-8.

Table E-8. Extracted sample stability data for perchloroethylene (tetrachloroethylene).

	punctured septa replaced recovery (%)		punctured septa retained recovery (%)	
time (days)	1	2	1	2
0	98.1	98.6	97.2	97.4
1	97.7	100.7	97.4	99.1
2	97.8	97.6	94.8	95.2
3	96.6	96.7	91.5	91.8

7 Sampler Capacity

Pre-existing data from OSHA Method 1001[1] are presented in this section.

The sampling capacity of the front section of a sorbent tube was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing perchloroethylene (tetrachloroethylene) nominally at two times the target concentration (calculated to be 192.7 ppm). The relative humidity and temperature of the air sampled were 65% and 26.1 °C, and the sampling flow rate was 50 mL/min. A sorbent tube testing system was made by placing a complete sorbent tube in series behind another tube, which contained only the front sorbent section. The rear tube was removed and analyzed at 570 min. Breakthrough was not observed after sampling for 9.5 hours (corresponding to 28.5 liters). Data from three sorbent tube testing systems were used to determine a recommended sampling volume of 12 liters for perchloroethylene (tetrachloroethylene) as described in OSHA Method 5000. This volume corresponds to a 240 min sampling period, which is the maximum recommended sampling time regardless of breakthrough.

8 Low Humidity

Pre-existing data from OSHA Method 1001[1] are presented in this section.

The effect of low humidity was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing perchloroethylene (tetrachloroethylene) nominally at two times the target concentration (calculated to be 198 ppm). The relative humidity and temperature of the air sampled were 3% and 26 °C, and the sampling flow rate was 50 mL/min. Samples were collected on three sorbent tubes for 240 min. After immediate analysis, results as a percentage of expected recovery were 100.0%, 99.3%, and 100.0%.

9 Chemical Interference

Pre-existing data from OSHA Method 1001[1] are presented in this section.

The effect of potential chemical sampling interference was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing perchloroethylene (tetrachloroethylene) nominally at the target concentration (calculated to be 100 ppm). The relative humidity and temperature of the air sampled were 63% and 27 °C, and the sampling flow rate was 50 mL/min. Methylene chloride, isopropyl alcohol, 2-butanone (methyl ethyl ketone), *n*-butyl acetate, dioxane, and *n*-amyl acetate were present as interferents (calculated to be at 83 ppm, 70 ppm, 71 ppm, 26 ppm, 17 ppm, and 16 ppm respectively). Samples were collected on three sorbent tubes for 240 min. After immediate analysis, results as a percentage of expected recovery were 101.6%, 100.0%, and 102.0%.

10 Analytical Method Reproducibility

Pre-existing data from OSHA Method 1001[1] are presented in this section.

Samples were prepared by repeatedly sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing perchloroethylene (tetrachloroethylene) nominally at the Z-2 8-hour TWA, Z-2 ceiling, and Z-2 peak target concentrations (calculated to be respectively 98.6 ppm, 197 ppm, and 296 ppm). The relative humidity and temperature of the air sampled were not reported. Samples were collected on six sorbent tubes at a flow rate of 50 mL/min for 240 min. The resulting samples were submitted to the OSHA Salt Lake Technical Center for analysis using the procedures described in OSHA Method 1001 after storage for 22 days at ambient temperature. The analytical results corrected for E_E are provided in Tables E-9 through E-11. No sample result for perchloroethylene (tetrachloroethylene) fell outside the permissible bounds set by the precision of the overall procedure determined in Section 5 of this appendix.

Table E-9. Reproducibility data for perchloroethylene (tetrachloroethylene) (Z-2 8-hour TWA).

sampled (mg/m^3)	recovered (mg/m^3)	recovery (%)	deviation (%)
668.5	652.7	97.6	-2.4
668.5	647.6	96.9	-3.1
668.5	649.2	97.1	-2.9
668.5	647.2	96.8	-3.2
668.5	634.6	94.9	-5.1
668.5	649.4	97.1	-2.9

Table E-10. Reproducibility data for perchloroethylene (tetrachloroethylene) (Z-2 ceiling).

sampled (mg/m^3)	recovered (mg/m^3)	recovery (%)	deviation (%)
1337	1365	102.1	+2.1
1337	1314	98.3	-1.7
1337	1324	99.0	-1.0
1337	1326	99.2	-0.8
1337	1326	99.2	-0.8
1337	1313	98.2	-1.8

Table E-11. Reproducibility data for perchloroethylene (tetrachloroethylene (Z-2 peak).

sampled (mg/m^3)	recovered (mg/m^3)	recovery (%)	deviation (%)
2005	1961	97.8	-2.2
2005	1970	98.3	-1.7
2005	1957	97.6	-2.4
2005	1969	98.2	-1.8
2005	1974	98.5	-1.5
2005	1976	98.6	-1.4

11 Effect of Sampling a Low Concentration

Pre-existing data from OSHA Method 1001[1] are presented in this section.

The effect of sampling a low concentration of perchloroethylene (tetrachloroethylene) vapor was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing perchloroethylene (tetrachloroethylene) nominally at one-tenth the target concentration (calculated to be 9.0 ppm). The relative humidity and temperature of the air sampled were 67% and 26 °C, and the sampling flow rate was 50 mL/min. Samples were collected on three sorbent tubes for 240 min. After immediate analysis, results for perchloroethylene (tetrachloroethylene) as a percentage of expected recovery were 100.2%, 100.2%, and 100.8%.

12 Estimation of Uncertainty

While systematic biases such as analyte storage loss are examined, and limits are placed on these, an estimation of uncertainty that encompasses both potential random and systematic error was not completed. Instead, the overall standard error of estimate was calculated from the random error inherent to the points about the regression line produced by the ambient storage test described in Section 5, as prescribed by the OSHA validation guidelines in use at the time OSHA Method 1001[1] was originally validated. See Section 5 of this appendix for details.

13 Controlled Test Atmosphere Procedure

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 perchloroethylene (tetrachloroethylene) 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 perchloroethylene (tetrachloroethylene) 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.

OSHA 5000, Appendix F
Toluene

Version:	1.0
OSHA PEL:	200 ppm (753 mg/m^3) Z-2 8-Hour TWA, General Industry, Construction, Shipyard; 300 ppm (1130 mg/m^3) Z-2 Ceiling (up to Peak Value, no more than 10 minutes), General Industry; 500 ppm (1883 mg/m^3) Z-2 Peak, General Industry
ACGIH TLV:	20 ppm (75 mg/m^3) 8-Hour TWA
Recommended sampling time and sampling rate:	240 min at 50 mL/min (12 L, 8-Hour TWA); 5-10 min at 50 mL/min (0.25 L, Ceiling); 1-5 min at 50 mL/min (0.05 L, Peak)
Reliable quantitation limit:	0.058 ppm (0.18 mg/m^3, 8-Hour TWA); 2.7 ppm (8.8 mg/m^3, Ceiling); 14 ppm (44 mg/m^3, Peak)
Standard error of estimate:	5.5% (8-Hour TWA); 5.2% (Ceiling); 5.2% (Peak)
Status:	Fully validated. Method 5000 has been subjected to the established validation procedures of the Method Development Team for sampling and analysis of toluene.

April 1998 (OSHA 111)	Carl J. Elskamp
February 2021 (OSHA 5000)	Anna Tang, Daren Pearce

1 Introduction

1.1 Previous Methods used by OSHA for Sampling and Analysis of Toluene

The specific analyte described in this appendix is toluene, CAS No. 108-88-3. The methodologies described in this appendix for toluene are based on OSHA Method 111.[1] That method requires the collection of samples using charcoal sorbent tubes, extraction using 60/40 v/v *N*,*N*-dimethylformamide/carbon disulfide, and analysis by gas chromatography using a flame ionization detector.

1.2 Changes to the Previously-Used Method

This appendix represents an update of OSHA Method 111[1], which was fully validated at the time it was published based on the validation guidelines in effect at that time. Compared to the previous method used this method includes new analytical parameters and extraction solvent. Data presented from the previously used method are identified by the statement “Pre-existing data from OSHA Method 111[1] are presented in this section”. The changes were made to allow the standardized collection and analysis of toluene with other analytes found in Organic Vapor Sampling Group 1, described in OSHA Method 5000.

---

[1] Elskamp, C. Toluene (OSHA Method 111), 1998. Occupational Safety and Health Administration Web site. https://www.osha.gov/dts/sltc/methods/organic/org111/org111.pdf (accessed October 2018).

1.3 Validation Parameters

The procedures used to develop the method validation data are described in Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis.[2] Air concentrations listed in ppm are referenced to 25 °C and 760 Torr. The target concentration for method evaluation was the OSHA Z-2 8-hour time-weighted average (TWA) permissible exposure limit (PEL) for toluene.

2 Detection and Quantification

2.1 Detection Limit of the Analytical Procedure (DLAP)

The DLAP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLAP $S_{y/x}$) divided by the slope of the line produced from analyses of ten analytical standards prepared with equally spaced increments of analyte mass. The standards were prepared in such a way that the highest standard concentration would produce a peak approximately 10 times the response of a reagent blank at or near the chromatographic retention time of the analyte. The standards and a reagent blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLAP $S_{y/x}$ and slope values for DLAP determination. Results obtained for these analyses are listed in Table F-1, and plotted in Figure F-1.

Table F-1. DLAP data for toluene.

concentration (µg/mL)	mass on column (pg)	area counts (µV·s)
0	0.00	0.00
0.416	2.77	0.138
0.831	5.54	0.189
1.25	8.33	0.236
1.66	11.1	0.324
2.08	13.9	0.428
2.49	16.6	0.537
2.91	19.4	0.638
3.33	22.2	0.775
3.75	24.9	0.857
4.16	27.7	0.961

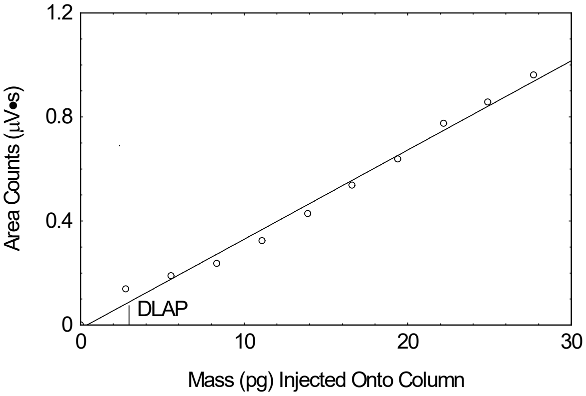

Figure F-1. Plot of data used to determine the DLAP for toluene ($y = 0.0343x - 0.0135$, DLAP $S_{y/x}$ = 0.0335, DLAP = 2.93 pg).

2.2 Detection Limit of the Overall procedure (DLOP) and Reliable Quantitation Limit (RQL)

The DLOP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLOP $S_{y/x}$) divided by the slope of the line produced from analyses of ten samples prepared from sorbent tubes spiked with equally spaced increments of analyte mass. 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 RQL is expressed as an air concentration that will provide sufficient analyte mass per sample that produces a response greater than 10× DLOP $S_{y/x}$ divided by the slope of the line described above. The spiked samplers and a sample blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLOP $S_{y/x}$ and slope values for DLOP and RQL determination. Results obtained from this analysis are listed in Table F-2, and plotted in Figure F-2.

---

[2] Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration Web site. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed December 2018).

Table F-2. DLOP and RQL data for toluene.

mass per sample (µg/sample)	area counts (µV·s)
0.00	0.00
0.416	0.214
0.831	0.164
1.25	0.257
1.66	0.382
2.08	0.484
2.49	0.527
2.91	0.644
3.33	0.666
3.74	0.790
4.16	0.833

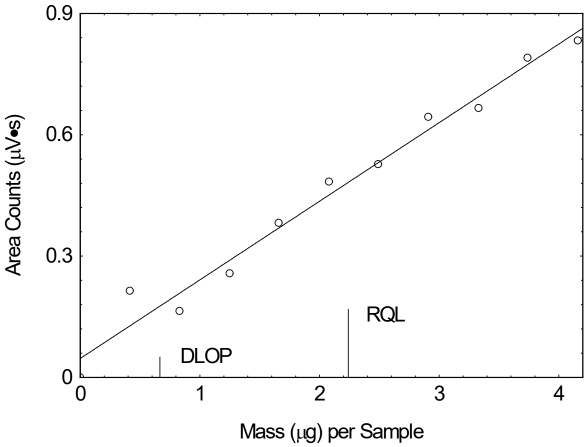

Figure F-2. Plot of data used to determine the DLOP and RQL for toluene ($y = 0.194x + 0.0468$, DLOP $S_{y/x}$ = 0.0428, DLOP = 0.665 µg/sample, RQL = 2.21 µg/sample or 0.0576 ppm).

3 Analytical Precision Across the Calibration Range

Fifteen analytical standards over a range of 0.1 to 2 times the analyte concentration in solvent that would be obtained from sampling for the recommended time at the target concentration were analyzed with the recommended analytical parameters described in OSHA Method 5000. An ordinary least-squares linear regression curve was created by plotting the analyte mass per sample versus the corresponding ratio of analyte peak area to internal standard (ISTD) peak area. The resulting data provided the standard error of estimate (Calibration $S_{y/x}$) value across the calibration range, which provides an indication of the imprecision attributable to the instrumental analysis of the target analyte. Results from these analyses are listed in Table F-3, and plotted in Figure F-3.

Table F-3. Analytical precision data for toluene.

× target	0.1×	0.5×	1.0×	1.5×	2.0×
concn (µg/sample)	900.6	4330	8660	12,990	17,320
area ratio	4.087	18.81	39.55	57.42	80.38
	4.034	19.44	39.87	59.96	80.11
	4.135	19.62	40.18	60.76	81.31

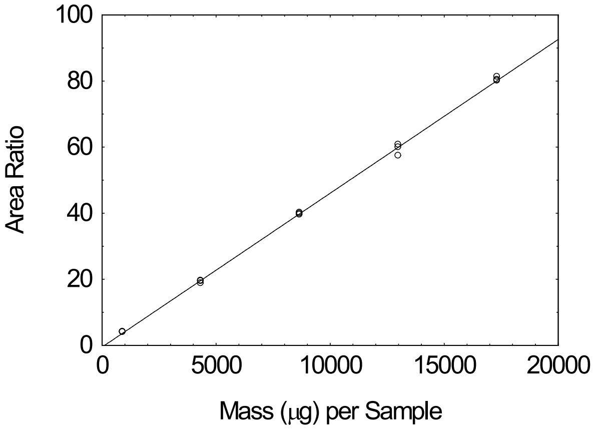

Figure F-3. Plot of data used to determine the precision of the analytical method for toluene ($y = 0.00466x - 0.512$, Calibration $S_{y/x}$ = 0.878).

4 Sampler Storage Stability

Pre-existing data from OSHA Method 111[1] are presented in this section.

Storage stability test samples for toluene were prepared by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13. Sampling from this system followed the recommended sampling parameters published in OSHA Method 111. The nominal concentration of toluene for both ambient and refrigerated storage testing was the target concentration (calculated to be 100 ppm (Z-2 8-hour TWA), 200 ppm (Z-2 ceiling, ambient storage only), and 300 ppm (Z-2 peak, ambient storage only)). The relative humidity and temperature of the air sampled were 80% and 22 °C for both tests. For each test, twenty-one samples were prepared, and six of these were analyzed on the day that samples were created. The remaining fifteen refrigerated storage test samples were stored at reduced temperature (0 °C), while the remaining ambient storage test samples were kept in a closed drawer at ambient temperatures (20-25 °C). For each storage condition, three samples were selected and analyzed from those remaining at 3-4 day intervals. The results of these analyses (extraction efficiency correction was not specified in OSHA Method 111[1]) are provided in Tables F-4 through F-6, and plotted in Figures F-4 through F-7.

The recovery of toluene calculated from the regression line generated for the 19-day Z-2 8-hour TWA ambient storage test was 99.9%.

Table F-4. Sampler storage stability data for toluene (Z-2 8-hour TWA).

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	100.6	102.0	99.9	100.6	102.0	99.9
0	102.8	100.4	101.3	102.8	100.4	101.3
3	100.2	90.7	99.2	99.7	99.1	101.4
6	100.0	99.7	100.2	101.7	101.3	101.3
11	99.5	100.1	100.1	99.8	100.4	99.4
14	99.6	99.8	100.6	99.4	101.4	99.9
19	100.3	99.8	100.8	98.1	99.5	100.8

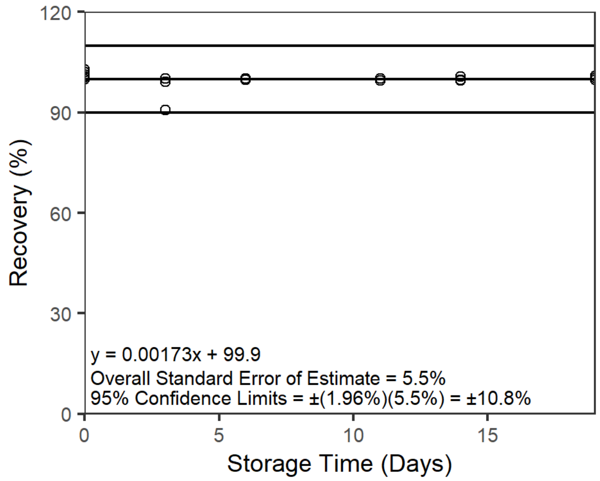

Figure F-4. Plot of Z-2 8-hour TWA ambient storage stability data for toluene.

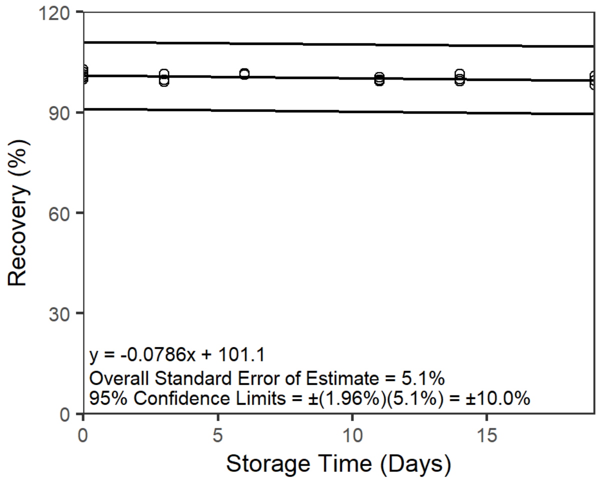

Figure F-5. Plot of Z-2 8-hour TWA refrigerated storage stability data for toluene.

Table F-5. Ambient sampler storage stability data for toluene (Z-2 ceiling).

time (days)	ambient storage recovery (%)		
0	97.9	99.7	101.4
0	99.2	98.6	99.7
3	99.9	100.2	97.2
6	97.3	94.7	98.0
10	98.5	97.1	100.0
12	97.0	99.4	97.5
15	98.8	98.0	98.4

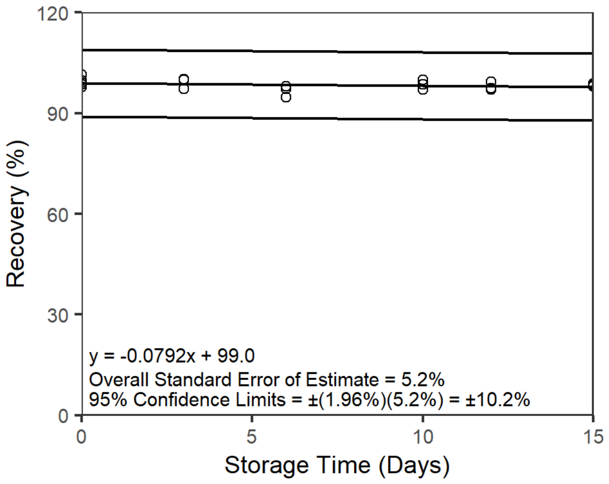

Figure F-6. Plot of Z-2 ceiling ambient storage stability data for toluene.

Table F-6. Ambient sampler storage stability data for toluene (Z-2 peak).

time (days)	ambient storage recovery (%)		
0	96.1	94.9	97.8
0	98.0	99.7	95.1
3	95.5	96.5	93.8
6	92.0	94.4	94.1
10	95.0	95.0	94.8
12	95.3	95.2	95.8
15	96.6	95.9	94.3

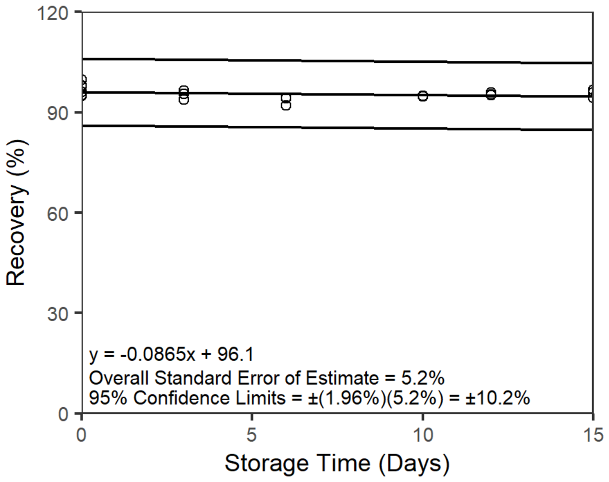

Figure F-7. Plot of Z-2 peak ambient storage stability data for toluene.

5 Precision of the Overall Procedure

Pre-existing data from OSHA Method 111[1] are presented in this section.

The overall standard error of estimate obtained from the ambient storage test analyses described in Section 4 and sampling pump variability were used to determine the precision of the overall procedure, where all aspects of sampling and analysis (sampling, sorbent tube handling and solvent extraction, and instrumental analysis) are considered. This value was obtained by taking the square root of the squared ambient storage stability standard error of estimate (Storage $S^2_{y/x}$) added to the squared sampling pump variability value (V^2_{SP}). The resulting precision of the overall procedure at the 95% confidence level for the Z-2 8-hour TWA ambient 19-day storage test for toluene was determined to be ±10.8% based on the observed ambient Storage $S_{y/x}$ value of 5.5% and V_{sp} value of 5.0%. The resulting precision of the overall procedure at the 95% confidence level for the Z-2 ceiling ambient 15-day storage test for toluene was determined to be ±10.2% based on the observed ambient Storage $S_{y/x}$ value of 5.2% and V_{SP} value of 5.0%. The resulting precision of the overall procedure at the 95% confidence level for the Z-2 peak ambient 15-day storage test for toluene was determined to be ±10.2% based on the observed ambient Storage $S_{y/x}$ value of 5.2% and V_{sp} value of 5.0%.

6 Recovery and Stability of Prepared Samples

Quantitative extraction 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 OSHA Method 5000. 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.

A value for extraction efficiency (E_E) was determined by liquid-spiking four replicate sorbent tubes across a range of analyte mass values that would be obtained from sampling 0.1 to 2 times the target concentration value for 240 min. Four sorbent tubes were also spiked in this fashion at the target concentration after drawing humid air (73.5% relative humidity at 25.0 °C) through these tubes at 50 mL/min for 4 hours. All of the samples described above were analyzed the following day after being kept overnight at ambient temperature. The E_E value at the RQL was 104.7%, while that of the working range samples (excluding the samples through which humid air had been drawn) was 98.6%. The data are shown in Table F-7. Pre-loading sorbent tubes with moisture ("wet" designation in the table) did not have an unacceptable effect on E_E.

Table F-7. Extraction efficiency data for toluene.

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.1	900.6	99.3	100.0	100.0	99.9	99.8
0.25	2598	97.5	98.9	100.5	97.4	98.6
0.5	4330	98.1	101.5	98.8	101.3	99.9
1.0	8660	98.6	99.3	97.2	98.2	98.3
1.5	12,990	98.1	98.6	98.3	96.9	98.0
2.0	17,320	97.2	96.7	97.6	95.9	96.8
RQL	1.66	104.2	108.4	98.1	108.2	104.7
1.0 (wet)	8660	99.0	97.2	97.7	98.1	98.0

The stability of sample extracts prepared according to OSHA Method 5000 was examined by retaining the sample solvent extracts for the target concentration samples described immediately above. Two of the four vials were immediately recapped with new septa following the initial analyses, and again following each re-analysis event. The other two vials retained the original punctured septa throughout. All four vials were re-analyzed at 24, 48, and 72 hours after the initial analyses, with all vials remaining in the autosampler tray kept at 22.2 °C. Freshly prepared standards were used for each analysis event, and each septum (whether new or previously used) was punctured four times for each injection. The resulting data are shown in Table F-8.

Table F-8. Extracted sample stability data for toluene.

	punctured septa replaced recovery (%)		punctured septa retained recovery (%)	
time (days)	1	2	1	2
0	94.9	96.7	97.0	97.9
1	96.2	95.3	94.6	96.7
2	94.9	95.8	95.1	95.8
3	95.2	95.7	104.7	95.1

7 Sampler Capacity

Pre-existing data from OSHA Method 111[1] are presented in this section.

The sampling capacity of the front section of a sorbent tube was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing toluene nominally at two times the target concentration (calculated to be 401.6 ppm), at 50 mL/min. The relative humidity and temperature of the air sampled were 73% and 29.1 °C, and the sampling flow rate was 50 mL/min. A sorbent tube testing system was made by placing a complete sorbent tube in series behind another tube, which contained only the front sorbent section. The rear tube was changed and analyzed at 210, 270, 330, 390, 450, and 510 min. Data from three sorbent tube testing systems, shown in Table F-9, were used to recommend a sampling volume of 12 liters for toluene as described in OSHA Method 5000. This volume corresponds to a 240 min sampling period, which is the maximum recommended sampling time regardless of breakthrough. The resulting data are plotted in Figure F-8.

Table F-9. Sampler capacity data for toluene.

sample no.	air vol (L)	sampling time (min)	cumulative downstream concn (mg/m^3)	break-through (%)
1	5.50	210	0.00	0.00
	12.56	270	0.00	0.00
	15.71	330	9.68	0.64
	18.84	390	410.6	27.1
	21.99	450	1301	86.0
	25.13	510	1461	96.6
2	5.28	210	0.00	0.00
	12.77	270	0.63	0.04
	15.96	330	9.75	0.65
	19.15	390	406.4	26.9
	22.34	450	1273	84.1
	25.54	510	1424	94.1
3	5.25	210	0.00	0.00
	11.97	270	0.00	0.00
	14.97	330	4.65	0.31
	17.96	390	248.8	16.4
	20.95	450	1136	75.1
	23.95	510	1495	98.8

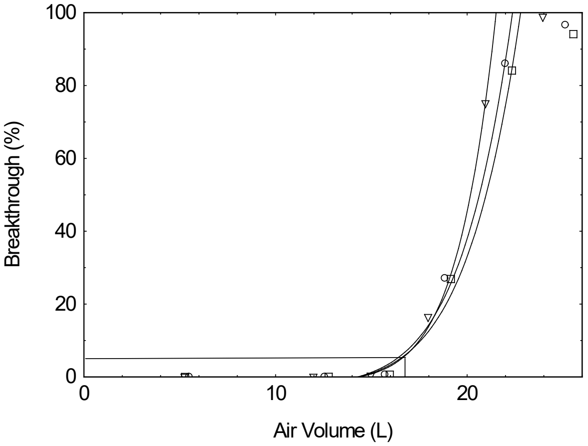

Figure F-8. Plot of data used to determine sampler capacity for toluene. The 5% breakthrough volumes shown are based on the curves in the figure, which are fit to the data provided in Table F-9.

8 Low Humidity

Pre-existing data from OSHA Method 111[1] are presented in this section.

The effect of low humidity was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing toluene nominally at two times the target concentration (calculated to be 403.2 ppm). The relative humidity and temperature of the air sampled were 9% and 25.3 °C, and the sampling flow rate was 50 mL/min. Samples were collected on six sorbent tubes for 240 min. Additional testing was completed to evaluate low humidity effects at the Z-2 peak concentration (calculated to be 499 ppm). For that testing, the relative humidity and temperature of the air sampled were 9% and 26.1 °C, and the sampling flow rate was 50 mL/min. Samples were collected on six sorbent tubes for 1 min. After immediate analysis, results as a percentage of expected recovery were 99.2%, 98.0%, 99.3%, 99.8%, 99.9%, and 98.8% with sampling at the target concentration for 240 min, and 98.6%, 98.0%, 97.7%, 100.3%, 97.5%, and 96.9% with sampling at the Z-2 peak concentration for 1 min.

9 Chemical Interference

Pre-existing data from OSHA Method 111[1] are presented in this section.

The effect of potential chemical sampling interference was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing toluene nominally at two times the target concentration (calculated to be 396 ppm). The relative humidity and temperature of the air sampled were 10% and 26 °C, and the sampling flow rate was 50 mL/min. 2-Butanone (methyl ethyl ketone), hexone (methyl isobutyl ketone), *n*-butyl alcohol, isobutyl acetate, and xylenes (*o*-, *m*-, *p*-isomers) were present as potential interferents (calculated to be at respective concentrations of 50 ppm, 20 ppm, 20 ppm, 30 ppm, and 30 ppm). Samples were collected on six sorbent tubes for 240 min. After immediate analysis, results for toluene as a percentage of expected recovery were 102.5%, 100.9%, 105.8%, 102.3%, 99.7%, and 102.0%.

The effect of short-term (1 min) chemical sampling interference was tested by sampling a dynamically generated controlled test atmosphere containing toluene nominally at the peak target concentration (calculated to be 495 ppm). The relative humidity and temperature of the air sampled were 10% and 25 °C, and the sampling flow rate was 50 mL/min. 2-Butanone (methyl ethyl ketone), hexone (methyl isobutyl ketone), *n*-butyl alcohol, isobutyl acetate, and xylenes (*o*-, *m*-, *p*-isomers) were present as potential interferents (calculated to be at respective concentrations of 50 ppm, 20 ppm, 20 ppm, 30 ppm, and 30 ppm). Samples were collected on six sorbent tubes for 240 min. After immediate analysis, results for toluene as a percentage of expected recovery were 96.5%, 98.1%, 97.8%, 100.7%, 94.8%, and 96.4%.

10 Analytical Method Reproducibility

Pre-existing data from OSHA Method 111[1] are presented in this section.

Samples were prepared by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing toluene nominally at the target concentration (calculated to be 197 ppm). The relative humidity and temperature of the air sampled were not reported. Samples were collected on six sorbent tubes at a flow rate of 50 mL/min for 240 min. The resulting samples were submitted to the OSHA Salt Lake Technical Center for analysis using the procedures described in OSHA Method 111 after ambient storage for 20 days. The analytical results are provided in Table F-10. No sample results for toluene fell outside the permissible bounds set by the precision of the overall procedure determined in Section 5 of this appendix.

Table F-10. Reproducibility data for toluene Z-2 TWA.

sampled (ppm)	recovered (ppm)	recovery (%)	deviation (%)
197	183	92.8	-7.2
197	183	92.9	-7.1
197	184	93.4	-6.6
197	181	91.9	-8.1
197	183	92.8	-7.2
197	182	92.4	-7.6

11 Effect of Sampling a Low Concentration

Pre-existing data from OSHA Method 111[1] are presented in this section.

The effect of sampling a low concentration of toluene vapor was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing toluene nominally at one-tenth the target concentration (calculated to be 19.8 ppm). The relative humidity and temperature of the air sampled were 74% and 26 °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 toluene as a percentage of expected recovery were 97.8%, 98.7%, 98.1%, 99.2%, 98.4%, and 98.4%.

The effect of sampling a low concentration of toluene vapor over a 1 min sampling period short-term sampling was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing toluene nominally at one-tenth the Z-2 peak concentration (calculated to be 49.3 ppm). The relative humidity values were 73% and 27.8 °C, and the sampling flow rate was 50 mL/min. Samples were collected on six sorbent tubes for 1 min. After immediate analysis, results for toluene as a percentage of expected recovery were 97.3%, 97.7%, 100.7%, 90.3%, 94.4%, and 92.4%.

12 Estimation of Uncertainty

While systematic biases such as analyte storage loss are examined, and limits are placed on these, an estimation of uncertainty that encompasses both potential random and systematic error was not completed. Instead, the overall standard error of estimate was calculated from the random error inherent to the points about the regression line produced by the ambient storage test described in Section 5, as prescribed by the OSHA validation guidelines in use at the time OSHA Method 111[1] was originally validated. See Section 5 of this appendix for details.

13 Controlled Test Atmosphere Procedure

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 toluene 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 toluene 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.

OSHA 5000, Appendix G
Ethyl Benzene

Version:	1.0
OSHA PEL:	100 ppm (435 mg/m^3) 8-Hour TWA, General Industry, Construction, Shipyard
ACGIH TLV:	20 ppm (87 mg/m^3) 8-Hour TWA
Recommended sampling time and sampling rate:	240 min at 50 mL/min (12 L)
Reliable quantitation limit:	0.023 ppm (0.10 mg/m^3)
Standard error of estimate:	5.4%
Status:	Fully validated. Method 5000 has been subjected to the established validation procedures of the Method Development Team for sampling and analysis of ethyl benzene.

August 1999 (OSHA 1002)	Warren Hendricks
February 2021 (OSHA 5000)	Uyen Bui, Daren Pearce

1 Introduction

1.1 Previous Methods used by OSHA for Sampling and Analysis of Ethyl Benzene

The specific analyte described in this appendix is ethyl benzene, CAS No. 100-41-4. The methodologies described in this appendix for ethyl benzene are based on OSHA Method 1002.[1] That method requires the collection of samples using charcoal sorbent tubes, extraction using carbon disulfide, and analysis by gas chromatography using a flame ionization detector.

1.2 Changes to the Previously-Used Method

This appendix represents an update of OSHA Method 1002, which was fully validated at the time it was published based on the validation guidelines in effect at that time. Compared to the previous method used this method includes new analytical parameters and internal standard (ISTD). Data presented from the previously used method are identified by the statement "Pre-existing data from OSHA Method 1002[1] are presented in this section". The changes were made to allow the standardized collection and analysis of ethyl benzene with other analytes found in Organic Vapor Sampling Group 1, described in OSHA Method 5000.

1.3 Validation Parameters

The procedures used to develop the method validation data are described in Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis.[2] Air concentrations listed in ppm are referenced to 25 °C and 760 Torr. The target concentration for the OSHA Method 1002 validation was 17 ppm. This concentration value was selected

---

[1] Hendricks, W. Xylenes (*o*-, *m*-, *p*-isomers) Ethylbenzene (OSHA Method 1002), 1999. United States Department of Labor, Occupational Safety & Health Administration Web site. https://www.osha.gov/dts/sltc/methods/mdt/mdt1002/1002.html (accessed October 2018).

[2] Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration Web site. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed December 2018).

because it was the concentration of ethyl benzene in a mixture of mixed xylenes. Both analytes were evaluated concurrently. The target concentration for subsequent OSHA Method 5000 evaluation was the OSHA 8-hour time-weighted average (TWA) permissible exposure limit (PEL) for ethyl benzene.

2 Detection and Quantification

2.1 Detection Limit of the Analytical Procedure (DLAP)

The DLAP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLAP $S_{y/x}$) divided by the slope of the line produced from analyses of ten analytical standards prepared with equally spaced increments of analyte mass. The standards were prepared in such a way that the highest standard concentration would produce a peak approximately 10 times the response of a reagent blank at or near the chromatographic retention time of the analyte. The standards and a reagent blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLAP $S_{y/x}$ and slope values for DLAP determination. Results obtained for these analyses are listed below in Table G-1, and plotted in Figure G-1.

Table G-1. DLAP data for ethyl benzene.

concentration (µg/mL)	mass on column (pg)	area counts (µV·s)
0.00	0.00	0.00
0.866	5.77	0.190
1.73	11.5	0.428
2.60	17.3	0.582
3.46	23.1	0.803
4.33	28.9	0.966
5.20	34.7	1.27
6.06	40.4	1.29
6.93	46.2	1.57
7.79	51.9	1.76
8.66	57.7	2.12

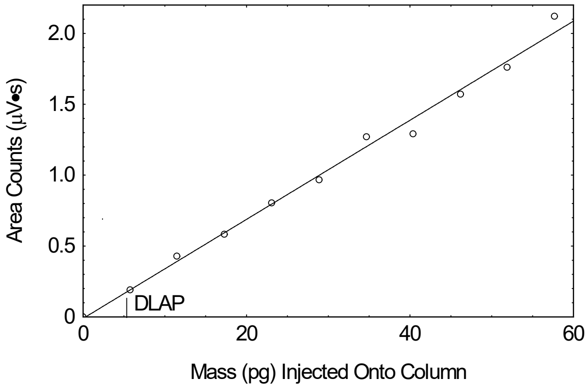

Figure G-1. Plot of data used to determine the DLAP for ethyl benzene ($y = 0.0349x - 0.0105$, DLAP $S_{y/x}$ = 0.0631, DLAP = 5.42 pg).

2.2 Detection Limit of the Overall Procedure (DLOP) and Reliable Quantitation Limit (RQL)

The DLOP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLOP $S_{y/x}$) divided by the slope of the line produced from analyses of ten samples prepared from sorbent tubes spiked with equally spaced increments of analyte mass. 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 RQL is expressed as an air concentration that will provide sufficient analyte mass per sample that produces a response greater than 10× DLOP $S_{y/x}$ divided by the slope of the line described above. The spiked samplers and a sample blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLOP $S_{y/x}$ and the slope values for DLOP and RQL determinations. Results obtained from these analyses are listed below in Table G-2 and plotted in Figure G-2.

Table G-2. DLOP and RQL data for ethyl benzene.

mass per sample (µg/sample)	area counts (µV·s)
0.00	0.00
0.433	0.103
0.866	0.129
1.30	0.204
1.73	0.268
2.17	0.356
2.60	0.403
3.03	0.483
3.46	0.518
3.90	0.565
4.33	0.675

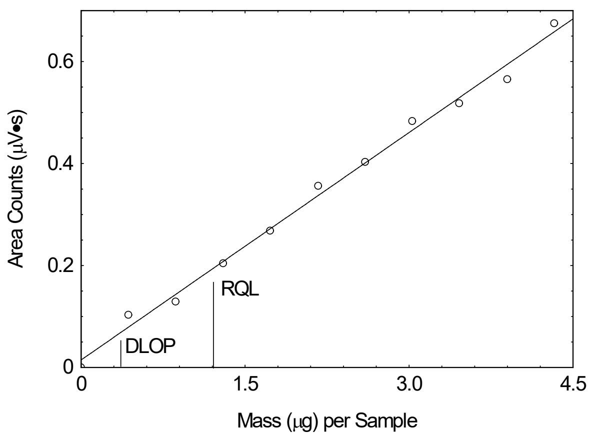

Figure G-2. Plot of data used to determine the DLOP and RQL for ethyl benzene ($y = 0.149x - 0.0147$, DLOP $S_{y/x}$ = 0.0182, DLOP = 0.367 µg/sample, RQL = 1.22 µg/sample or 0.0234 ppm).

3 Analytical Precision Across the Calibration Range

Fifteen analytical standards over a range of 0.1 to 2 times the analyte concentration in solvent that would be obtained from sampling for the recommended time at the target concentration were analyzed with the recommended analytical parameters described in OSHA Method 5000. An ordinary least-squares linear regression curve was created by plotting the analyte mass per sample versus the corresponding ratio of analyte peak area to internal standard (ISTD) peak area. The resulting data provided the standard error of estimate (Calibration $S_{y/x}$) value across the calibration range, which provides an indication of the imprecision attributable to the instrumental analysis of the target analyte. Results from these analyses are listed in Table G-3, and plotted in Figure G-3.

Table G-3. Analytical precision data for ethyl benzene.

× target	0.1×	0.5×	1.0×	1.5×	2.0×
concn (µg/sample)	519.6	2598	5196	7794	10,392
area ratio	2.275	11.53	23.06	34.36	47.05
	2.274	11.43	22.92	34.38	47.02
	2.292	11.50	22.97	34.28	46.96

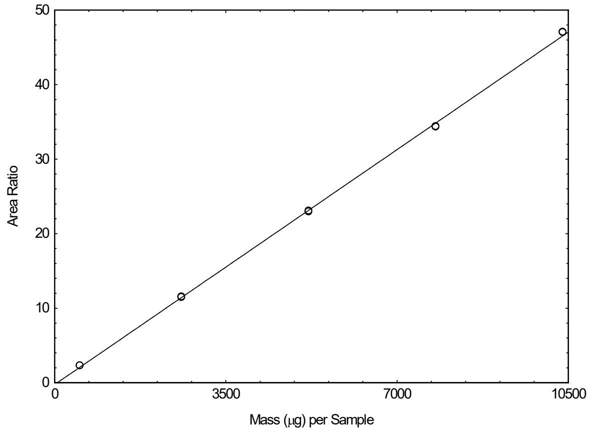

Figure G-3. Plot of data used to determine the precision of the analytical method for ethyl benzene ($y = 0.00450x - 0.255$, Calibration $S_{y/x}$ = 0.355).

4 Sampler Storage Stability

Pre-existing data from OSHA Method 1002[1] are presented in this section.

Storage stability test samples for ethyl benzene were prepared by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13. Sampling from this system followed the recommended sampling procedures published in OSHA Method 1002. The nominal concentration of ethyl benzene for both ambient and refrigerated storage testing was calculated to be 17 ppm. The test atmosphere also included xylene (*m* isomer) at 48 ppm, xylene (*o* isomer) at 22 ppm, and xylene (*p* isomer) at 21 ppm. The relative humidity and temperature of the air sampled were 83% and 20 °C for both tests. For each test, eighteen samples were prepared, and three of these were analyzed on the same day that samples were created. The remaining fifteen refrigerated storage test samples were stored at reduced temperature, while the remaining fifteen ambient storage test samples were stored at ambient temperature. For each storage condition, three samples were selected and analyzed from those remaining at 2-4 day intervals. The results of these analyses (corrected for extraction efficiency) are provided in Table G-4 and plotted in Figures G-4 through G-5.

The recovery of ethyl benzene calculated from the regression line generated for the 16-day ambient storage test was 100.2%.

Table G-4. Sampler storage stability data for ethyl benzene.

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	98.2	99.7	98.3	98.2	99.7	98.3
3	102.1	103.6	101.6	104.0	102.3	101.3
7	103.1	99.0	103.9	97.5	101.9	102.2
10	98.2	99.3	100.3	101.6	100.1	100.3
14	102.5	98.6	100.8	102.3	100.6	101.2
16	100.0	97.5	101.4	102.6	93.5	103.0

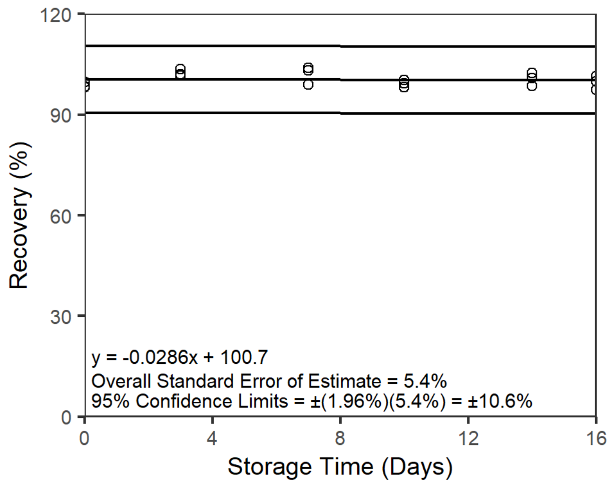

Figure G-4. Plot of ambient storage stability data for ethyl benzene.

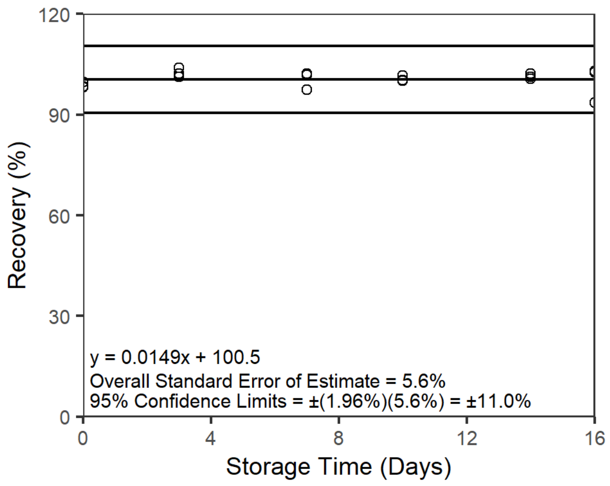

Figure G-5. Plot of refrigerated storage stability data for ethyl benzene.

5 Precision of the Overall Procedure

Pre-existing data from OSHA Method 1002[1] are presented in this section.

The overall standard error of estimate obtained from the ambient storage test analyses described in Section 4 and sampling pump variability were used to determine the precision of the overall procedure, where all aspects of sampling and analysis (sampling, sorbent tube handling and solvent extraction, and instrumental analysis) are considered. This value was obtained by taking the square root of the squared ambient storage stability standard error of estimate

(Storage $S^2_{y/x}$) added to the squared sampling pump variability value (V^2_{SP}). The resulting precision of the overall procedure at the 95% confidence level for the ambient 16-day storage test (at the target concentration) for ethyl benzene was determined to be ±10.6% based on the observed ambient Storage $S_{y/x}$ value of 5.4% and V_{SP} value of 5.0%.

6 Recovery and Stability of Prepared Samples

Quantitative extraction 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 OSHA Method 5000. 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.

A value for extraction efficiency (E_E) was determined by liquid-spiking four replicate sorbent tubes across a range of analyte mass values that would be obtained from sampling at 0.1 to 2 times the target concentration value for 240 min. Four sorbent tubes were also spiked in this fashion at the target concentration after drawing humid air (74.7% relative humidity at 23.3 °C) through these tubes at 50 mL/min for 4 hours. All of the samples described above were analyzed the following day after being kept overnight at ambient temperature. The E_E value at the RQL was 94.8%, while that of the working range samples (excluding the samples through which humid air had been drawn) was 100.4%. The data are shown in Table G-5. Pre-loading sorbent tubes with moisture ("wet" designation in the table) did not have an unacceptable effect on E_E.

Table G-5. Extraction efficiency data for ethyl benzene.

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.1	519.6	101.1	98.7	99.2	98.4	99.4
0.25	1299	101.9	99.4	101.6	102.7	101.4
0.5	2598	100.5	100.3	99.6	99.9	100.1
1.0	5196	99.8	98.7	99.8	99.6	99.5
1.5	7794	100.1	99.8	100.8	100.9	100.4
2.0	10,392	100.3	102.9	99.5	102.6	101.3
RQL	1.21	91.5	106.7	90.5	90.5	94.8
1.0 (wet)	5196	99.2	99.4	104.5	97.8	100.2

The stability of sample extracts prepared according to OSHA Method 5000 was examined by retaining the sample solvent extracts for the target concentration samples described immediately above. Two of the four vials were immediately recapped with new septa following the initial analyses, and again following each re-analysis event. The other two vials retained the original punctured septa throughout. All four 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 septum (whether new or previously used) was punctured four times for each injection. The resulting data are shown in Table G-6.

Table G-6. Extracted sample stability data for ethyl benzene.

	punctured septa replaced recovery (%)		punctured septa retained recovery (%)	
time (days)	1	2	1	2
0	98.7	97.8	98.7	98.6
1	98.0	97.4	98.3	98.2
2	98.2	97.9	98.6	99.2
3	98.3	98.2	98.0	98.0

7 Sampler Capacity

Pre-existing data from OSHA Method 1002[1] are presented in this section.

The sampling capacity of the front section of a sorbent tube was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing ethyl benzene at nominally two times the target concentration (calculated to be 37 ppm). The atmosphere also contained xylenes (*o*-, *m*-, *p*-isomers) at 105 ppm for xylene (*m* isomer), 49 ppm for xylene (*o* isomer), and 46 ppm for xylene (*p* isomer). The relative humidity and temperature of the air sampled were 78% and 21 °C, and the sampling flow rate was 50 mL/min. A sorbent tube testing system was made by placing a complete sorbent tube in series behind another tube, which contained only the front sorbent section. The rear tube was changed and analyzed at 5, 10, 15, 30, 60, 120, 180, 240, 360, 480, and 600 min. Breakthrough was not observed after sampling for 600 min (corresponding to 30 liters). Data from three sorbent tube testing systems were used to determine a recommended sampling volume of 12 liters for ethyl benzene as described in OSHA Method 5000. This volume corresponds to a 240 min sampling period, which is the maximum recommended sampling time regardless of breakthrough

8 Low Humidity

Pre-existing data from OSHA Method 1002[1] are presented in this section.

The effect of low humidity was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing ethyl benzene nominally at two times the target concentration (calculated to be 38.2 ppm). The atmosphere also contained xylenes (*o*-, *m*-, *p*-isomers) at 108 ppm for xylene (*m* isomer), 50.2 ppm for xylene (*o* isomer), and 47.0 ppm for xylene (*p* isomer). The relative humidity and temperature of the air sampled were 5% and 20 °C, and the sampling flow rate was 50 mL/min. Samples were collected on three sorbent tubes for 240 min. After immediate analysis, results as a percentage of expected recovery were 102.5%, 100.8%, and 100.4%.

9 Chemical Interference

Pre-existing data from OSHA Method 1002[1] are presented in this section.

The effect of potential chemical sampling interference was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing ethyl benzene nominally at the target concentration (calculated to be 18.9 ppm). The relative humidity and temperature of the air sampled were 81% and 21 °C, and the sampling flow rate was 50 mL/min. Xylenes (*o*-, *m*-, *p*-isomers), toluene, and *n*-butyl acetate were present as potential interferents, (calculated to be at respective concentrations of 53 ppm, 25 ppm, 23 ppm, 97 ppm, and 79 ppm). Samples were collected on three sorbent tubes for 240 min. After immediate analysis, results for ethyl benzene as a percentage of expected recovery were 104.1%, 103.4%, and 102.6%.

10 Analytical Method Reproducibility

Pre-existing data from OSHA Method 1002[1] are presented in this section.

Samples were prepared by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing ethyl benzene nominally at the target concentration (calculated to be about 17.3 ppm). The relative humidity and temperature of the air sampled were not reported. Samples were collected on six sorbent tubes at a flow rate of 50 mL/min for 240 min. The resulting samples were submitted to the OSHA Salt Lake Technical Center for analysis using the procedures described in OSHA Method 1002 after storage for 16 days at ambient temperature. The analytical results corrected for E_E are provided in Table G-7. No sample result for ethyl benzene fell outside the permissible bounds set by the precision of the overall procedure determined in Section 5 of this appendix.

Table G-7. Reproducibility data for ethyl benzene.

sampled (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
904.8	929.4	102.7	+2.7
918.9	944.2	102.8	+2.8
929.0	895.4	96.4	-3.6
905.6	939.1	103.7	+3.7
911.8	945.6	103.7	+3.7
929.0	944.3	101.6	+1.6

11 Effect of Sampling a Low Concentration

Pre-existing data from OSHA Method 1002[1] are presented in this section.

The effect of sampling a low concentration of ethyl benzene vapor was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing ethyl benzene nominally at one-tenth the target concentration (calculated to be 1.84 ppm). The atmosphere also contained xylenes (*o*-, *m*-, *p*-isomers) at 5.07 ppm for xylene (*m* isomer), 2.30 ppm for xylene (*o* isomer), and 2.30 ppm for xylene (*p* isomer). 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 three sorbent tubes for 240 min. After immediate analysis, results for ethyl benzene as a percentage of expected recovery were 96.1%, 98.6%, and 102.5%.

12 Estimation of Uncertainty

While systematic biases such as analyte storage loss are examined, and limits are placed on these, an estimation of uncertainty that encompasses both potential random and systematic error was not completed. Instead, the overall standard error of estimate was calculated from the random error inherent to the points about the regression line produced by the ambient storage test described in Section 5, as prescribed by the OSHA validation guidelines in use at the time OSHA Method 1002 was originally validated. See Section 5 of this appendix for details.

13 Controlled Test Atmosphere Procedure

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 ethyl benzene and xylenes (*o*-, *m*-, *p*-isomers) 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 vapors of ethyl benzene and xylenes (*o*-, *m*-, *p*-isomers), 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.

OSHA 5000, Appendix H
Xylenes (*o*-, *m*-, *p*-isomers)

Version:	1.0
OSHA PEL:	100 ppm (435 mg/m^3) 8-Hour TWA, General Industry, Construction, Shipyard
ACGIH TLV:	100 ppm (434 mg/m^3) 8-Hour TWA, 150 ppm (651 mg/m^3) 15-Minute STEL
Recommended sampling time and sampling rate:	240 min at 50 mL/min (12 L)
Reliable quantitation limit:	0.026 ppm (0.11 mg/m^3 xylene (*m* isomer)); 0.021 ppm (0.093 mg/m^3, xylene (*o* isomer)); 0.034 ppm (0.15 mg/m^3, xylene (*p* isomer))
Standard error of estimate:	5.5% xylene (*m* isomer); 5.6% xylene (*o* isomer); 5.7% xylene (*p* isomer)
Status of method:	Fully validated. Method 5000 has been subjected to the established validation procedures of the Method Development Team for sampling and analysis of xylenes (*o*-, *m*-, *p*-isomers).

August 1999 (OSHA 1002)	Warren Hendricks
February 2021 (OSHA 5000)	Uyen Bui, Carmen Riberas, Daren Pearce

1 Introduction

1.1 Previous Methods used by OSHA for Sampling and Analysis of Xylenes (*o*-, m-, *p*-isomers)

The specific analyte described in this appendix is xylenes (*o*-, *m*-, *p*-isomers), CAS No. 1330-20-7, the concentration of which is determined by considering the combined concentrations of xylene (*o* isomer) CAS No. 95-47-6, xylene (*m* isomer) CAS No. 108-38-3, and xylene (*p* isomer) CAS No. 106-42-3. The methodologies described in this appendix for xylenes (*o*-, *m*-, *p*-isomers) are based on OSHA Method 1002.[1] That method requires the collection of samples using charcoal sorbent tubes, extraction using carbon disulfide, and analysis by gas chromatography using a flame ionization detector.

1.2 Changes to the Previously-Used Method

This appendix represents an update of OSHA Method 1002[1], which was fully validated at the time it was published based on the validation guidelines in effect at that time. Compared to the previous method used this method includes new analytical parameters and internal standard (ISTD). Data presented from the previously used method are identified by the statement "Pre-existing data from OSHA Method 1002[1] are presented in this section". The changes were made to allow the standardized collection and analysis of *xylenes* (*o-, m-, p*-isomers) with other analytes found in Organic Vapor Sampling Group 1, described in OSHA Method 5000.

---

[1] Hendricks, W. Xylenes (*o*-, *m*-, *p*-isomers) Ethylbenzene (OSHA Method 1002), 1999. United States Department of Labor, Occupational Safety & Health Administration Web site. https://www.osha.gov/dts/sltc/methods/mdt/mdt1002/1002.html (accessed October 2018).

1.3 Validation Parameters

The procedures used to develop the method validation data are described in Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis.[2] Air concentrations listed in ppm are referenced to 25 °C and 760 Torr. The target concentration for method evaluation was the OSHA 8-hour time-weighted average (TWA) permissible exposure limit (PEL) for xylenes (*o*-, *m*-, *p*-isomers).

2 Detection and Quantification

2.1 Detection Limit of the Analytical Procedure (DLAP)

The DLAP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLAP $S_{y/x}$) divided by the slope of the line produced from analyses of ten analytical standards prepared with equally descending increments of analyte mass. The standards were prepared in such a way that the highest standard concentration would produce a peak approximately 10 times the response of a reagent blank at or near the chromatographic retention time of the analyte. The standards and a reagent blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLAP $S_{y/x}$ and slope for values for DLAP determination. Results obtained for these analyses are listed in Tables H-1 through H-3, and plotted in Figures H-1 through H-3.

Table H-1. DLAP data for xylene *(m* isomer).

concentration (µg/mL)	mass on column (pg)	area counts (µV·s)
0.00	0.00	0.00
0.868	5.79	0.188
1.74	11.6	0.389
2.61	17.4	0.599
3.47	23.1	0.786
4.34	28.9	0.987
5.21	34.7	1.19
6.08	40.5	1.34
6.95	46.3	1.63
7.82	52.1	1.80
8.68	57.9	2.06

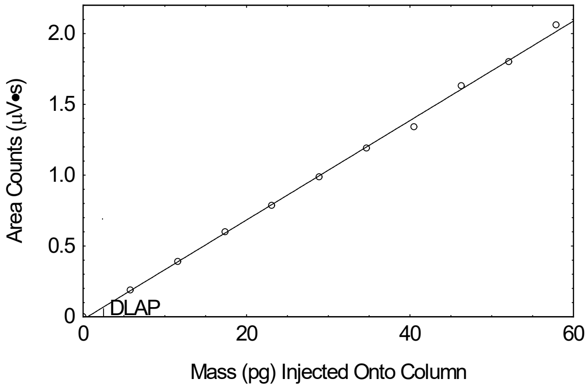

Figure H-1. Plot of data used to determine the DLAP for xylene *(m* isomer, $y = 0.351x - 0.00190$, DLAP $S_{y/x}$ = 0.0286, DLAP = 2.44 pg).

---

[2] Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration Web site. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed December 2018).

Table H-2. DLAP data for xylene (*o* isomer).

concentration (µg/mL)	mass on column (pg)	area counts (µV·s)
0.00	0.00	0.00
0.880	5.87	0.238
1.76	11.7	0.407
2.64	17.6	0.637
3.52	23.5	0.841
4.40	29.3	1.03
5.28	35.2	1.26
6.16	41.1	1.39
7.04	46.9	1.66
7.92	52.8	1.81
8.80	58.7	2.11

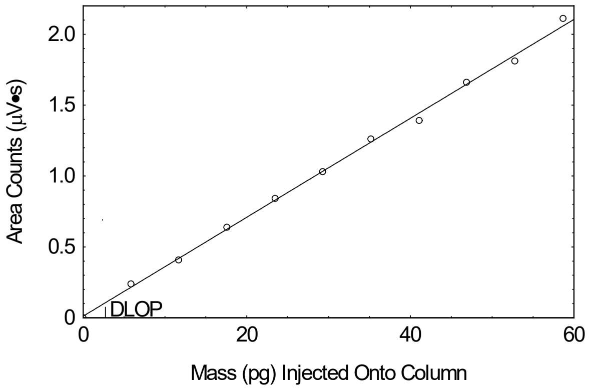

Figure H-2. Plot of data used to determine the DLAP for xylene (*o* isomer, $y = 0.349x + 0.0114$, DLAP $S_{y/x} = 0.0318$, DLAP = 2.73 pg).

Table H-3. DLAP data for xylene (*p* isomer).

concentration (µg/mL)	mass on column (pg)	area counts (µV·s)
0.00	0.00	0.00
0.414	2.76	0.00
0.828	5.52	0.0960
1.24	8.27	0.173
1.66	11.1	0.223
2.07	13.8	0.324
2.48	16.5	0.360
2.90	19.3	0.400
3.31	22.1	0.482
3.73	24.9	0.566
4.41	29.4	0.632

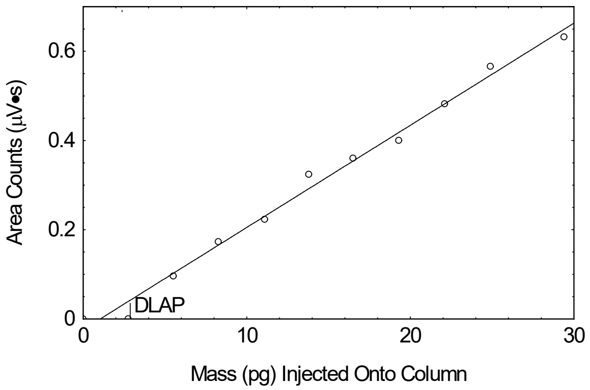

Figure H-3. Plot of data used to determine the DLAP for xylene (*p* isomer, $y = 0.0229x - 0.0239$, DLAP $S_{y/x} = 0.0220$, DLAP = 2.87 pg).

2.2 Detection Limit of the Overall Procedure (DLOP) and Reliable Quantitation Limit (RQL)

The DLOP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLOP $S_{y/x}$) divided by the slope of the line produced from analyses of ten samples prepared from sorbent tubes spiked with equally spaced increments of analyte mass. 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 RQL is expressed as an air concentration that will provide sufficient analyte mass per sample that produces a response greater than 10× DLOP $S_{y/x}$ divided by the slope of the line described above. The spiked samplers and a sample blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLOP $S_{y/x}$ and the slope values for DLOP and RQL determinations. Results obtained from these analyses are listed below in Tables H-4 through H-6, and plotted in Figures H-4 through H-6.

Table H-4. DLOP and RQL data for xylene *(m* isomer).

mass per sample (µg/sample)	area counts (µV·s)
0.00	0.00
0.434	0.0670
0.869	0.142
1.30	0.226
1.74	0.251
2.17	0.337
2.61	0.403
3.04	0.475
3.47	0.487
3.91	0.557
4.34	0.661

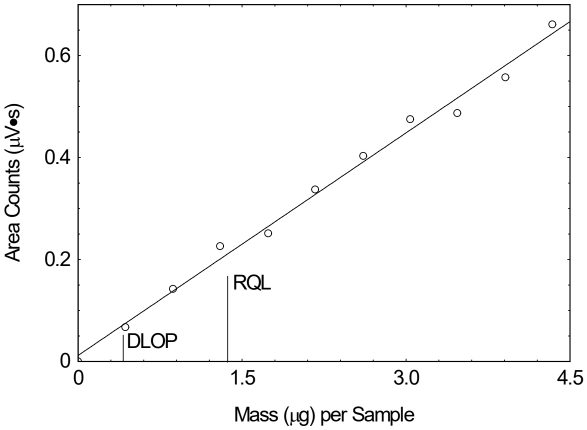

Figure H-4. Plot of data used to determine the DLOP and RQL for xylene *(m* isomer, $y = 0.146x + 0.0119$, DLOP $S_{y/x}$ is 0.0196, DLOP is 0.403 µg/sample, RQL is 1.34 µg/sample or 0.0258 ppm).

Table H-5. DLOP and RQL data for xylene (*o* isomer).

mass per sample (µg/sample)	area counts (µV·s)
0.00	0.00
0.440	0.0770
0.880	0.124
1.32	0.205
1.76	0.263
2.20	0.334
2.64	0.410
3.08	0.464
3.52	0.493
3.96	0.552
4.40	0.620

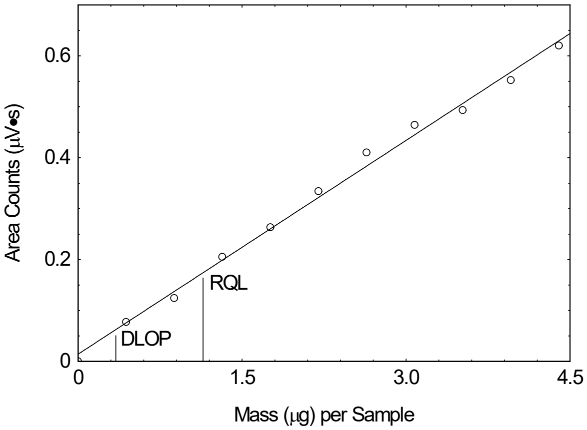

Figure H-5. Plot of data used to determine the DLOP and RQL for xylene (*o* isomer, $y = 0.140x + 0.0142$, DLOP $S_{y/x}$ is 0.0155, DLOP is 0.332 µg/sample, RQL is 1.11 µg/sample or 0.0214 ppm).

Table H-6. DLOP and RQL data for xylene (*p* isomer).

mass per sample (µg/sample)	area counts (µV·s)
0.00	0.00
0.414	0.00
0.828	0.114
1.24	0.173
1.66	0.262
2.07	0.308
2.48	0.418
2.90	0.405
3.31	0.502
3.73	0.588
4.14	0.610

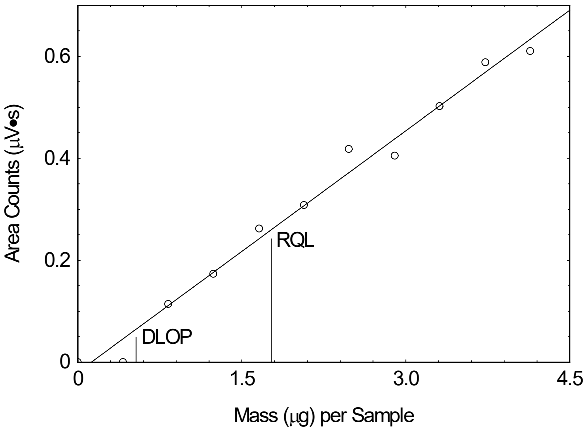

Figure H-6. Plot of data used to determine the DLOP and RQL for xylene (*p* isomer, $y = 0.158x - 0.0193$, DLOP $S_{y/x}$ is 0.0280, DLOP is 0.532 µg/sample, RQL is 1.77 µg/sample or 0.0341 ppm).

3 Analytical Precision Across the Calibration Range

Fifteen analytical standards over a range of 0.1 to 2 times the analyte concentration in solvent that would be obtained from sampling for the recommended time at the target concentration were analyzed with the recommended analytical parameters described in OSHA Method 5000. An ordinary least-squares linear regression curve was created by plotting the analyte mass per sample versus the corresponding ratio of analyte peak area to internal standard (ISTD) peak area for *m*- and *o*- isomers. The resulting data provided the standard error of estimate (Calibration $S_{y/x}$) values across the calibration range, which provide an indication of the imprecision attributable to the instrumental analysis of the target analytes. Results from these analyses are listed in Tables H-7 and H-8, and plotted in Figures H-7 and H-8. Since xylene (*m* isomer) and xylene (*p* isomer) co-elute on the column used, only calibrate for xylene (*m* isomer). There will be a slight error in the results for xylene (*p* isomer), but it is deemed acceptable due to the similarities in the recovery, DLAP, DLOP, and RQL values.

Table H-7. Analytical precision data for xylene *(m* isomer).

× target	0.1×	0.5×	1.0×	1.5×	2.0×
concn (µg/sample)	521.0	2605	5210	7816	10,421
area ratio	2.321	11.74	23.29	34.96	47.73
	2.502	11.63	23.16	34.99	47.73
	2.338	11.69	23.22	34.88	47.66

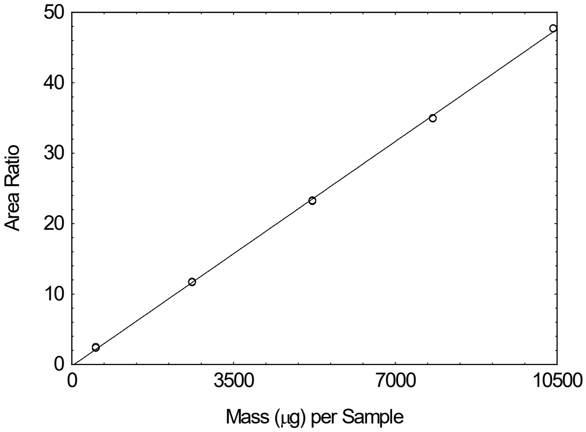

Figure H-7. Plot of data used to determine the precision of the analytical method for xylene *(m* isomer, $y = 0.00456x - 0.222$, Calibration $S_{y/x}$ = 0.359)

Table H-8. Analytical precision data for xylene (*o* isomer).

× target concn (µg/sample)	0.1× 528.1	0.5× 2640	1.0× 5281	1.5× 7921	2.0× 10,561
area ratio	2.451	11.86	23.62	35.29	48.42
	2.452	11.84	23.53	35.32	48.42
	2.471	11.91	23.60	35.20	48.34

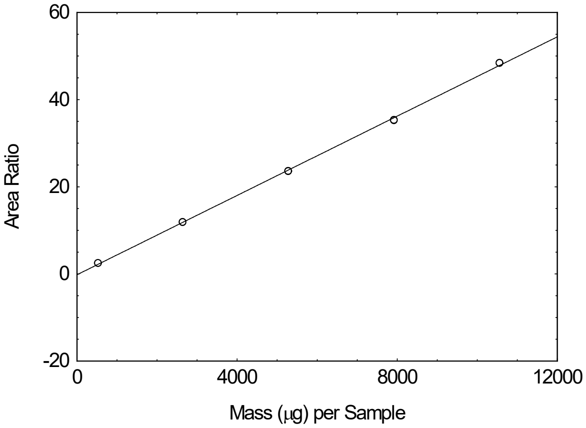

Figure H-8. Plot of data used to determine the precision of the analytical method for xylene (*o* isomer, $y = 0.00455x - 0.191$, Calibration $S_{y/x}$ = 0.417).

4 Sampler Storage Stability

Pre-existing data from OSHA Method 1002[1] are presented in this section.

Storage stability test samples for xylenes (*o*-, *m*-, *p*-isomers) were prepared by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13. Sampling from this system followed the recommended sampling parameters published in OSHA Method 1002. The nominal concentration of xylenes (*o*-, *m*-, *p*-isomers) sampled for both ambient and refrigerated storage testing was the target concentration (calculated to be 48 ppm for xylene (*o* isomer), 22 ppm for xylene (*m* isomer), and 21 ppm for xylene (*p* isomer)). The atmosphere also contained ethyl benzene at 17 ppm. The relative humidity and temperature of the air sampled were 83% and 20 °C for both tests. For each test, eighteen samples were prepared and three of these were analyzed on the same day that samples were created. The remaining fifteen refrigerated storage test samples were stored at reduced temperature, while the remaining fifteen ambient storage test samplers were stored at ambient temperature. For each storage condition, three samples were selected and analyzed from those remaining at 2-4 day intervals. The results of these analyses (corrected for extraction efficiency) are provided in Tables H-9 through H-12 and in Figures H-9 through H-15.

The recoveries of xylenes (*o*-, *m*-, *p*-isomers) calculated from the regression line generated for the 16-day ambient storage test were 99.1% for xylenes (*o*-, *m*-, *p*-isomers), 100.1% for xylene (*m* isomer), 98.5% for xylene (*o* isomer), and 98.5% for xylene (*p* isomer).

Table H-9. Sampler storage stability data for xylenes *(o*-, *m*-, *p*-isomers).

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	97.0	98.9	96.8	97.0	98.9	96.8
3	101.1	102.5	100.3	103.1	101.3	100.3
7	102.2	97.4	103.1	96.3	100.2	100.8
10	96.5	97.9	99.2	100.4	98.2	98.8
14	101.6	96.7	97.9	101.3	99.4	100.2
16	99.8	97.0	101.1	101.7	93.8	102.0

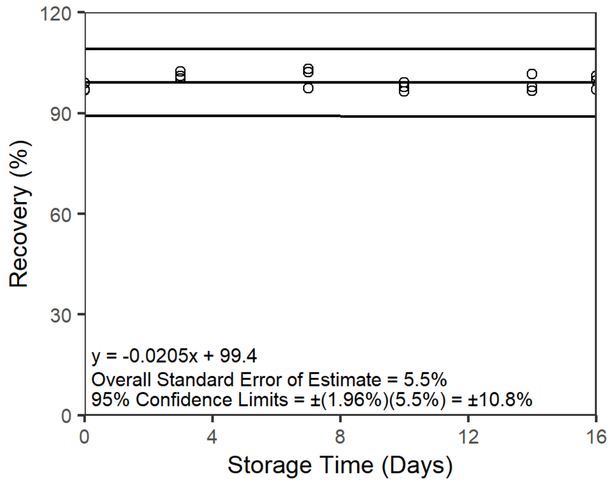

Figure H-9. Plot of ambient storage stability data for xylenes *(o-*, *m-*, *p*-isomers).

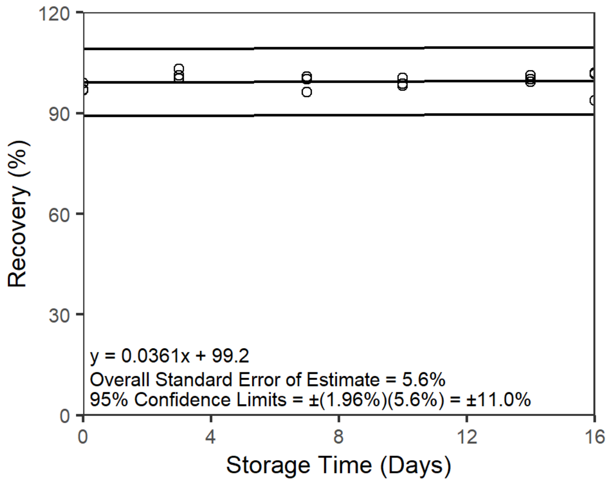

Figure H-10. Plot of refrigerated storage stability data for xylenes *(o-*, *m-*, *p*-isomers).

Table H-10. Sampler storage stability data for xylene *(m* isomer).

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	97.3	99.1	97.2	97.3	99.1	97.2
3	101.4	102.8	100.6	103.3	101.6	100.6
7	102.5	97.8	103.3	97.6	100.7	101.2
10	97.0	98.3	99.5	100.7	98.7	99.2
14	101.9	97.2	99.8	101.6	99.7	100.5
16	100.6	98.7	101.9	102.0	93.7	102.3

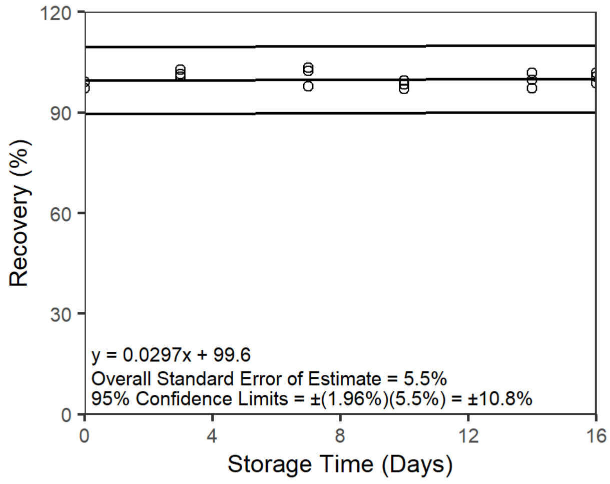

Figure H-11. Plot of ambient storage stability data for xylene *(m* isomer).

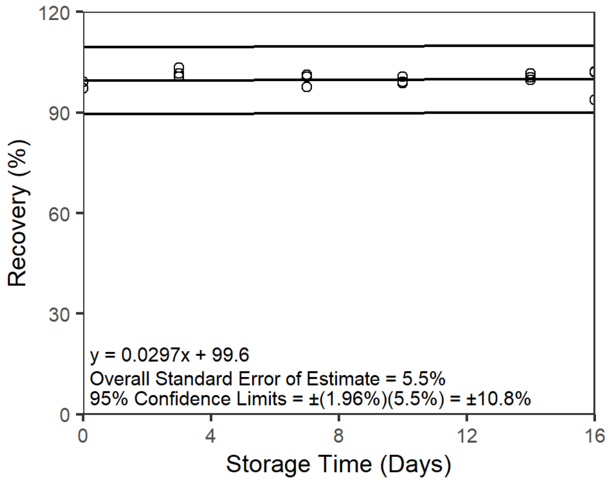

Figure H-12. Plot of refrigerated storage stability data for xylene *(m* isomer).

Table H-11. Sampler storage stability data for xylene (*o* isomer).

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	96.1	98.4	95.9	96.1	98.4	95.9
3	100.7	101.8	99.5	102.5	100.7	99.6
7	101.5	96.3	102.6	95.6	99.2	100.0
10	95.2	97.0	98.4	99.6	96.9	97.7
14	101.0	95.6	98.5	100.6	98.8	99.5
16	99.5	95.8	100.6	101.1	94.4	101.4

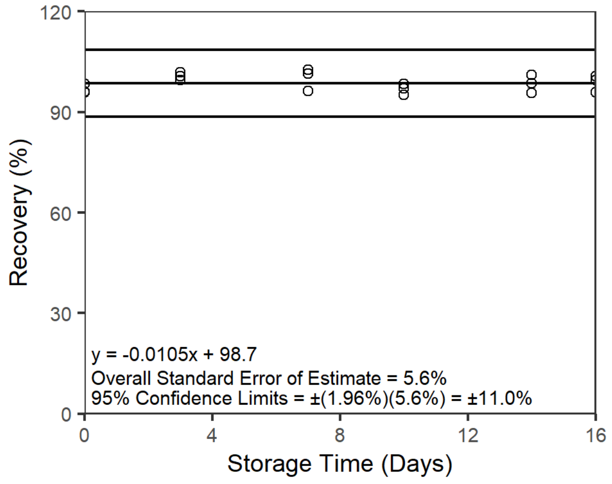

Figure H-13. Plot of ambient storage stability data for xylene (*o* isomer).

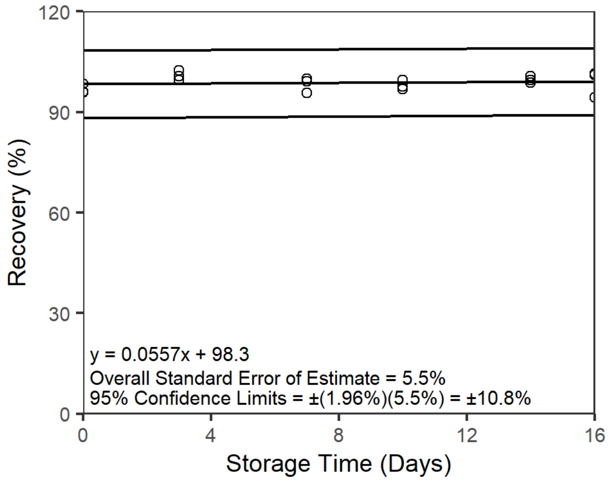

Figure H-14. Plot of refrigerated storage stability data for xylene (*o* isomer).

Table H-12. Sampler storage stability data for xylene (*p* isomer).

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	97.0	98.8	96.8	97.0	98.8	96.8
3	101.1	102.5	100.3	103.0	101.3	100.3
7	102.1	97.5	103.0	96.4	100.3	100.9
10	96.6	98.0	99.2	100.4	98.3	98.9
14	101.6	96.8	93.1	101.3	99.4	100.2
16	99.6	97.0	101.1	101.7	93.5	101.9

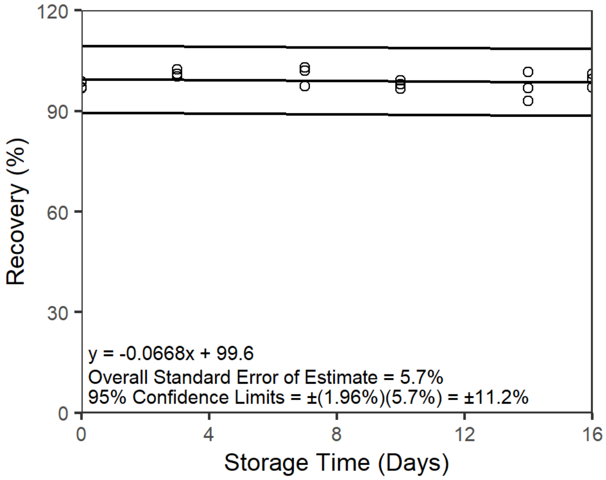

Figure H-15. Plot of ambient storage stability data for xylene (*p* isomer).

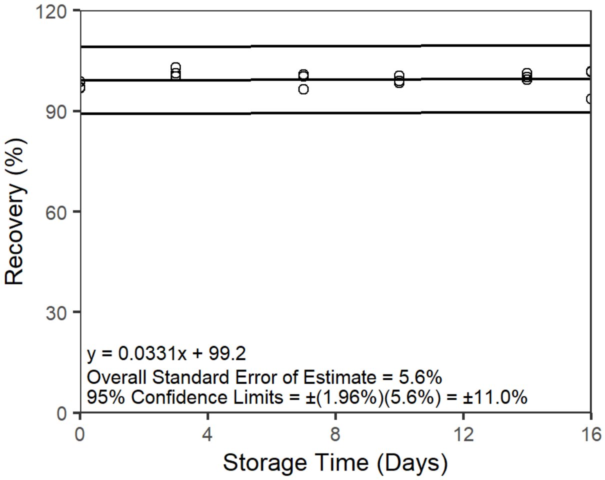

Figure H-16. Plot of refrigerated storage stability data for xylene (*p* isomer).

5 Precision of the Overall Procedure

Pre-existing data from OSHA Method 1002[1] are presented in this section.

The overall standard error of estimate obtained from the ambient storage test analyses described in Section 4 and sampling pump variability were used to determine the precision of the overall procedure, where all aspects of sampling and analysis (sampling, sorbent tube handling and solvent extraction, and instrumental analysis) are considered. This value was obtained by taking the square root of the squared ambient storage stability standard error of estimate (Storage $S_{y/x}^2$) added to the squared sampling pump variability value (V_{SP}^2). The resulting precision of the overall procedure at the 95% confidence level for the ambient 16-day storage test (at the target concentration) for xylenes (*o*-, *m*-, *p*-isomers) was determined to be ±10.8%, ±10.8% for xylene *(m* isomer), ±11.0% for xylene (*o* isomer), and ±11.2% for xylene (*p* isomer) based on the observed ambient Storage $S_{y/x}$ values of 5.5%, 5.5%, 5.6% and 5.7%, respectively, and V_{SP} value of 5.0%.

6 Recovery and Stability of Prepared Samples

Quantitative extraction 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 OSHA Method 5000. 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.

Values for extraction efficiency (E_E) of xylene (*o* isomer),, xylene (*m* isomer), and xylene (*p* isomer) were determined by liquid-spiking four replicate sorbent tubes across a range of analyte mass values that would be obtained from sampling at 0.1 to 2 times the target concentration value for 240 min. Four sorbent tubes were also spiked in this fashion at the target concentration after drawing humid air (78.1% relative humidity at 21.3 °C) through these tubes at 50 mL/min for 4 hours. All of the samples described above were analyzed the following day after being kept overnight at ambient temperature. The E_E values at the RQL were 96.7% for xylene *(m* isomer), 91.8% for xylene (*o* isomer), and 92.2% for xylene (*p* isomer), while that of the working range samples (excluding the samples through which humid air had been drawn) were 99.5% for xylene *(m* isomer), 94.9% for xylene (*o* isomer), and 98.2% for xylene (*p* isomer). The resulting data are shown Tables H-13 through H-15. Pre-loading sorbent tubes with moisture (“wet” designation in the table) did not have an unacceptable effect on E_E.

Table H-13. Extraction efficiency data for xylene *(m* isomer).

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.1	550.1	99.5	98.5	100.7	99.2	99.5
0.25	1320	99.1	98.4	98.5	98.9	98.7
0.5	2640	100.9	99.7	99.5	100.7	100.2
1.0	5281	99.4	99.1	99.7	98.3	99.1
1.5	7921	99.9	101.6	100.8	100.5	100.7
2.0	10,561	99.7	98.6	98.3	99.3	99.0
RQL	1.39	97.4	101.6	96.5	91.3	96.7
1.0 (wet)	5281	98.7	99.2	99.0	100.8	99.4

Table H-14. Extraction efficiency data for xylene (*o* isomer).

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.1	550.1	97.7	95.9	95.9	94.7	96.0
0.25	1320	94.4	95.4	95.3	95.9	95.2
0.5	2640	93.4	92.6	94.4	93.9	93.6
1.0	5281	96.5	96.4	93.8	92.0	94.7
1.5	7921	94.8	93.4	94.3	94.3	94.2
2.0	10,561	96.7	96.3	95.8	94.6	95.9
RQL	1.06	88.4	89.9	93.4	95.4	91.8
1.0 (wet)	5281	97.3	96.7	95.4	94.1	95.9

Table H-15. Extraction efficiency data for xylene (*p* isomer).

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.1	538.2	98.7	99.0	97.9	98.2	98.5
0.25	1292	99.4	98.8	99.0	98.9	99.0
0.5	2583	97.8	98.4	98.5	98.7	98.4
1.0	5166	97.5	99.3	96.5	97.7	97.8
1.5	7749	98.4	98.1	96.2	97.3	97.5
2.0	10,332	98.0	96.5	98.3	97.9	97.7
RQL	1.72	96.6	95.1	86.0	91.2	92.2
1.0 (wet)	5166	97.9	96.1	97.3	95.0	96.6

The stability of sample extracts prepared according to OSHA Method 5000 was examined by retaining the sample solvent extracts for the target concentration samples described immediately above. Two of the four vials were immediately recapped with new septa following the initial analyses, and again following each re-analysis event. The other two vials retained the original punctured septa throughout. All four vials were re-analyzed at 24, 48, and 72 hours after the initial analyses with all vials remaining in an autosampler tray kept at 22 °C. Freshly prepared standards were used in each analysis event and each septum (whether new or previously used) was punctured four times for each injection. The resulting data are shown in Tables H-16 through H-18.

Table H-16. Extracted sample stability data for xylene *(m* isomer).

	punctured septa replaced recovery (%)		punctured septa retained recovery (%)	
time (days)	1	2	1	2
0	97.8	97.4	97.1	97.4
1	96.8	96.4	95.8	97.0
2	97.0	96.4	96.0	96.5
3	96.9	96.5	96.0	96.2

Table H-17. Extracted sample stability data for xylene (*o* isomer).

	punctured septa replaced recovery (%)		punctured septa retained recovery (%)	
time (days)	1	2	1	2
0	96.4	96.7	96.5	96.0
1	95.8	96.4	96.3	95.9
2	95.5	96.1	95.5	95.5
3	95.6	95.8	95.2	95.3

Table H-18. Extracted sample stability data for xylene (*p* isomer).

	punctured septa replaced recovery (%)		punctured septa retained recovery (%)	
time (days)	1	2	1	2
0	99.6	101.1	98.5	97.9
1	100.0	101.5	99.4	98.1
2	100.0	101.2	99.1	98.6
3	100.4	101.1	98.5	98.3

7 Sampler Capacity

Pre-existing data from OSHA Method 1002[1] are presented in this section.

The sampling capacity of the front section of a sorbent tube was tested by sampling a dynamically generated test atmosphere, using the system described in Section 13, containing xylenes (*o*-, *m*-, *p*-isomers) at nominally two times the target concentration (calculated to be 105 ppm for xylene (*m* isomer), 49 ppm for xylene (*o* isomer), and 46 ppm for xylene (*p* isomer)).The test atmosphere also contained ethyl benzene at 37 ppm. The relative humidity and temperature of the air sampled were 78% relative and 21 °C, and the sampling flow rate was 50 mL/min. A sorbent tube testing system was made by placing a complete sorbent tube in series behind another tube, which contained only the front sorbent section. The rear tube was changed and analyzed at 5, 10, 15, 30, 60, 120, 180, 240, 360, 480, and 600 min. Breakthrough was not observed after sampling for 600 min (corresponding to 30 liters). Data from three sorbent tube testing systems were used to determine a recommended sampling volume of 12 liters for xylenes (*o*-, *m*-, *p*-isomers) as described in OSHA Method 5000. This volume corresponds to a 240 min sampling period, which is the maximum recommended sampling time regardless of breakthrough.

8 Low Humidity

Pre-existing data from OSHA Method 1002[1] are presented in this section.

The effect of low humidity was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing xylenes (*o*-, *m*-, *p*-isomers) nominally at two times the target value (calculated to be 108 ppm for xylene (*m* isomer), 50.2 ppm for xylene (*o* isomer), and 47.0 ppm for xylene (*p* isomer)). The atmosphere also contained ethyl benzene at 38.2 ppm. The relative humidity and temperature were 5% and 20 °C, and the sampling flow rate was 50 mL/min. Samples were collected on three sorbent tubes for 240 min. After immediate analysis, results as a percentage of expected recovery were 102.0%, 100.4%, and 99.8% for xylene (*m* isomer); 101.4%, 100.4%, and 99.2% for xylene (*o* isomer); and 101.6%, 100.1%, and 99.6% for xylene (*p* isomer).

9 Chemical Interference

Pre-existing data from OSHA Method 1002[1] are presented in this section.

The effect of potential chemical sampling interference was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing xylenes (*o*-, *m*-, *p*-isomers) nominally at two times the target concentration (calculated to be 108 ppm for xylene (*m* isomer), 50.2 ppm for xylene (*o* isomer), and 47.0 ppm for xylene (*p* isomer)). The relative humidity and temperature of the air sampled were 81% and 21 °C, and the sampling flow rate was 50 mL/min. Ethyl benzene, toluene, and *n*-butyl acetate were present as potential interferents (calculated to be at respective concentrations of 18.9 ppm, 96.9 ppm, and 78.3 ppm). Samples were collected on three sorbent tubes for 240 min. After immediate analysis, results as a percentage of expected recovery were 103.3%, 102.9%, and 101.8% for xylene (*m* isomer); 102.8%, 102.5%, and 101.2% for xylene (*o* isomer); and 103.2%, 102.6%, and 101.6% for xylene (*p* isomer).

10 Analytical Method Reproducibility

Pre-existing data from OSHA Method 1002[1] are presented in this section.

Samples were prepared by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing xylenes (*o*-, *m*-, *p*-isomer) nominally at the target concentration (calculated to be 53.0 ppm for xylene (*m* isomer), 24.7 ppm for xylene (*o* isomer), and 23.0 ppm for xylene (*p* isomer)). The relative humidity and temperature of the air sampled were not reported. Samples were collected on six sorbent tubes at a flow rate of 50 mL/min for 240 min (conditions similar to those used for storage stability testing). The resulting samples were submitted to the OSHA Salt Lake Technical Center for analysis using the procedures described OSHA Method 1002 after storage for 16 days at ambient temperature. The analytical results corrected for E_E are provided in Tables H-19 through H-22. No sample result for xylenes (*o*-, *m*-, *p*-isomers) fell outside the permissible bounds set by the precision of the overall procedure determined in Section 5 of this appendix.

Table H-19. Reproducibility data for xylene (*m* isomer).

sampled (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
2555	2552	99.9	-0.1
2595	2593	99.9	-0.1
2623	2427	92.5	-7.5
2557	2580	100.9	+0.9
2564	2593	101.1	+1.1
2623	2610	99.5	-0.5

Table H-20. Reproducibility data for xylene (*o* isomer).

sampled (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
1189	1245	104.7	+4.7
1207	1266	104.9	+4.9
1221	1158	94.8	-5.2
1190	1262	106.1	+6.1
1193	1263	105.9	+5.9
1221	1275	104.4	+4.4

Table H-21. Reproducibility data for xylene (*p* isomer).

sampled (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
1112	1140	102.5	+2.5
1129	1158	102.6	+2.6
1142	1082	94.7	-5.3
1129	1152	102.0	+2.0
1116	1159	103.9	+3.9
1142	1166	102.1	+2.1

Table H-22. Reproducibility data for xylene (*o*-, *m*-, *p*-isomers).

sampled (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
4856	4937	101.7	+1.7
4931	5017	101.7	+1.7
4986	4667	93.6	-6.4
4876	4994	102.4	+2.4
4873	5014	102.9	+2.9
4986	5051	101.3	+1.3

11 Effect of Sampling a Low Concentration

Pre-existing data from OSHA Method 1002[1] are presented in this section.

The effect of sampling a low concentration of xylenes (*o*-, *m*-, *p*-isomers) vapor was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing xylenes (*o*-, *m*-, *p*-isomers) nominally at one-tenth the target concentration (calculated to be 5.07 ppm or xylene (*m* isomer), 2.30 ppm for xylene (*o* isomer), and 2.30 ppm for xylene (*p* isomer)). The atmosphere also contained ethyl benzene at 1.84 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 three sorbent tubes for 240 min. After immediate analysis, results as a percentage of expected recovery were 95.2%, 97.6%, and 102.2% for xylene (*m* isomer); 94.6%, 96.1%, and 101.2% for xylene (*o* isomer); and 95.0%, 97.2%, and 101.8% for xylene (*p* isomer).

12 Estimation of Uncertainty

While systematic biases such as analyte storage loss are examined, and limits are placed on these, an estimation of uncertainty that encompasses both potential random and systematic error was not completed. Instead, the overall standard error of estimate was calculated from the random error inherent to the points about the regression line produced by the ambient storage test described in Section 5, as prescribed by the OSHA validation guidelines in use at the time OSHA Method 1002 was originally validated. See Section 5 of this appendix for details.

13 Controlled Test Atmosphere Procedure

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 ethyl benzene and xylenes (*o*-, *m*-, *p*-isomers) 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 ethyl benzene and xylenes (*o*-, *m*-, *p*-isomers) 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.

OSHA 5000. Appendix I
Benzene

Version:	1.0
OSHA PEL:	1 ppm (3.19 mg/m^3) 8-Hour TWA; 5 ppm (16.0 mg/m^3) 15-Minute STEL; 0.5 ppm (1.60 mg/m^3) Action Level, General Industry, Construction, Shipyard 10 ppm (31.9 mg/m^3) 8-Hour TWA; 25 ppm (79.8 mg/m^3) Ceiling (up to Peak Value, no more than 10 minutes); 50 ppm (160 mg/m^3) Peak, General Industry segments exempt from the 1 ppm 8-Hour TWA and 5 ppm STEL of the benzene standard 29 CFR 1910.1028
ACGIH TLV:	0.5 ppm (1.6 mg/m^3) 8-Hour TWA; 2.5 ppm (8.0 mg/m^3) 15-Minute STEL
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); 10 min at 50 mL/min (0.5 L, Peak)
Reliable quantitation limit:	0.043 ppm (0.14 mg/m^3, 8-Hour TWA); 0.69 ppm (2.2 mg/m^3, 15-Minute STEL) 1.0 ppm (3.3 mg/m^3, Peak)
Standard error of estimate:	5.1%
Status:	Fully validated. Method 5000 has been subjected to the established validation procedures of the Method Development Team for sampling and analysis of benzene.

November 2001 (OSHA 1005)
September 2002 (OSHA 1005)
February 2021 (OSHA 5000)

Mary Eide
Daren Pearce

1 Introduction

1.1 Previous Methods used by OSHA for Sampling and Analysis of Benzene

The specific analyte described in this appendix is benzene, CAS No. 71-43-2. The methodologies described in this appendix for benzene are based on OSHA Method 1005.[1] That method requires the collection of samples using charcoal sorbent tubes, extraction using carbon disulfide, and analysis by gas chromatography using a flame ionization detector. Prior to the use of OSHA Method 1005, OSHA routinely collected and analyzed samples for benzene using OSHA Method 12.[2] OSHA Method 1005 made changes to the analytical column type (from packed) and stationary phase compared to OSHA Method 12. Version 2 of OSHA Method 1005 added sampling and analysis of surface wipes.

1.2 Changes to the Previously-Used Method

This appendix represents an update of OSHA Method 1005[1], which was fully validated at the time it was published based on the validation guidelines in effect at that time. Compared to the previous method used this method includes new analytical parameters and internal standard (ISTD). Data presented from the previously used method are identified by the statement "Pre-existing data from OSHA Method 1005[1] are presented in this section". The changes were made

---

[1] Eide, M. Benzene (OSHA Method 1005), 2002. United States Department of Labor, Occupational Safety & Health Administration Web site. https://www.osha.gov/dts/sltc/methods/validated/1005/1005.html (accessed October 2019).

[2] Elskamp, C.J. Benzene (OSHA Method 12), 1980. United States Department of Labor, Occupational Safety & Health Administration Web site. https://www.osha.gov/dts/sltc/methods/archive/org012/org012.pdf (accessed October 2019).

to allow the standardized collection and analysis of benzene with other analytes found in Organic Vapor Sampling Group 1, described in OSHA Method 5000.

1.3 Validation Parameters

The procedures used to develop the method validation data are described in Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis.[3] Air concentrations listed in ppm are referenced to 25 °C and 760 Torr. The target concentration for method evaluation was the OSHA Table Z-1 8-hour time-weighted average (TWA) permissible exposure limit (PEL) for benzene.

2 Detection and Quantification

2.1 Detection Limit of the Analytical Procedure (DLAP)

The DLAP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLAP $S_{y/x}$) divided by the slope of the line produced from analyses of ten analytical standards prepared with equally spaced increments of analyte mass. The standards were prepared in such a way that the highest standard concentration would produce a peak approximately 10 times the response of a reagent blank at or near the chromatographic retention time of the analyte. The standards and a reagent blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLAP $S_{y/x}$ and slope values for DLAP determination. Results obtained for these analyses are listed in Tables I-1, and plotted in Figure I-1.

Table I-1. DLAP data for benzene.

concentration (µg/mL)	mass on column (pg)	area counts (µV·s)
0	0.00	0.00
0.282	1.88	0.332
0.565	3.77	0.366
0.847	5.65	0.430
1.13	7.53	0.555
1.41	9.40	0.593
1.69	11.3	0.700
1.98	13.2	0.800
2.26	15.1	0.836
2.54	16.9	0.935
2.82	18.8	1.00

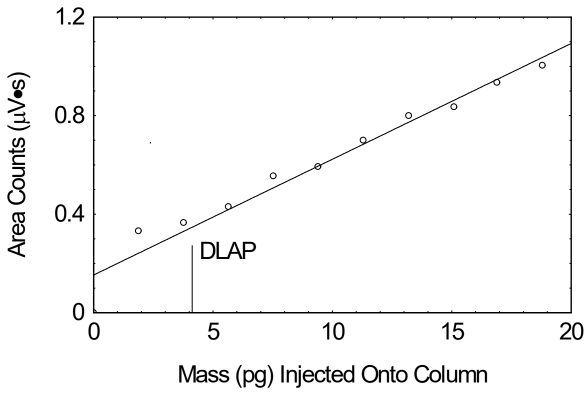

Figure I-1. Plot of data used to determine the DLAP for benzene ($y = 0.0468x + 0.154$, DLAP $S_{y/x}$ = 0.06541, DLAP = 4.18 pg).

2.2 Detection Limit of the Overall Procedure (DLOP) and Reliable Quantitation Limit (RQL)

The DLOP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLOP $S_{y/x}$) divided by the slope of the line produced from analyses of ten samples prepared from sorbent tubes spiked with equally spaced increments of analyte mass. 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 RQL is expressed as an air concentration that will provide sufficient analyte mass per sample that produces a response greater than 10× DLOP $S_{y/x}$ divided by the slope of the line described above. The spiked samplers and a sample blank were analyzed with the recommended analytical

---

[3] Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration Web site. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed December 2018).

parameters described in OSHA Method 5000. The resulting data provided the DLOP $S_{y/x}$ and the slope values for DLOP and RQL determinations. Results obtained from these analyses are listed in Table I-2 and, plotted in Figure I-2.

Table I-2. DLOP and RQL data for benzene.

mass per sample (µg/sample)	area counts (µV·s)
0.00	0.00
0.702	0.090
1.05	0.167
1.40	0.171
1.76	0.278
2.11	0.337
2.46	0.361
2.81	0.361
3.16	0.461
3.51	0.506
3.86	0.547

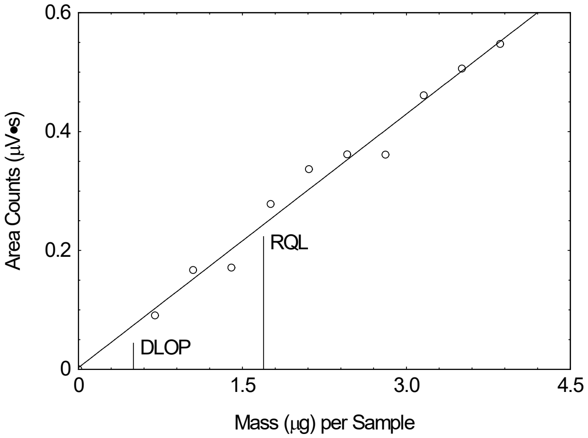

Figure I-2. Plot of data used to determine the DLOP and RQL for benzene ($y = 0.142x + 0.00279$, DLOP $S_{y/x} = 0.0236$, DLOP = 0.499 µg/sample, RQL = 1.66 µg/sample or 0.0432 ppm).

3 Analytical Precision Across the Calibration Range

Fifteen analytical standards over a range of 0.1 to 2 times the analyte concentration in solvent that would be obtained from sampling for the recommended time at the target concentration were analyzed with the recommended analytical parameters described in OSHA Method 5000. An ordinary least-squares linear regression curve was created by plotting the analyte mass per sample versus the corresponding ratio of analyte peak area to internal standard (ISTD) peak area. The resulting data provided the standard error of estimate (Calibration $S_{y/x}$) value across the calibration range, which provides an indication of the imprecision attributable to the instrumental analysis of the target analyte. Results from these analyses are listed in Table I-3, and plotted in Figure I-3.

Table I-3. Analytical precision data for benzene.

× target	0.1×	0.5×	1.0×	1.5×	2.0×
concn (µg/sample)	3.95	19.76	39.51	59.27	79.02
area ratio	0.0244	0.1077	0.2136	0.3131	0.4175
	0.0239	0.1096	0.2229	0.3313	0.4322
	0.0242	0.1129	0.2274	0.3147	0.4400

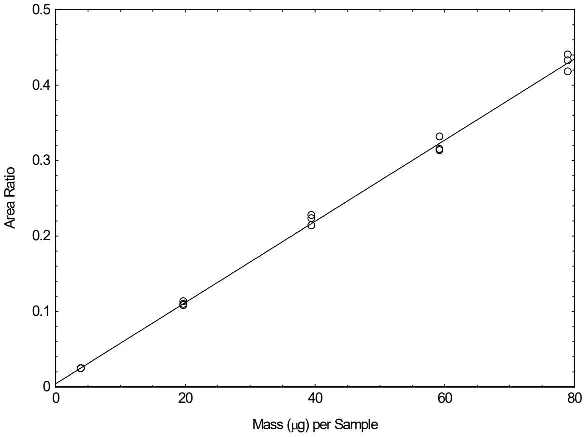

Figure I-3. Plot of data used to determine the precision of the analytical method for benzene ($y = 0.00538x - 0.0409$, Calibration $S_{y/x}$ = 0.00723).

4 Sampler Storage Stability

Pre-existing data from OSHA Method 1005[1] are presented in this section.

Storage stability test samples for benzene were prepared by sampling a dynamically generated controlled test atmosphere using the system described in Section 13. Sampling from this system followed the recommended sampling parameters published in OSHA Method 1005. The nominal concentration of benzene for both ambient and refrigerated storage testing was the target concentration (calculated to be 0.999 ppm). The relative humidity and temperature of the air sampled were about 80% and 22 °C for both tests. For each test, eighteen samples were prepared, and three of these were analyzed on the same day that samples were created. The remaining fifteen refrigerated storage test samples were stored at reduced temperature (4 °C), while the remaining fifteen ambient storage test samples were stored in a closed drawer at ambient temperature (22 °C). For each storage condition, three of the samples were selected and analyzed from those remaining at 3-5 day intervals. The results of these analyses (uncorrected for extraction efficiency) are provided in Table I-4 and in Figures I-4 through I-5.

The recovery of benzene calculated from the regression line generated for the 19-day ambient storage test was 98.0%. This result was not corrected for extraction efficiency.

Table I-4. Sampler storage stability data for benzene.

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	98.9	99.9	100.4	98.9	99.9	100.4
5	99.4	98.9	97.9	98.8	100.3	99.7
8	97.9	99.4	99.1	99.5	100.4	98.8
12	98.1	99.9	97.9	100.1	99.9	97.9
15	98.5	98.9	96.9	97.7	99.1	98.5
19	96.8	99.1	98.4	97.9	99.8	98.4

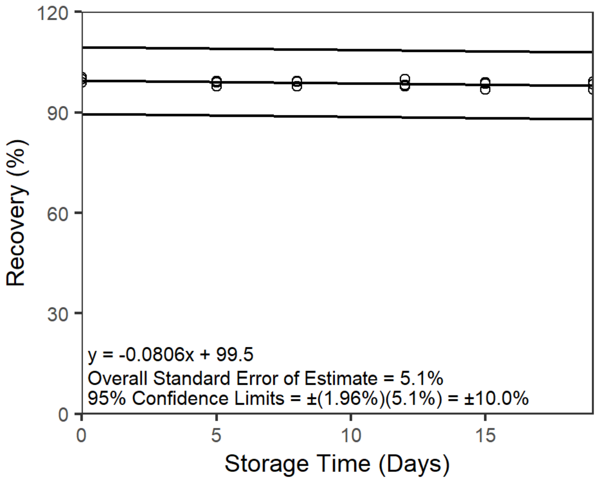

Figure I-4. Plot of ambient storage stability data for benzene.

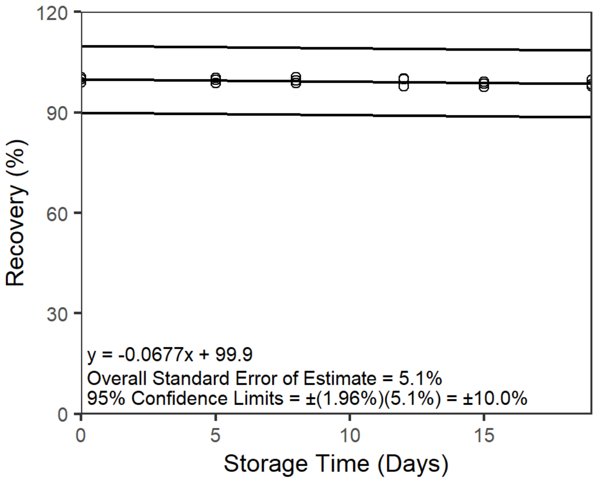

Figure I-5. Plot of refrigerated storage stability data for benzene.

5 Precision of the Overall Procedure

Pre-existing data from OSHA Method 1005[1] are presented in this section.

The overall standard error of estimate obtained from the ambient storage test analyses described in Section 4 and sampling pump variability were used to determine the precision of the overall procedure, where all aspects of sampling and analysis (sampling, sorbent tube handling and solvent extraction, and instrumental analysis) are considered. This value was obtained by taking the square root of the squared ambient storage stability standard error of estimate (Storage $S_{y/x}^2$) added to the squared sampling pump variability value (V_{SP}^2). The resulting precision of the overall procedure at the 95% confidence level for the ambient 19-day storage test (at the target concentration) for benzene was determined to be ±10.0% based on the observed ambient Storage $S_{y/x}$ value of 5.1% and V_{SP} value of 5.0%.

6 Recovery and Stability of Prepared Samples

Pre-existing data from OSHA Method 1005[1] are presented in this section.

Quantitative extraction 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 OSHA Method 1005. 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.

A value for extraction efficiency (E_E) was determined by liquid-spiking four replicate sorbent tubes across a range of analyte mass values that would be obtained from sampling at 0.25 to 2 times the target concentration value for 240 min. Four sorbent tubes were also spiked in this fashion at the target concentration after drawing humid air (80% relative humidity at 21 °C) through these tubes at 50 mL/min for 240 min. All of the samples described above were analyzed the following day after being kept overnight at ambient temperature. The E_E value at the RQL was 96.6%, while that of the working range samples (excluding the samples through which humid air had been drawn) was 97.1%. The data are shown in Table I-5. Pre-loading sorbent tubes with moisture ("wet" designation in the table) did not have an unacceptable effect on E_E.

Table I-5. Extraction efficiency data for benzene.

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.25	9.9	98.6	95.3	96.6	97.3	97.0
0.5	19.8	97.6	98.2	97.6	98.2	97.9
1.0	39.5	96.7	97.1	96.3	97.0	96.8
1.5	59.3	96.9	95.5	96.9	97.3	96.7
2.0	79.1	97.2	96.5	97.2	97.1	97.0
RQL	0.13	98.5	97.3	95.3	95.1	96.6
1.0 (wet)	39.5	97.1	95.6	96.8	97.2	96.7

Stability in OSHA Method 1005[1] was only performed for 24 hours; this study was expanded to 72 hours.

The stability of sample extracts prepared according to OSHA Method 1005 was examined by retaining the sample solvent extracts for the target concentration samples described immediately above. Two of the four vials were immediately recapped with new septa following the initial analyses, and again following each re-analysis event. The other two vials retained the original punctured septa throughout. All four vial were re-analyzed at 24, 48, and 72 hours after the initial analyses, with all vials remaining in an autosampler tray kept at 22 °C. Freshly prepared standards were used for each analysis event and each septum (whether new or previously used) was punctured four times for each injection. The resulting data are shown in Table I-6.

Table I-6. Extracted sample stability data for benzene.

	punctured septa replaced recovery (%)		punctured septa retained recovery (%)	
time (days)	1	2	1	2
0	100.4	101.4	101.8	103.1
1	97.9	95.1	94.2	94.0
2	101.4	99.6	96.0	98.5
3	102.1	101.2	95.8	98.4

7 Sampler capacity

Pre-existing data from OSHA Method 1005[1] are presented in this section.

The sampling capacity of the front section of a sorbent tube was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing benzene nominally at two times the target concentration (calculated to be 23.0 ppm). The relative humidity and temperature of the air sampled were about 80% and 22 °C, and the sampling flow rate was 50 mL/min. A sorbent tube testing system was made by placing a complete sorbent tube in series behind another tube, which contained only the front sorbent section. The rear tube was changed and analyzed at 5, 10, 15, 30, 60, 120, 180, 240, 360, 480, and 600 min. Data from three sorbent tube testing systems were used to determine a recommended sampling volume of 12 liters for benzene as described in OSHA Method 5000. This volume corresponds to a 240 min sampling period, which is the maximum recommended sampling time regardless of breakthrough.

8 Low Humidity

Pre-existing data from OSHA Method 1005[1] are presented in this section.

The effect of low humidity was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing benzene at nominally at two times the target concentration (calculated to be 23.0 ppm). The relative humidity and temperature of the air sampled were about 10% and 22 °C, and the sampling flow rate was 50 mL/min. Samples were collected on three sorbent tubes for 240 min. After immediate analysis, results as a percentage of expected recovery were 99.4%, 99.8%, and 99.7%.

9 Chemical Interference

Pre-existing data from OSHA Method 1005[1] are presented in this section.

The effect of potential chemical sampling interference was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing benzene nominally at the target concentration (calculated to be 9.99 ppm). The relative humidity and temperature of the air sampled were about 80% and 22 °C, and the sampling flow rate was 50 mL/min. Gasoline was present as a potential interferent (concentration calculated to be 890 mg/m^3). Samples were collected on three sorbent tubes for 240 min. After immediate analysis, results as a percentage of expected recovery were 99.8%, 100.1%, and 98.9%.

10 Analytical Method Reproducibility

Pre-existing data from OSHA Method 1005[1] are presented in this section.

Samples were prepared by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing benzene nominally at twice the target concentration. The relative humidity and temperature of the air sampled were not reported. Samples were collected on six sorbent tubes at a flow rate of 50 mL/min for 190 min (conditions similar to those used for storage stability testing). The resulting samples were submitted to the OSHA Salt Lake Technical Center for analysis using the procedure described in OSHA Method 1005 after storage for 7 days at reduced temperature (4 °C). The analytical results corrected for E_E are provided in Table I-7. No sample result for benzene fell outside the permissible bounds set by the precision of the overall procedure determined in Section 5 of this appendix.

Table I-7. Reproducibility data for benzene.

sampled (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
76.91	73.61	95.7	-4.3
83.34	81.58	97.9	-2.1
77.84	75.17	96.6	-3.4
88.56	85.62	96.7	-3.3
79.73	75.29	94.4	-5.6
78.98	74.88	94.8	-5.2

11 Effects of Sampling a Low Concentration

Pre-existing data from OSHA Method 1005[1] are presented in this section.

The effect of sampling a low concentration of benzene vapor was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing benzene nominally at one-tenth the target concentration (calculated to be 0.10 ppm). The relative humidity and temperature of the air sampled were about 80% and 22.2 °C, and the sampling flow rate was 50 mL/min. Samples were collected on three sorbent tubes for 240 min. After immediate analysis, results for benzene as a percentage of expected recovery were 100.4%, 98.5%, and 98.9%.

12 Estimation of Uncertainty

While systematic biases such as analyte storage loss are examined, and limits are placed on these, an estimation of uncertainty that encompasses both potential random and systematic error was not completed. Instead, the overall standard error of estimate was calculated from the random error inherent to the points about the regression line produced by the ambient storage test described in Section 5, as prescribed by the OSHA validation guidelines in use at the time OSHA Method 1005 was originally validated. See Section 5 of this appendix for details.

13 Controlled Test Atmosphere Procedure

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 benzene 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 benzene 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.

OSHA 5000. Appendix J
n-Butyl Acetate

Version:	1.0
OSHA PEL:	150 ppm (710 mg/m^3) 8-Hour TWA, General Industry, Construction, Shipyard
ACGIH TLV:	50 ppm (238 mg/m^3) 8-Hour TWA; 150 ppm (712 mg/m^3) 15-Minute STEL
Recommended sampling time and sampling rate:	240 min at 50 mL/min (12 L, 8-Hour TWA)
Reliable quantitation limit:	0.055 ppm (0.26 mg/m^3)
Standard error of estimate:	5.0%
Status:	Fully validated. Method 5000 has been subjected to the established validation procedures of the Method Development Team for sampling and analysis of *n*-butyl acetate.

January 2007 (OSHA 1009)	Mary Eide
February 2021 (OSHA 5000)	Carmen Riberas, Daren Pearce

1 Introduction

1.1 Previous Methods used by OSHA for Sampling and Analysis of *n*-butyl acetate

The specific analyte described in this appendix is *n*-butyl acetate, CAS No. 123-86-4. The methodologies described in this appendix for *n*-butyl acetate are based on OSHA Method 1009.[1] That method requires the collection of samples using charcoal sorbent tubes, extraction using carbon disulfide, and analysis by gas chromatography using a flame ionization detector.

1.2 Changes to the Previously-Used Method

This appendix represents an update of OSHA Method 1009[1], which was fully validated at the time it was published based on the validation guidelines in effect at that time. Compared to the previous method used this method includes new analytical parameters. Data presented from the previously used method are identified by the statement "Pre-existing data from OSHA Method 1009[1] are presented in this section". The change was made to allow the standardized collection and analysis of *n*-butyl acetate with other analytes found in Organic Vapor Sampling Group 1, described in OSHA Method 5000.

1.3 Validation Parameters

The procedures used to develop the method validation data are described in Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis.[2] Air concentrations listed in ppm are referenced to 25 °C and 760 Torr.

---

[1] Eide, M. *n*-butyl acetate, isobutyl acetate, *sec*-butyl acetate, and *tert*-butyl acetate (OSHA Method 1009), 2007. United States Department of Labor, Occupational Safety & Health Administration Web site. https://www.osha.gov/dts/sltc/methods/validated/1009/1009.html (accessed March 2019).

[2] Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration Web site. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed December 2018).

The target concentration for method evaluation was the OSHA 8-hour time-weighted average (TWA) permissible exposure limit (PEL) for *n*-butyl acetate.

2 Detection and Quantification

2.1 Detection Limit of the Analytical Procedure (DLAP)

The DLAP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLAP $S_{y/x}$) divided by the slope of the line produced from analyses of ten analytical standards prepared with equally spaced increments of analyte mass. The standards were prepared in such a way that the highest standard concentration would produce a peak approximately 10 times the response of a reagent blank at or near the chromatographic retention time of the analyte. The standards and a reagent blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLAP $S_{y/x}$ and slope values for DLAP determination. Results obtained for these analyses are listed below in Table J-1, and plotted in Figure J-1.

Table J-1. DLAP data for *n*-butyl acetate.

concentration (µg/mL)	mass on column (pg)	area counts (µV·s)
0.00	0.00	0.00
0.424	2.83	0.00
0.848	5.65	0.0361
1.27	8.48	0.0514
1.70	11.3	0.0678
2.12	14.1	0.0887
2.54	17.0	0.1184
2.97	19.8	0.1374
3.39	22.6	0.1731
3.82	25.4	0.1823
4.24	28.3	0.1992

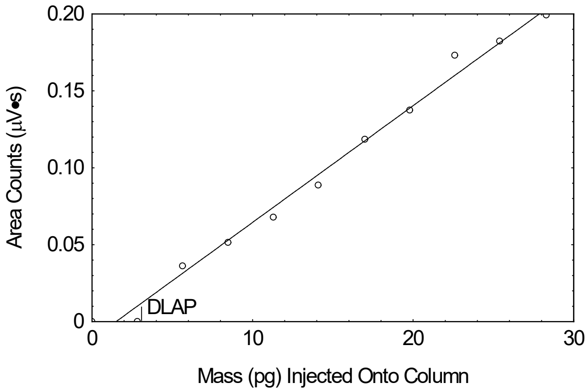

Figure J-1. Plot of data used to determine the DLAP for *n*-butyl acetate ($y = 0.00759x - 0.0113$, DLAP $S_{y/x}$ = 0.00771, DLAP = 3.05 pg).

2.2 Detection Limit of the Overall Procedure (DLOP) and Reliable Quantitation Limit (RQL)

The DLOP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLOP $S_{y/x}$) divided by the slope of the line produced from analyses of ten samples prepared from sorbent tubes spiked with equally spaced increments of analyte mass. 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 RQL is expressed as an air concentration that will provide sufficient analyte mass per sample that produces a response greater than 10× DLOP $S_{y/x}$ divided by the slope of the line described above. The spiked samplers and a sample blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLOP $S_{y/x}$ and the slope values for DLOP and RQL determinations. Results obtained from these analyses are listed in Table J-2, and plotted in Figure J-2.

Table J-2. DLOP and RQL data for *n*-butyl acetate.

mass per sample (µg/sample)	area counts (µV·s)
0.00	0.00
0.424	0.00
0.848	0.0237
1.27	0.0595
1.70	0.0711
2.12	0.0972
2.54	0.1304
2.97	0.1227
3.39	0.1359
3.82	0.1969
4.24	0.1753

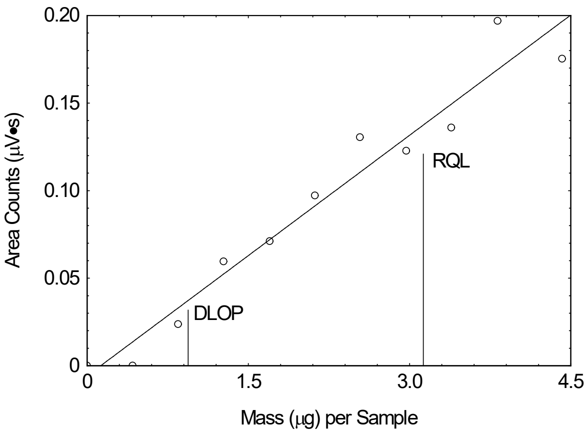

Figure J-2. Plot of data used to determine the DLOP and RQL for *n*-butyl acetate ($y = 0.0469x - 0.00731$, DLOP $S_{y/x}$ = 0.0147, DLOP = 0.940 µg/sample, RQL = 3.13 µg/sample or 0.055 ppm).

3 Analytical Precision Across the Calibration Range

Fifteen analytical standards over a range of 0.1 to 2 times the analyte concentration in solvent that would be obtained from sampling for the recommended time at the target concentration were analyzed with the recommended analytical parameters described in OSHA Method 5000. An ordinary least-squares linear regression curve was created by plotting the analyte mass per sample versus the corresponding ratio of analyte peak area to internal standard (ISTD) peak area. The resulting data provided the standard error of estimate (Calibration $S_{y/x}$) value across the calibration range, which provides an indication on the imprecision attributable to the instrumental analysis of the target analyte. Results from these analyses are listed in Table J-3, and plotted in Figure J-3.

Table J-3. Analytical precision data for n-butyl acetate.

× target	0.1×	0.5×	1.0×	1.5×	2.0×
concn (µg/sample)	882.6	4413	8826	13,239	17,652
area ratio	1.750	9.006	18.61	28.57	38.20
	1.758	8.970	18.56	28.58	38.91
	1.767	8.988	18.58	28.55	38.66

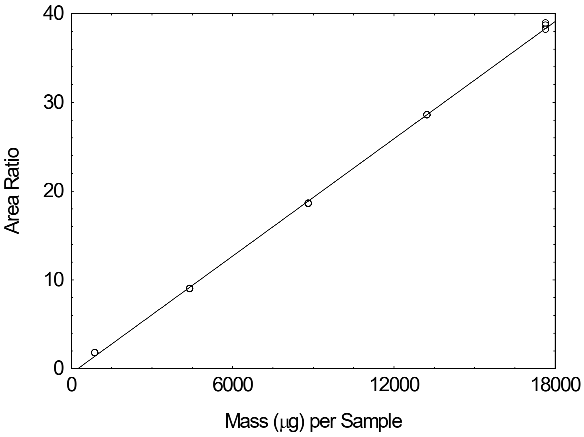

Figure J-3. Plot of data used to determine the precision of the analytical method for *n*-butyl acetate ($y = 0.00220x - 0.531$, Calibration $S_{y/x}$ = 0.309).

4 Sampler Storage Stability

Pre-existing data from OSHA Method 1009[1] are presented in this section.

Storage stability test samples for *n*-butyl acetate were prepared by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13. Sampling from this system followed the recommended sampling parameters published in OSHA Method 1009. The nominal concentration of *n*-butyl acetate for both ambient and refrigerated storage testing was the target concentration (calculated to be 151 ppm). The relative humidity and temperature of the air sampled were 80% and 23 °C for both tests. For each test, eighteen samples were prepared and three of these were analyzed on the same day that samples were created. The remaining fifteen refrigerated storage test samples were stored at reduced temperature (4 °C), while the remaining fifteen ambient storage test samples were stored in a closed drawer at ambient temperature (about 22 °C). For each storage condition, three samples were selected and analyzed from those remaining at 3-4 day intervals. The results of these analyses (uncorrected for extraction efficiency) are provided in Table J-4 and plotted in Figures J-4 through J-5.

The recovery of *n*-butyl acetate calculated from the regression line generated for the 17-day ambient storage test was 96.0%.

Table J-4. Sampler storage stability data for *n*-butyl acetate.

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	100.2	100.4	99.8	100.2	100.4	99.8
3	99.3	98.6	99.4	99.7	99.4	99.8
7	98.8	99.0	98.4	100.1	99.8	99.4
10	97.3	98.1	96.9	98.6	98.7	97.9
14	96.9	97.5	96.6	98.5	98.9	97.6
17	95.7	96.9	95.1	97.3	98.6	97.9

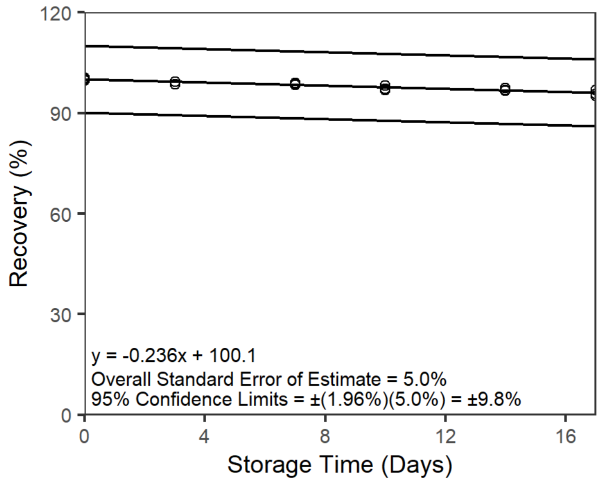

Figure J-4. Plot of ambient storage stability data for *n*-butyl acetate.

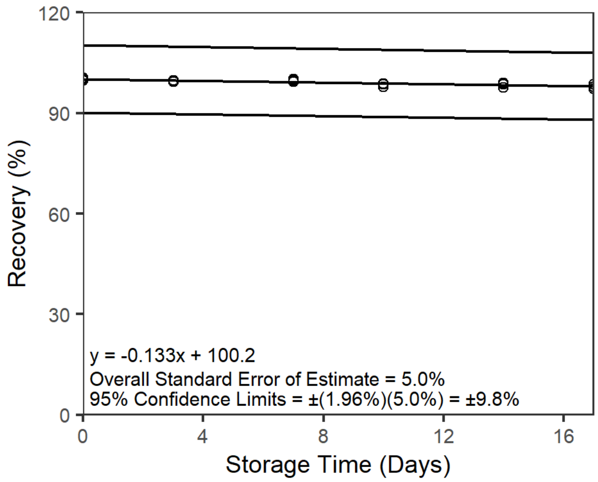

Figure J-5. Plot of refrigerated storage stability data for *n*-butyl acetate.

5 Precision of the Overall Procedure

Pre-existing data from OSHA Method 1009[1] are presented in this section.

The overall standard error of estimate obtained from the ambient storage test analyses described in Section 4 and sampling pump variability were used to determine the precision of the overall procedure, where all aspects of sampling and analysis (sampling, sorbent tube handling and solvent extraction, and instrumental analysis) are considered. This value was obtained by taking the square root of the squared ambient storage stability standard error of estimate (Storage $S_{y/x}^2$) added to the squared sampling pump variability value (V_{SP}^2). The resulting values for precision of the overall procedure at the 95% confidence level for the ambient 17-day storage test (at the target concentration) for *n*-butyl acetate was determined to be ±9.8% based on the observed ambient Storage $S_{y/x}$ value of 5.0% and V_{SP} value of 5.0%.

6 Recovery and Stability of Prepared Samples

Quantitative extraction 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 OSHA Method 5000. 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.

A value for extraction efficiency (E_E) was determined by liquid-spiking four replicate sorbent tubes across a range of analyte mass values that would be obtained from sampling at 0.1 to 2 times the target concentration value for 240 min. Four sorbent tubes were also spiked in this fashion at the target concentration after drawing humid air (79.4% relative humidity at 22.3 °C) through these tubes at 50 mL/min for 240 min. All of the samples described above were analyzed the following day after being kept overnight at ambient temperature. The E_E value at the RQL was 91.3%, while that of the working range samples (excluding the samples through which humid air had been drawn) was 98.0%. The data are shown in Table J-5. Pre-loading sorbent tubes with moisture ("wet" designation in the table) did not have an unacceptable effect on E_E.

Table J-5. Extraction efficiency data for *n*-butyl acetate.

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.1	882.6	98.2	96.6	97.8	97.1	97.4
0.25	2207	97.8	97.4	96.8	97.0	97.3
0.5	4413	96.3	94.6	93.4	95.3	94.9
1.0	8826	99.0	99.1	98.7	98.3	98.8
1.5	13,239	98.5	99.4	100.3	100.3	99.6
2.0	17,652	99.5	100.6	100.1	100.4	100.2
RQL	3.18	88.0	90.1	92.2	95.0	91.3
1.0 (wet)	8826	94.3	94.9	95.4	93.4	94.5

The stability of sample extracts prepared according to OSHA Method 5000 was examined by retaining the sample solvent extracts for the target concentration samples described immediately above. Two of the four vials were immediately recapped with new septa following the initial analyses, and again following each re-analysis event. The other two vials retained the original punctured septa throughout. All four vials were re-analyzed at 24, 48, and 72 hours after the initial analyses, with all the vials remaining in an autosampler tray kept at 22 °C. Freshly prepared standards were used with each analysis event and each septum (whether new or previously used) was punctured four times for each injection. The resulting data are shown in Table J-6.

Table J-6. Extracted sample stability data for *n*-butyl acetate.

	punctured septa replaced recovery (%)		punctured septa retained recovery (%)	
time (days)	1	2	1	2
0	99.9	98.5	98.7	98.5
1	97.9	98.3	99.0	98.1
2	97.8	97.9	97.7	97.8
3	98.2	99.2	95.7	96.6

7 Sampler Capacity

Pre-existing data from OSHA Method 1009[1] are presented in this section.

The sampling capacity of the front section of a sorbent tube was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing *n*-butyl acetate nominally at two times the target concentration (calculated to be 302 ppm). The relative humidity and temperature of the air sampled were 80% and 23 °C, and the sampling flow rate was 50 mL/min. A sorbent tube testing system was made by placing a complete sorbent tube in series behind another tube, which contained only the front sorbent section. The rear tube was changed and analyzed at 180, 240, 300, 360, 390, 420, 450, and 480 min. Breakthrough was observed after sampling for 500 min (corresponding to 25.0 liters). Data from two sorbent tube testing systems, shown in Table J-7, were used to determine a recommended sampling volume of 12 liters for *n*-butyl acetate. This volume corresponds to a 240 min sampling period, which is the maximum recommended sampling time regardless of breakthrough. Results are plotted in Figure J-7.

Table J-7. Sampler capacity data for *n*-butyl acetate.

test no.	air vol (L)	sampling time (min)	break-through (%)
1	9.22	180	0.00
	12.3	240	0.00
	15.4	300	0.00
	18.4	360	0.00
	20.0	390	0.00
	21.5	420	0.30
	23.0	450	1.9
	24.6	480	5.9
2	9.65	180	0.00
	12.9	240	0.00
	16.1	300	0.00
	19.3	360	0.00
	20.9	390	0.00
	22.5	420	0.50
	24.1	450	2.5
	25.7	480	7.1

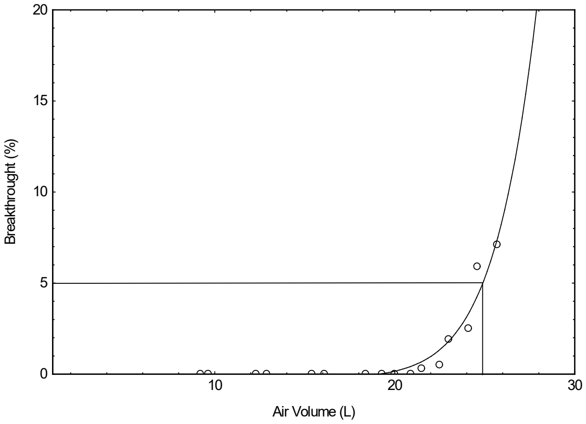

Figure J-7. Plot of data used to determine sampler capacity for *n*-butyl acetate. The 5% breakthrough volume shown is based on the curve in the figure, which is fit to the data provided in Table J-7.

8 Low Humidity

Pre-existing data from OSHA Method 1009[1] are presented in this section.

The effect of low humidity was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing *n*-butyl acetate nominally at two times the target concentration (calculated to be 302 ppm). The relative humidity and temperature of the air sampled were 20% and 23 °C, and the sampling flow rate was 50 mL/min. Samples were collected on three sorbent tubes for 240 min. After immediate analysis, results as a percentage of expected recovery were 99.6%, 99.9%, and 98.7%.

9 Chemical Interference

Pre-existing data from OSHA Method 1009[1] are presented in this section.

The effect of potential chemical sampling interference was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing *n*-butyl acetate nominally at the target concentration (calculated to be 151 ppm). The relative humidity and temperature of the air sampled were 80% and 23 °C, and the sampling flow rate was 50 mL/min. Hexone, *n*-butyl alcohol, and toluene were present as potential interferents, nominally at their permissible exposure limits of 100 ppm (calculated to be at 99 ppm, 101 ppm, and 100 ppm respectively). Samples were collected on three sorbent tubes for 240 min. After immediate analysis, results for *n*-butyl acetate as a percentage of expected recovery were 100.1%, 99.2%, and 97.6%.

10 Analytical Method Reproducibility

Pre-existing data from OSHA Method 1009[1] are presented in this section.

Samples were prepared by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing *n*-butyl acetate nominally at the target concentration (calculated to be 157.8 ppm). The relative humidity and temperature of the air sampled were not reported. Samples were collected on six sorbent tubes at a flow rate of 50 mL/min for 240 min. The resulting samples were submitted to the OSHA Salt Lake Technical Center for analysis using the procedures described in OSHA Method 1009 after storage for 5 days at 4 °C. The analytical results corrected for E_E are provided in Table J-8. No sample result for *n*-butyl acetate fell outside the permissible bounds set by the precision of the overall procedure determined in Section 5 of this appendix.

Table J-8. Reproducibility data for *n*-butyl acetate.

sampled (mg/sample)	recovered (mg/sample)	recovery (%)	deviation (%)
8.99	9.04	100.6	+0.6
8.99	8.88	98.8	-1.2
8.99	9.24	102.8	+2.8
8.99	8.98	99.9	-0.1
8.99	8.94	99.4	-0.6
8.99	8.53	94.9	-5.1

11 Effect of Sampling a Low Concentration

Pre-existing data from OSHA Method 1009[1] are presented in this section.

The effect of sampling a low concentration of *n*-butyl acetate vapor was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing *n*-butyl acetate nominally at one-tenth the target concentration (calculated to be 15 ppm). The relative humidity and temperature of the air sampled were 80% and 23 °C, and the sampling flow rate was 50 mL/min. Samples were collected on three sorbent tubes for 240 min. After immediate analysis, results for *n*-butyl acetate as a percentage of expected recovery were 100.9%, 99.5%, and 98.9%.

12 Estimation of Uncertainty

While systematic biases such as analyte storage loss are examined, and limits are placed on these, an estimation of uncertainty that encompasses both potential random and systematic error was not completed. Instead, the overall standard error of estimate was calculated from the random error inherent to the points about the regression line produced by the ambient storage test described in Section 5, as prescribed by the OSHA validation guidelines in use at the time OSHA Method 1009 was originally validated. See Section 5 of this appendix for details.

13 Controlled Test Atmosphere Procedure

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 *n*-butyl acetate 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 *n*-butyl acetate 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.

OSHA 5000, Appendix K
Isobutyl Acetate

Version:	1.0
OSHA PEL:	150 ppm (700 mg/m^3) 8-Hour TWA, General Industry, Construction, Shipyard
ACGIH TLV:	50 ppm (238 mg/m^3) 8-Hour TWA; 150 ppm (712 mg/m^3) 15-Minute STEL
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, STEL)
Reliable quantitation limit:	0.040 ppm (0.19 mg/m^3)
Standard error of estimate:	5.1%
Status of method:	Fully validated. Method 5000 has been subjected to the established validation procedures of the Method Development Team for sampling and analysis of isobutyl acetate.

January 2007 (OSHA 1009)	Mary Eide
February 2021 (OSHA 5000)	Uyen Bui, Daren Pearce

1 Introduction

1.1 Previous Methods used by OSHA for Sampling and Analysis of Isobutyl Acetate

The specific analyte described in this appendix is isobutyl acetate, CAS No. 110-19-0. The methodologies described in this appendix for isobutyl acetate are based on OSHA Method 1009.[1] That method requires the collection of samples using charcoal sorbent tubes, extraction using carbon disulfide, and analysis by gas chromatography using a flame ionization detector.

1.2 Changes to the Previously-Used Method

This appendix represents an update of OSHA Method 1009[1], which was fully validated at the time it was published based on the validation guidelines in effect at that time. Compared to the previous method used this method includes new analytical parameters. Data presented from the previously used method are identified by the statement "Pre-existing data from OSHA Method 1009[1] are presented in this section". The change was made to allow the standardized collection and analysis of isobutyl acetate with other analytes found in Organic Vapor Sampling Group 1, described in OSHA Method 5000.

1.3 Validation Parameters

The procedures used to develop the method validation data are described in Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis.[2] Air concentrations listed in ppm are referenced to 25 °C and 760 Torr.

---

[1] Eide, M. *n*-butyl acetate, isobutyl acetate, *sec*-butyl acetate, and *tert*-butyl acetate (OSHA Method 1009), 2007. United States Department of Labor, Occupational Safety & Health Administration Web site. https://www.osha.gov/dts/sltc/methods/validated/1009/1009.html (accessed March 2019).

[2] Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration Web site. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed December 2018).

The target concentration for method evaluation was the OSHA 8-hour time-weighted average (TWA) permissible exposure limit (PEL) for isobutyl acetate.

2 Detection and Quantification

2.1 Detection Limit of the Analytical Procedure (DLAP)

The DLAP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLAP $S_{y/x}$) divided by the slope of the line produced from analyses of ten analytical standards prepared with equally spaced increments of analyte mass. The standards were prepared in such a way that the highest standard concentration would produce a peak approximately 10 times the response of a reagent blank at or near the chromatographic retention time of the analyte. The standards and a reagent blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLAP $S_{y/x}$ and slope values for DLAP determination. Results obtained for these analyses are listed in Tables K-1 and plotted in Figure K-1.

Table K-1. DLAP data for isobutyl acetate.

concentration (µg/mL)	mass on column (pg)	area counts (µV·s)
0.00	0.00	0.00
0.871	5.81	0.0494
1.74	11.6	0.1377
2.61	17.4	0.2009
3.48	23.2	0.3108
4.36	29.0	0.3768
5.26	34.8	0.4551
6.10	40.6	0.5074
6.97	46.5	0.5725
7.84	52.3	0.6239
8.71	58.1	0.7159

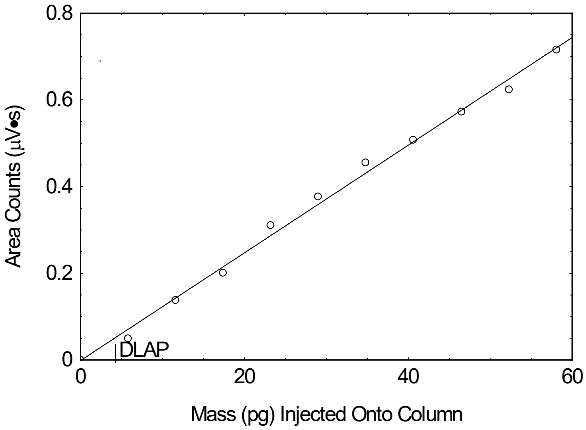

Figure K-1. Plot of data used to determine the DLAP for isobutyl acetate ($y = 0.0124x - 0.00141$, DLAP $S_{y/x}$ = 0.0177, DLAP = 4.28 pg).

2.2 Detection Limit of the Overall Procedure (DLOP) and Reliable Quantitation Limit (RQL)

The DLOP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLOP $S_{y/x}$) divided by the slope of the line produced from analyses of ten samples prepared from sorbent tubes spiked with equally spaced increments of analyte mass. 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 RQL is expressed as an air concentration that will provide sufficient analyte mass per sample that produces a response greater than 10× the $S_{y/x}$ divided by the slope of the line described above. The spiked samplers and a sample blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLOP $S_{y/x}$ and slope values for DLOP and RQL determinations. Results obtained from these analyses are listed in Table K-2 and plotted in Figure K-2.

Table K-2. DLOP and RQL data for isobutyl acetate.

mass per sample (µg/sample)	area counts (µV·s)
0.00	0.00
0.871	0.0590
1.74	0.139
2.61	0.211
3.48	0.309
4.36	0.329
5.23	0.409
6.10	0.475
6.97	0.513
7.84	0.605
8.71	0.652

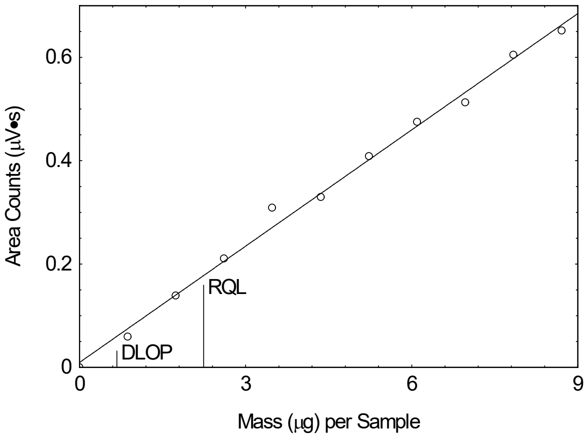

Figure K-2. Plot of data used to determine the DLOP and RQL for isobutyl acetate ($y = 0.0751x + 0.00955$, DLOP $S_{y/x}$ = 0.0169, DLOP = 0.675 µg/sample, RQL = 2.25 µg/sample or 0.040 ppm).

3 Analytical Precision Across the Calibration Range

Fifteen analytical standards over a range of 0.1 to 2 times the analyte concentration in solvent that would be obtained from sampling for the recommended time at the target concentration were analyzed with the recommended analytical parameters described in OSHA Method 5000. An ordinary least-squares linear regression curve was created by plotting the analyte mass per sample versus the corresponding ratio of analyte peak area to internal standard (ISTD) peak area. The resulting data provided the standard error of estimate (Calibration $S_{y/x}$) value across the calibration range, which provides an indication of the imprecision attributable to the instrumental analysis of the target analyte. Results from these analyses are listed in Table K-3, and plotted in Figure K-3.

Table K-3. Analytical precision data for isobutyl acetate.

× target	0.1×	0.5×	1.0×	1.5×	2.0×
concn (µg/sample)	871	4355	8710	13,065	17,420
area ratio	1.957	9.884	19.36	28.68	39.38
	1.958	9.866	19.41	28.53	39.41
	1.956	9.881	19.36	28.55	39.46

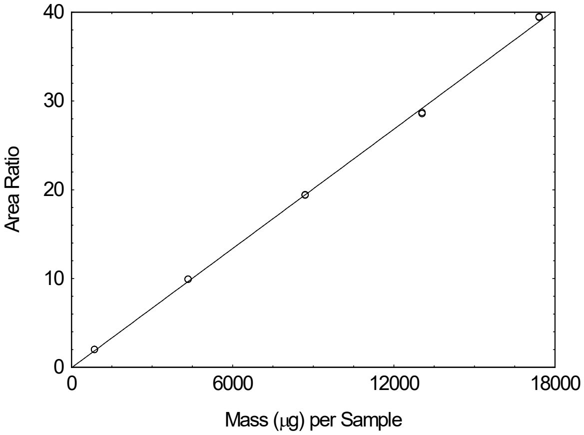

Figure K-3. Plot of data used to determine the precision of the analytical method for isobutyl acetate ($y = 0.00224x - 0.0560$, Calibration $S_{y/x}$ = 0.384).

4 Sampler Storage Stability

Pre-existing data from OSHA Method 1009[1] are presented in this section.

Storage stability test samples for isobutyl acetate were prepared by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13. Sampling from this system followed the recommended sampling parameters published in OSHA Method 5000. The nominal concentration of isobutyl acetate for both ambient and refrigerated storage testing was the target concentration (calculated to be 149 ppm). The relative humidity and temperature of the air sampled were 80% and 23 °C for both tests. For each test, eighteen samples were prepared and three of these were analyzed on the day that samples were created. The remaining fifteen refrigerated storage test samples were stored at reduced temperature (4 °C), while the remaining fifteen ambient storage test samples were kept in a closed drawer at ambient temperature (about 23 °C). For each storage condition, three samples were selected and analyzed from those remaining at 3-4 day intervals. The results of these analyses (uncorrected for extraction efficiency) are provided in Table K-4, and plotted in Figures K-4 through K-5.

The recovery of isobutyl acetate calculated from the regression line generated for the 17-day ambient storage test was 96.7%.

Table K-4. Sampler storage stability data for isobutyl acetate.

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	99.9	99.7	100.3	99.9	99.7	100.3
3	98.6	99.3	99.4	99.4	99.6	100.1
7	97.4	97.3	98.4	99.6	99.2	99.5
10	97.5	98.1	98.0	99.2	98.7	98.5
14	98.4	97.9	97.6	98.9	98.8	99.3
17	96.1	97.8	95.3	97.9	98.4	98.9

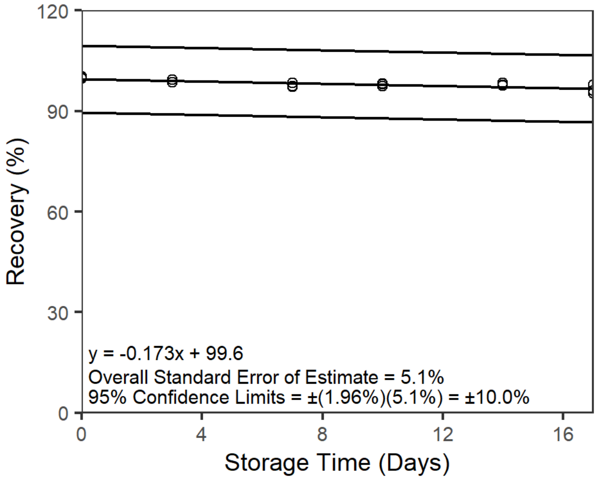

Figure K-4. Plot of ambient storage stability data for isobutyl acetate.

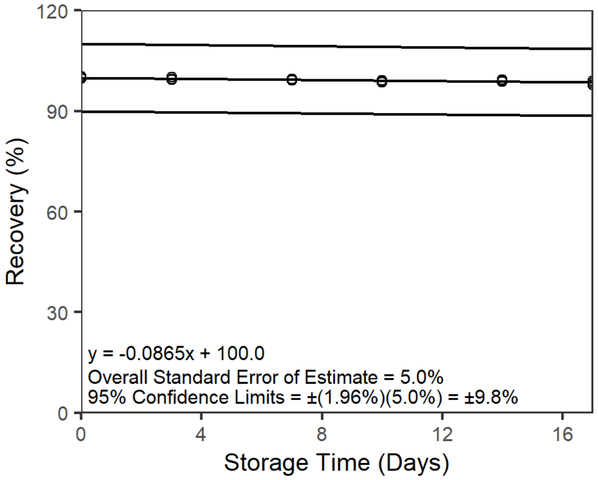

Figure K-5. Plot of refrigerated storage stability data for isobutyl acetate.

5 Precision of the Overall Procedure

Pre-existing data from OSHA Method 1009[1] are presented in this section.

The overall standard error of estimate obtained from the ambient storage test analyses described in Section 4 and sampling pump variability were used to determine the precision of the overall procedure, where all aspects of sampling and analysis (sampling, sorbent tube handling and solvent extraction, and instrumental analysis) are considered. This value was obtained by taking the square root of the squared ambient storage stability standard error of estimate (Storage $S_{y/x}^2$) added to the squared sampling pump variability value (V_{SP}^2). The resulting precision of the overall procedure at the 95% confidence level for the ambient 17-day storage test (at the target concentration) for isobutyl acetate was determined to be ±10.0% based on the observed ambient Storage $S_{y/x}$ value of 5.1% and V_{SP} value of 5.0%.

6 Recovery and Stability of Prepared Samples

Quantitative extraction 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 OSHA Method 5000. 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.

A value for extraction efficiency (E_E) was determined by liquid-spiking four replicate sorbent tubes across a range of analyte mass values that would be obtained from sampling at 0.1 to 2 times the target concentration value for 240 min. Four sorbent tubes were also spiked in this fashion at the target concentration after drawing humid air (80.2% relative humidity at 20.9 °C) through these tubes at 50 mL/min for 240 min. All of the samples described above were analyzed the following day after being kept overnight at ambient temperature. The E_E value at the RQL was 92.2%, while that of the working range samples (excluding the samples through which humid air had been drawn) was 101.4%. The data are shown in Table K-5. Pre-loading sorbent tubes with moisture ("wet" designation in the table) did not have an unacceptable effect on E_E.

Table K-5. Extraction efficiency data for isobutyl acetate.

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.1	871.0	101.3	102.1	101.2	100.9	101.4
0.25	2178	100.8	101.3	101.2	100.3	100.9
0.5	4355	99.9	98.8	99.3	98.3	99.1
1.0	8710	101.9	102.1	101.5	101.7	101.8
1.5	13065	102.4	102.2	101.8	102.9	102.3
2.0	17420	102.7	102.5	102.4	103.3	102.7
RQL	2.27	91.8	88.8	95.9	92.1	92.2
1.0 (wet)	8710	99.5	100.0	101.4	99.3	100.1

The stability of extracted samples prepared according to OSHA Method 5000 was examined retaining the sample solvent extracts for the target concentration samples described immediately above. Two of the four vials were immediately recapped with new septa following the initial analyses, and again following each re-analysis event. The other two vials retained the original punctured septa throughout. All four vials were re-analyzed at 24, 48, and 72 hours after the initial analyses, with all vials remaining in an autosampler tray kept at 22 °C. Freshly prepared standards were used for each analysis event, and each septum (whether new or previously used) was punctured four times for each injection. The resulting data are shown in Table K-6.

Table K-6. Extracted sample stability data for isobutyl acetate.

	punctured septa replaced recovery (%)		punctured septa retained recovery (%)	
time (days)	1	2	1	2
0	97.8	97.6	97.4	96.4
1	100.1	98.3	98.8	97.9
2	96.7	97.4	95.3	94.4
3	98.3	99.3	95.7	95.3

7 Sampler Capacity

Pre-existing data from OSHA Method 1009[1] are presented in this section.

The sampling capacity of the front section of a sorbent tube was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing isobutyl acetate nominally at two times the target concentration (calculated to be 298 ppm). The relative humidity and temperature of the air sampled were 80% and 23 °C, and the sampling flow rate was 50 mL/min. A sorbent tube testing system was made by placing a complete sorbent tube in series behind another tube containing only the front sorbent section. The rear tube was changed and analyzed at 180, 240, 300, 360, 390, 420, 450, and 480 min. Breakthrough was observed after sampling for 504 min (corresponding to 25.2 liters). Data from two sorbent tube testing systems, shown in Table K-7, were used to determine a recommended sampling volume of 12 liters for isobutyl acetate as described in OSHA Method 5000. This volume corresponds to a 240 min sampling period, which is the maximum recommended sampling time regardless of breakthrough. Results are plotted in Figure K-7.

Table K-7. Sampler capacity data for isobutyl acetate.

test no.	air vol (L)	sampling time (min)	break-through (%)
1	9.59	180	0.00
	12.8	240	0.00
	16.0	300	0.00
	19.2	360	0.00
	20.8	390	0.10
	22.4	420	0.50
	24.0	450	2.1
	25.6	480	8.6
2	10.2	180	0.00
	13.6	240	0.00
	17.0	300	0.00
	20.4	360	0.00
	22.1	390	0.40
	23.8	420	1.1
	25.5	450	3.9
	27.2	480	10.5

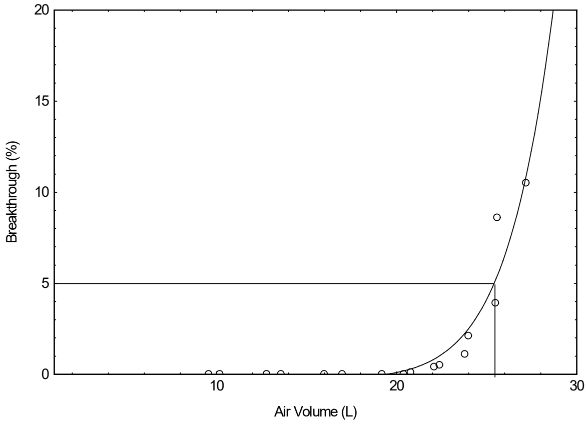

Figure K-7. Plot of data used to determine sampler capacity for isobutyl acetate. The 5% breakthrough volume shown is based on the curve in the figure, which is fit to the data provided in Table K-7.

8 Low Humidity

Pre-existing data from OSHA Method 1009[1] are presented in this section.

The effect of low humidity was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing isobutyl acetate nominally at two times the target concentration (calculated to be 298 ppm). The relative humidity and temperature of the air sampled were 20% and 23 °C, and the sampling flow rate was 50 mL/min. Samples were collected on three sorbent tubes for 240 min. After immediate analysis, results as a percentage of expected recovery were 99.9%, 99.1%, and 99.2%.

9 Chemical Interference

Pre-existing data from OSHA Method 1009[1] are presented in this section.

The effect of potential chemical sampling interference was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing isobutyl acetate nominally at the target concentration (calculated to be 149 ppm). The relative humidity and temperature of the air sampled were 80% and 23 °C, and the sampling flow rate was 50 mL/min. Hexone, *n*-butyl alcohol, and toluene were present as potential interferents, nominally at their permissible exposure limits (calculated to be at 99 ppm, 101 ppm, and 100 ppm respectively). Samples were collected on three sorbent tubes for 240 min. After immediate analysis, results for isobutyl acetate as a percentage of expected recovery were 100.8%, 99.3%, and 98.5%.

10 Analytical Method Reproducibility

Pre-existing data from OSHA Method 1009[1] are presented in this section.

Samples were prepared by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing isobutyl acetate nominally at the target concentration (calculated to be 157.8 ppm). The relative humidity and temperature of the air sampled were not reported, 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 Salt Lake Technical Center for analysis using the procedures described in OSHA Method 1009 after storage for 5 days at 4 °C. The analytical results corrected for E_E are provided in Table K-8. No sample result for isobutyl acetate fell outside the permissible bounds set by the precision of the overall procedure determined in Section 5 of this appendix.

Table K-8. Reproducibility data for isobutyl acetate.

sampled (mg/sample)	recovered (mg/sample)	recovery (%)	deviation (%)
8.90	8.78	98.7	-1.3
8.90	8.67	97.4	-2.6
8.90	8.98	100.9	+0.9
8.90	8.73	98.1	-1.9
8.90	8.66	97.3	-2.3
8.90	8.29	93.1	-6.9

11 Effect of Sampling a Low Concentration

Pre-existing data from OSHA Method 1009[1] are presented in this section.

The effect of sampling a low concentration of isobutyl acetate vapor was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing isobutyl acetate nominally at one-tenth the target concentration (calculated to be 15 ppm). The relative humidity and temperature of the air sampled were 80% and 23 °C, and the sampling flow rate was 50 mL/min. Samples were collected on three sorbent tubes for 240 min. After immediate analysis, results for isobutyl acetate as a percentage of expected recovery were 101.2%, 99.8%, and 99.3%.

12 Estimation of Uncertainty

While systematic biases such as analyte storage loss are examined, and limits are placed on these, an estimation of uncertainty that encompasses both potential random and systematic error was not completed. Instead, the overall standard error of estimate was calculated from the random error inherent to the points about the regression line produced by the ambient storage test described in Section 5, as prescribed by the OSHA validation guidelines in use at the time OSHA Method 1009 was originally validated. See Section 5 of this appendix for details.

13 Controlled Test Atmosphere Procedure

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 isobutyl acetate 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 isobutyl acetate 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.

OSHA 5000, Appendix L
Ethyl Acetate

Version:	1.0
OSHA PEL:	400 ppm (1400 mg/m^3) 8-Hour TWA, General industry, Construction, Shipyard
ACGIH TLV:	400 ppm (1400 mg/m^3) 8-Hour TWA
Recommended sampling time and sampling rate:	120 min at 50 mL/min (6 L)
Reliable quantitation limit:	0.051 ppm (0.18 mg/m^3)
Standard error of estimate:	5.8%
Status:	Partially validated. Method 5000 has been subjected to the established validation procedures of the Method Development Team for sampling and analysis of ethyl acetate.

February 2021 (OSHA 5000)

Anna Tang, Daren Pearce

1 Introduction

1.1 Previous Methods used by OSHA for Sampling and Analysis of Ethyl Acetate

The specific analyte described in this appendix is ethyl acetate, CAS No. 141-78-6. The methodologies described in this appendix for ethyl acetate replace OSHA Method 7, Organic Vapors[1], which simply described a modification of NIOSH Method 1457.[2] OSHA Method 7 required collection of samples using charcoal sorbent tubes, extraction using carbon disulfide containing 1% *N,N*-dimethylformamide, and analysis by gas chromatography using flame ionization detector.

1.2 Changes to the Previously-Used Method

This appendix represents a new method to replace OSHA Method 7, Organic Vapors[1] for sampling and analysis of ethyl acetate. Compared to the previous method used this method includes new analytical parameters, a new internal standard (ISTD), and a new sample collection flow rate and collection time. Data presented from the previously used method are identified by the statement "Pre-existing data from NIOSH Method 1457[2] are presented in this section". The changes were made to allow the standardized collection and analysis of ethyl acetate with other analytes found in Organic Vapor Sampling Group 1, described in OSHA Method 5000.

1.3 Validation Parameters

The procedures used to develop the method validation data are described in Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis.[3] Air concentrations listed in ppm are referenced to 25 °C and 760 Torr. The target concentration for method evaluation was the OSHA 8-hour time-weighted average (TWA) permissible exposure limit (PEL) for ethyl acetate.

---

[1] OSHA Method 7 Organic Vapors. United States Department of Labor, Occupational Safety & Health Administration Web site. https://www.osha.gov/dts/sltc/methods/archive/org007/org007.pdf (accessed March 2019).

[2] Pendegrass, S. Ethyl Acetate (NIOSH Method 1457, Issue 4), 1994. Center for Disease Control, The National Institute for Occupational Safety and Health (NIOSH) Web site. https://www.cdc.gov/niosh/docs/2003-154/pdfs/1457.pdf (accessed March 2019).

[3] Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration Web site. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed December 2018).

2 Detection and Quantification

2.1 Detection Limit of the Analytical Procedure (DLAP)

The DLAP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLAP $S_{y/x}$) divided by the slope of the line produced from analyses of ten analytical standards prepared with equally spaced increments of analyte mass. The standards were prepared in such a way that the highest standard concentration would produce a peak approximately 10 times the response of a reagent blank at or near the chromatographic retention time of the analyte. The standards and a reagent blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLAP $S_{y/x}$ and slope values for DLAP determination. Results obtained for these analyses are listed in Tables L-1, and plotted in Figure L-1.

Table L-1. DLAP data for ethyl acetate.

concentration (µg/sample)	mass on column (pg)	area counts (µV·s)
0.00	0.00	0.00
0.433	2.89	0.0660
0.866	5.77	0.120
1.30	8.67	0.142
1.73	11.5	0.158
2.16	14.4	0.228
2.60	17.3	0.267
3.03	20.2	0.302
3.46	23.1	0.346
3.90	26.0	0.410
4.33	28.9	0.436

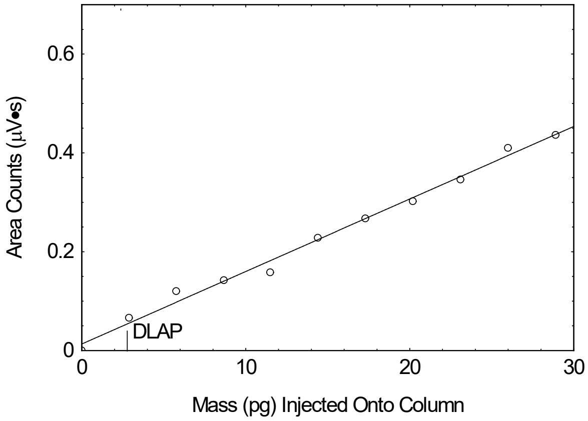

Figure L-1. Plot of data used to determine the DLAP for ethyl acetate ($y = 0.0147x + 0.0132$, DLAP $S_{y/x}$ = 0.0137, DLAP = 2.80 pg).

2.2 Detection Limit of the Overall Procedure (DLOP) and Reliable Quantitation Limit (RQL)

The DLOP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLOP $S_{y/x}$) divided by the slope of the line produced from analyses of ten samples prepared from sorbent tubes spiked with equally spaced increments of analyte mass. 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 RQL is expressed as an air concentration that will provide sufficient analyte mass per sample that produces a response greater than 10× DLOP $S_{y/x}$ divided by the slope of the line described above. The spiked samplers and a sample blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLOP $S_{y/x}$ and the slope values for DLOP and RQL determinations. Results obtained from these analyses are listed in Table L-2, and plotted in Figure L-2.

Table L-2. DLOP and RQL data for ethyl acetate.

mass per sample (µg/sample)	area counts (µV·s)
0.00	0.00
0.433	0.0500
0.866	0.0810
1.30	0.135
1.73	0.149
2.16	0.185
2.60	0.234
3.03	0.311
3.46	0.311
3.90	0.332
4.33	0.404

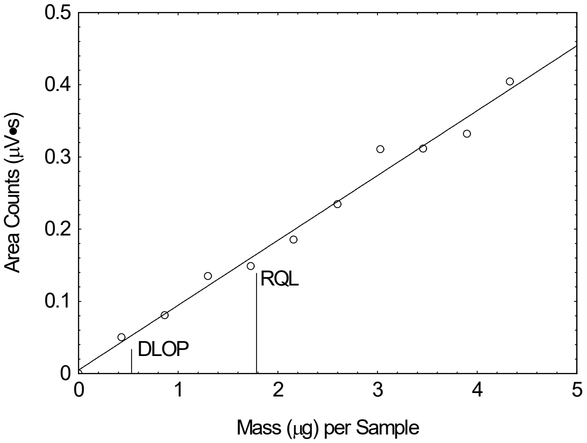

Figure L-2. Plot of data used to determine the DLOP and RQL for ethyl acetate ($y = 0.0898x + 0.00500$, DLOP $S_{y/x}$ = 0.0163, DLOP = 0.545 µg/sample, RQL = 1.82 µg/sample or 0.051 ppm).

3 Analytical Precision Across the Calibration Range

Fifteen analytical standards over a range of 0.1 to 2 times the analyte concentration in solvent that would be obtained from sampling for the recommended time at the target concentration were analyzed with the recommended analytical parameters described in OSHA Method 5000. An ordinary least-squares linear regression curve was created by plotting the analyte mass per sample versus the corresponding ratio of analyte peak area to internal standard (ISTD) peak area. The resulting data provided the standard error of estimate (Calibration $S_{y/x}$) value across the calibration range, which provides an indication of the imprecision attributable to the instrumental analysis of the target analyte. Results from these analyses are listed in Table L-3, and plotted in Figure L-3.

Table L-3. Analytical precision data for ethyl acetate.

× target	0.1×	0.5×	1.0×	1.5×	2.0×
concn (µg/sample)	798.9	4161	8015	12,608	16,043
area ratio	1.383	7.381	14.016	22.274	28.912
	1.389	8.020	14.795	22.538	28.674
	1.429	7.644	14.477	22.290	28.563

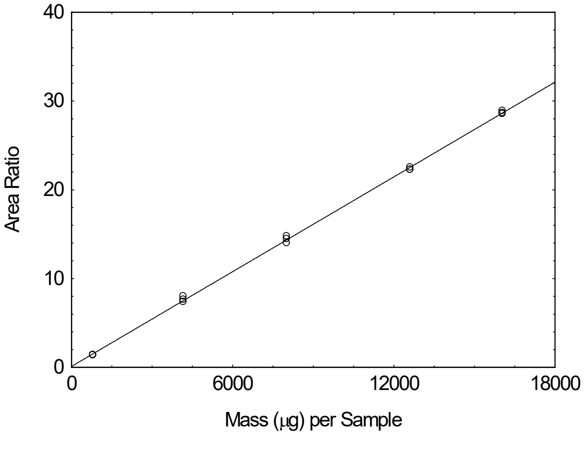

Figure L-3. Plot of data used to determine the precision of the analytical method for ethyl acetate ($y = 0.00178x + 0.107$, Calibration $S_{y/x}$ = 0.259).

4 Sampler Storage Stability

Pre-existing data from NIOSH Method 1457[2] are presented in this section.

Recovery of ethyl acetate following storage of analyte-laden sorbent tubes for 6 days at 5 °C was determined to be 91.0%. See NIOSH 1457[2] for details. Information regarding migration of ethyl acetate between sorbent tube sections is not available.

5 Precision of the Overall Procedure

Pre-existing data from NIOSH Method 1457[2] are presented in this section.

Based on the overall precision of NIOSH Method 1457 of 0.058 as reported by NIOSH researchers, the estimate of precision of the overall procedure was stated to be ±11.8% with 0.05 pump error added. [4]

6 Recovery and Stability of Prepared Samples

Quantitative extraction 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 OSHA Method 5000. 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.

A value for extraction efficiency (E_E) was determined by liquid-spiking four replicate sorbent tubes across a range of analyte mass values that would be obtained from sampling at 0.1 to 2 times the target concentration value for 240 min. Four sorbent tubes were also spiked in this fashion at the target concentration after drawing humid air (73.5% relative humidity at 25.0 °C) through these tubes at 50 mL/min for 4 hours. All of the samples described above were analyzed the following day after being kept overnight at ambient temperature. The E_E value at the RQL was 103.6%, while that of the working range samples (excluding the samples through which humid air had been drawn) was 96.4%. The data are shown in Table L-4. Pre-loading sorbent tubes with moisture ("wet" designation in the table) did not have an unacceptable effect on E_E.

Table L-4. Extraction efficiency data for ethyl acetate.

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.1	811.8	94.7	96.0	93.7	93.8	94.6
0.25	1804	91.4	94.8	92.2	95.1	93.4
0.5	4510	97.1	97.5	95.9	92.8	95.8
1.0	8118	95.1	98.9	98.1	98.0	97.5
1.5	12,628	98.3	97.3	98.9	99.5	98.5
2.0	16,236	98.2	98.7	100.1	97.1	98.5
RQL	1.73	107.1	100.0	107.1	100.0	103.6
1.0 (wet)	8118	99.0	97.0	95.9	96.7	97.2

The stability of sample extracts prepared according to OSHA Method 5000 was examined by retaining the sample solvent extracts for the target concentration samples described immediately above. Two of the four vials were immediately recapped with new septa following the initial analyses, and again following each re-analysis event. The other two vials retained the original punctured septa throughout. All four vials were re-analyzed at 24, 48, and 72 hours after the initial analyses, with all vials remaining in an autosampler tray kept at 22 °C. Freshly prepared standards were used for each analysis event, and each septum (whether new or previously used) was punctured four times for each injection. The resulting data are shown in Table L-5.

---

[4] NIOSH Manual of Analytical Methods, 2nd ed., V. 2, S49, U.S. Dept. of Health, Education, and Welfare, Publ. (NIOSH) 77-157B (1977).

Table L-5. Extracted sample stability data for ethyl acetate.

	punctured septa replaced recovery (%)		punctured septa retained recovery (%)	
time (days)	1	2	1	2
0	94.5	94.5	98.3	98.2
1	92.6	97.0	96.3	96.4
2	92.3	97.5	91.2	92.9
3	92.7	96.3	84.5	87.8

7 Sampler capacity

Pre-existing data from NIOSH Method 1457[2] are presented in this section.

Breakthrough (minimum of 5% of the front section recovery detected on rear sorbent section) was observed with a sampling volume of 8.55-L specified as “dry air”.[5] There is a comment in NIOSH Method 1457 that states that the applicability range was evaluated over 6 liters air volume. NIOSH Method S49 modified P&CAM 127 by reducing the air volume to 6 liters due to breakthrough.

8 Low Humidity

A study has not been undertaken to verify that sampling under low humidity conditions for ethyl acetate at the target concentration does not produce anomalous results.

9 Chemical Interference

A study has not been undertaken to verify that sampling another common organic vapor at high concentration concurrently with the sampling of ethyl acetate at the target concentration does not produce anomalous results.

10 Analytical Method Reproducibility

A study has not been undertaken to verify that independent analysis of sorbent tubes used to sample ethyl acetate does not produce results outside the boundaries of the precision of the overall procedure, described in Section 5 of this appendix.

11 Effect of Sampling a Low Concentration

A study has not been undertaken to verify the effect of sampling low concentrations of ethyl acetate.

12 Estimation of Uncertainty

While systematic biases are reported by NIOSH researchers, and limits are placed on these, an estimation of uncertainty that encompasses both potential random and systematic error was not completed by OSHA. See Section 5 of this appendix for details.

13 Controlled Test Atmosphere Procedure

A test atmosphere for ethyl acetate is mentioned in NIOSH Method S49[4], but details regarding the procedures used to create the test atmosphere are not available.

---

[5] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185(1977).

OSHA 5000, Appendix M
Heptane (*n*-Heptane)

Version:	1.0
OSHA PEL:	500 ppm (2000 mg/m^3) 8-Hour TWA, General Industry, Construction, Shipyard
ACGIH TLV:	400 ppm (1640 mg/m^3) 8-Hour TWA; 500 ppm (2050 mg/m^3) 15-Minute STEL
Recommended sampling time and sampling rate:	80 min at 50 mL/min (4 L)
Reliable quantitation limit:	0.076 ppm (0.31 mg/m^3)
Standard error of estimate:	5.9%
Status:	Partially validated. Method 5000 has been subjected to the established validation procedures of the Method Development Team for sampling and analysis of heptane (*n*-heptane).

February 2021 (OSHA 5000) Chelsea Burke, Daren Pearce

1 Introduction

1.1 Previous Methods used by OSHA for Sampling and Analysis of Heptane (*n*-Heptane)

The specific analyte described in this appendix is heptane (*n*-heptane), CAS No. 142-82-5. The methodologies described in this appendix for heptane (*n*-heptane) replace OSHA Method 7, Organic Vapors[1], which simply described a modification of NIOSH Method 1500.[2] OSHA Method 7 required collection of samples using charcoal sorbent tubes, extraction using carbon disulfide containing 1% *N,N*-dimethylformamide, and analysis by gas chromatography using a flame ionization detector.

1.2 Changes to the Previously-Used Method

This appendix represents a new method to replace OSHA Method 7, Organic Vapors[1] for sampling and analysis of heptane (*n*-heptane). Compared to the previous method used this method includes new analytical parameters, internal standard (ISTD), and sample collection flow rate and collection time. Data presented from the previously used method are not used. The changes were made to allow the standardized collection and analysis of heptane (*n*-heptane) with other analytes found in Organic Vapor Sampling Group 1, described in OSHA Method 5000.

1.3 Validation Parameters

The procedures used to develop the method validation data are described in Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis.[3] Air concentrations listed in ppm are referenced to 25 °C and 760 Torr.

---

[1] OSHA Method 7 Organic Vapors. United States Department of Labor, Occupational Safety & Health Administration Web site. https://www.osha.gov/dts/sltc/methods/archive/org007/org007.pdf (accessed March 2019).

[2] Pendegrass, S.; May, L. Hydrocarbons, BP 36 ºC-216 ºC (NIOSH Method 1500, Issue 3), 2003. Center for Disease Control, The National Institute for Occupational Safety and Health (NIOSH) Web site. http://www.cdc.gov/niosh/docs/2003-154/pdfs/1500.pdf (accessed October 2018).

[3] Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration Web site. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed December 2018).

The target concentration for method evaluation was the OSHA 8-hour time-weighted average (TWA) permissible exposure limit (PEL) for heptane (*n*-heptane).

2 Detection and Quantification

2.1 Detection Limit of the Analytical Procedure (DLAP)

The DLAP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLAP $S_{y/x}$) divided by the slope of the line produced from analyses of ten analytical standards prepared with equally spaced increments of analyte mass. The standards were prepared in such a way that the highest standard concentration would produce a peak approximately 10 times the response of a reagent blank at or near the chromatographic retention time of the analyte. The standards and a reagent blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLAP $S_{y/x}$ and slope values for DLAP determination. Results obtained for these analyses are listed in Tables M-1 and plotted in Figure M-1.

Table M-1. DLAP data for heptane (*n*-heptane).

concentration (µg/mL)	mass on column (pg)	area counts (µV·s)
0.00	0.00	0.00
0.342	2.28	0.0780
0.684	4.56	0.125
0.958	6.39	0.123
1.23	8.20	0.169
1.64	10.9	0.220
1.92	12.8	0.271
2.33	15.5	0.304
2.60	17.3	0.364
2.87	19.1	0.391
3.28	21.9	0.443

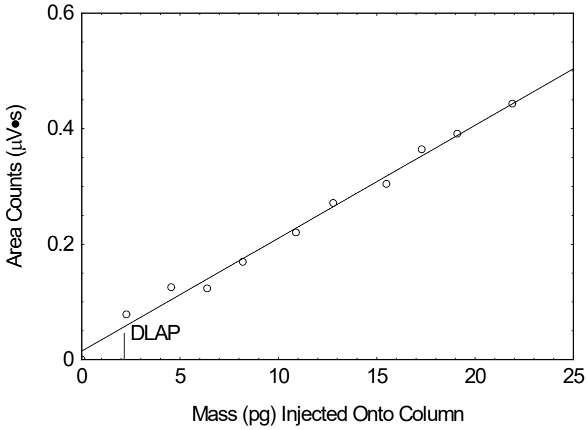

Figure M-1. Plot of data used to determine the DLAP for heptane (*n*-heptane, $y = 0.0196x + 0.0148$, DLAP $S_{y/x}$ = 0.0139, DLAP = 2.13 pg).

2.2 Detection Limit of the Overall Procedure (DLOP) and Reliable Quantitation Limit (RQL)

The DLOP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLOP $S_{y/x}$) divided by the slope of the line produced from analyses of ten samples prepared from sorbent tubes spiked with equally spaced increments of analyte mass. 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 RQL is expressed as an air concentration that will provide sufficient analyte mass per sample that produces a response greater than 10× DLOP $S_{y/x}$ divided by the slope of the line described above. The spiked samplers and a sample blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLOP $S_{y/x}$ and the slope values for DLOP and RQL determinations. Results obtained for this analysis are listed in Table M-2, and plotted in Figure M-2.

Table M-2. DLOP and RQL data for heptane (*n*-heptane).

mass per sample (µg/sample)	area counts (µV·s)
0.00	0.00
0.342	0.0410
0.684	0.0660
0.958	0.130
1.23	0.164
1.64	0.221
1.92	0.217
2.33	0.321
2.60	0.366
2.87	0.413
3.28	0.451

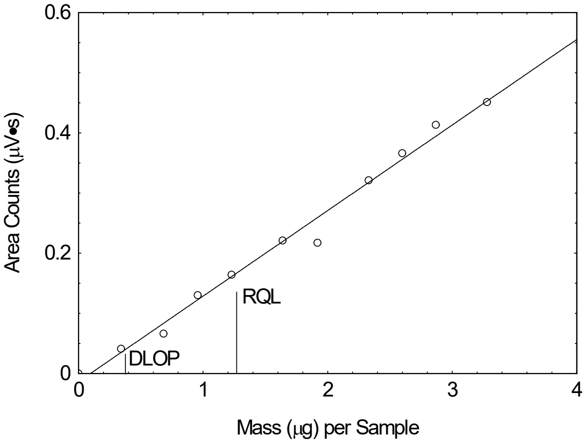

Figure M-2. Plot of data used to determine the DLOP and RQL for heptane (*n*-heptane, $y = 0.142x - 0.0142$, DLOP $S_{y/x}$ = 0.0178, DLOP = 0.376 µg/sample, RQL = 1.25 µg/sample or 0.076 ppm).

3 Analytical Precision Across the Calibration Range

Fifteen analytical standards over a range of 0.1 to 2 times the analyte concentration in solvent that would be obtained from sampling for the recommended time at the target concentration were analyzed with the recommended analytical parameters described in OSHA Method 5000. An ordinary least-squares linear regression curve was created by plotting the analyte mass per sample versus the corresponding ratio of analyte peak area to internal standard (ISTD) peak area. The resulting data provided the standard error of estimate (Calibration $S_{y/x}$) value across the calibration range, which provides an indication of the imprecision attributable to the instrumental analysis of the target analyte. Results from these analyses are listed in Table M-3, and plotted in Figure M-3.

Table M-3. Analytical precision data for heptane (*n*-heptane).

× target	0.1×	0.5×	1.0×	1.5×	2.0×
concn (µg/sample)	820.8	4104	8208	12,312	16,416
area ratio	3.295	16.51	32.84	48.71	64.86
	3.279	16.74	32.38	48.43	64.66
	3.305	16.23	32.77	48.78	64.57

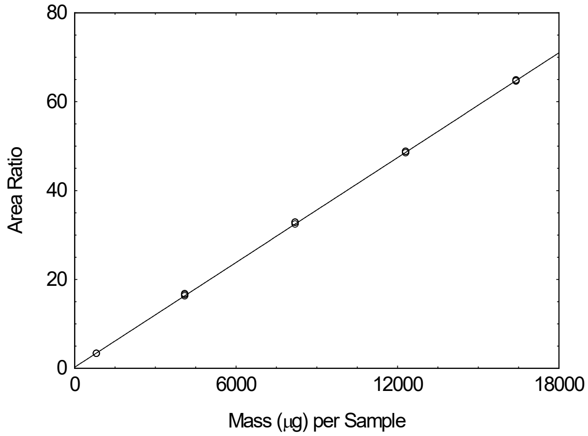

Figure M-3. Plot of data used to determine the precision of the analytical method for heptane (*n*-heptane, $y = 0.0039x + 0.237$, Calibration $S_{y/x}$ = 0.21)

4 Sampler Storage Stability

Storage stability test samples for heptane (*n*-heptane) were prepared by liquid-spiking sorbent tubes. The mass of heptane (*n*-heptane) spiked was equivalent to the mass that would be sampled at the target concentration in air for 80 min at a flow rate of 50 mL/min (calculated to be 501 ppm). Humid air (81.2% relative humidity at 20.3 °C) was drawn through the spiked sorbent tubes at 50 mL/min for 80 min. Twelve storage samples were prepared and three of these were analyzed on the day that samples were created. The remaining nine ambient storage test samples were stored in a closed drawer at ambient temperature (about 22°C). Three samples were selected and analyzed from those remaining at 4-7 day intervals. The results of these analyses (uncorrected for extraction efficiency) are provided in Table M-4 and plotted in Figure M-4. In eight of the samples, measurable analyte was found on the respective back sorbent tube sections. In seven of these cases, the analyte mass found on the back section was < 1.25% of the value detected from the front section, and in one case, the relative mass detected was 5.1% that of the front section recovery.

The recovery of heptane (*n*-heptane) calculated from the regression line generated for the 16-day ambient storage test was 101.8%.

Table M-4. Sampler storage stability data for heptane (*n*-heptane).

time (days)	ambient storage recovery (%)		
0	100.2	98.5	93.2
7	93.5	98.6	99.0
12	96.4	101.3	104.9
16	102.9	101.8	102.3

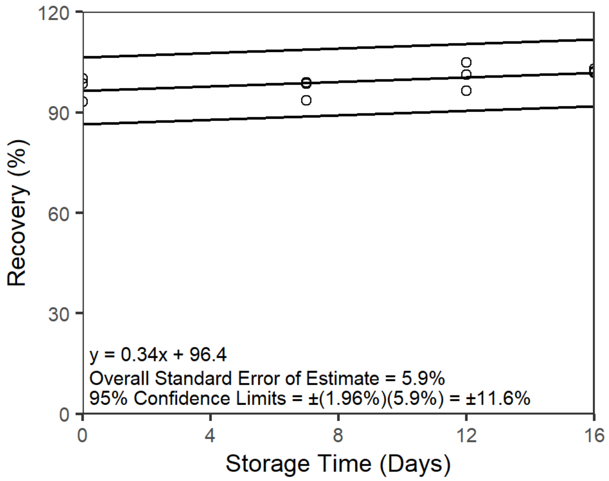

Figure M-4. Plot of the ambient storage stability data for heptane (*n*-heptane).

5 Precision of the Overall Procedure

The overall standard error of estimate obtained from the ambient storage test analyses described in Section 4 and sampling pump variability were used to determine the precision of the overall procedure, where all aspects of sampling and analysis (sampling, sorbent tube handling and solvent extraction, and instrumental analysis) are considered. This value was obtained by taking the square root of the squared ambient storage stability standard error of estimate (Storage $S^2_{y/x}$) added to the squared sampling pump variability value (V^2_{SP}). The resulting precision of the overall procedure at the 95% confidence level for the ambient 16-day storage test (at the target concentration) for heptane (*n*-heptane) was determined to be ±11.6% based on the observed ambient Storage $S_{y/x}$ value of 5.9% and V_{SP} value of 5.0%.

6 Recovery and Stability of Prepared Samples

Quantitative extraction 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 OSHA Method 5000. 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.

A value for extraction efficiency (E_E) was determined by liquid-spiking four replicate sorbent tubes across a range of analyte mass values that would be obtained from sampling at 0.1 to 2 times the target concentration value for 80 min. Four sorbent tubes were also spiked in this fashion at the target concentration after drawing humid air (76.0% relative humidity at 24.8 °C) through these tubes at 50 mL/min for 80 min. All of the samples described above were analyzed the following day after being kept overnight at ambient temperature The *E_E* value at the RQL was 100.1%, while that of the working range (excluding the sample through which humid air had been drawn) was 101.4%. The data are shown in Table M-5. Pre-loading sorbent tubes with moisture (“wet” designation in the table) did not have an unacceptable effect on *E_E*.

Table M-5. Extraction efficiency data for heptane (*n*-heptane).

level		sample number				
× target concn	µg per sample	1	2	3	4	Mean
0.1	820.8	102.0	101.1	101.3	101.0	101.4
0.25	2052	101.1	101.6	101.5	101.8	101.5
0.5	4104	101.5	102.7	100.6	100.3	101.3
1.0	8208	99.2	99.4	98.7	100.2	99.4
1.5	12,312	103.5	103.2	102.0	101.7	102.6
2.0	16,416	101.9	102.0	101.0	103.3	102.1
RQL	1.23	87.6	89.3	106.0	117.6	100.1
1.0 (wet)	8208	100.8	103.0	101.2	105.7	102.7

The stability of sample extracts prepared according to OSHA Method 5000 was examined by retaining the sample solvent extracts for the target concentration samples described immediately above. Two of the four vials were immediately recapped with new septa following the initial analyses, and again following each re-analysis event. The other two vials retained the original punctured septa throughout. All for vials were re-analyzed at 24, 48, and 72 hours after the initial analyses, with all vials remaining in an autosampler tray kept at 22 °C. Freshly prepared standards were used for each analysis event and each septum (whether new or previously used) was punctured four times for each injection. The data are shown in Table M-6.

Table M-6. Extracted sample stability data for heptane (*n*-heptane).

	punctured septa replaced recovery (%)		punctured septa retained recovery (%)	
time (days)	1	2	1	2
0	102.5	101.4	100.5	101.9
1	102.6	101.8	100.1	100.8
2	101.8	103.0	98.5	99.0
3	103.8	102.5	98.1	97.8

7 Sampler Capacity

The sampling capacity of the front section of a sorbent tube was tested by performing a sample media analyte retention test. Six sorbent tubes were spiked with heptane (n-heptane) at nominally twice the target concentration (calculated to be 1002 ppm). Air was then drawn through these sorbent tubes with a flow rate of 50 mL/min for 300 min. The relative humidity and temperature were 80.0% and 22.1 °C. Breakthrough was not observed after sampling for 300 min (corresponding to 15.0 liters). Data from six sorbent tubes, as shown in Table M-7, were used to determine the recommended sampling volume of 4 liters for heptane (*n*-heptane) as described in OSHA Method 5000. This volume corresponds to an 80 min sampling period, which is the maximum recommended sampling time regardless of breakthrough.

Table M-7. Retention data for heptane (n-heptane).

sample no.	air volume (L)	recovery front (%)	recovery back (%)
1	15	101.5	0.0
2	15	99.4	0.0
3	15	102.1	0.0
4	15	101.0	0.0
5	15	102.0	0.0
6	15	100.9	0.0

8 Low Humidity

A study has not been undertaken to verify that sampling under low humidity conditions for heptane (*n*-heptane) at the target concentration does not produce anomalous results.

9 Chemical Interference

A study has not been undertaken to verify that sampling another common organic vapor at high concentration concurrently with the sampling of heptane (*n*-heptane) at the target concentration does not produce anomalous results.

10 Analytical Method Reproducibility

A study has not been undertaken to verify that independent analysis of sorbent tubes used to sample heptane (*n*-heptane) does not produce results outside the boundaries of the precision of the overall procedure, described in Section 5 of this appendix.

11 Effect of Sampling a Low Concentration

A study has not been undertaken to verify the effect of sampling low concentrations of heptane (*n*-heptane).

12 Estimation of Uncertainty

While systematic biases such as analyte storage loss are examined, and limits are placed on these, an estimation of uncertainty that encompasses both potential random and systematic error was not completed. Instead, the overall standard error of estimate was calculated from the random error inherent to the points about the regression line produced by the ambient storage test described in Section 5, as prescribed by the OSHA validation guidelines in use at the time OSHA Method 5000 was originally validated. See Section 5 of this appendix for details.

13 Controlled Test Atmosphere Procedure

A controlled test atmosphere containing heptane (*n*-heptane) is not mentioned in validation work for NIOSH Method 1500[2].

OSHA 5000, Appendix N
sec-Butyl Acetate

Version:	1.0
OSHA PEL:	200 ppm (950 mg/m^3) 8-Hour TWA, General Industry, Construction, Shipyard
ACGIH TLV:	50 ppm (238 mg/m^3) 8-Hour TWA; 150 ppm (712 mg/m^3) 15-Minute STEL
Recommended sampling time and sampling rate:	240 min at 50 mL/min (12 L, 8-Hour TWA)
Reliable quantitation limit:	0.055 ppm (0.26 mg/m^3)
Standard error of estimate:	5.0%
Status of method:	Fully validated. Method 5000 has been subjected to the established validation procedures of the Method Development Team for sampling and analysis of *sec*-butyl acetate.

January 2007 (OSHA 1009)	Mary Eide
February 2021 (OSHA 5000)	Chelsea Burke, Daren Pearce

1 Introduction

1.1 Previous Methods used by OSHA for Sampling and Analysis of *sec*-Butyl Acetate

The specific analyte described in this appendix is *sec*-butyl acetate, CAS No. 105-46-4. The methodologies described in this appendix for *sec*-butyl acetate are based on OSHA Method 1009.[1] That method requires the collection of samples using charcoal sorbent tubes, extraction using carbon disulfide, and analysis by gas chromatography using a flame ionization detector.

1.2 Changes to the Previously-Used Method

This appendix represents an update of OSHA Method 1009[1], which was fully validated at the time it was published based on the validation guidelines in effect at that time. Compared to the previous method used this method includes new analytical parameters. Data presented from the previously used method are identified by the statement "Pre-existing data from OSHA Method 1009[1] are presented in this section". The changes were made to allow the standardized collection and analysis of *sec*-butyl acetate with other analytes found in Organic Vapor Sampling Group 1, described in OSHA Method 5000.

1.3 Validation Parameters

The procedures used to develop the method validation data are described in Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis.[2] Air concentrations listed in ppm are referenced to 25 °C and 760 Torr.

---

[1] Eide, M. *n*-butyl acetate, isobutyl acetate, *sec*-butyl acetate, and *tert*-butyl acetate (OSHA Method 1009), 2007. United States Department of Labor, Occupational Safety & Health Administration Web site. https://www.osha.gov/dts/sltc/methods/validated/1009/1009.html (accessed March 2019).

[2] Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration Web site. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed December 2018).

The target concentration for method evaluation was the OSHA 8-hour time-weighted average (TWA) permissible exposure limit (PEL) for *sec*-butyl acetate.

2 Detection and Quantification

2.1 Detection Limit of the Analytical Procedure (DLAP)

The DLAP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLAP $S_{y/x}$) divided by the slope of the line produced from analyses of ten analytical standards prepared with equally spaced increments of analyte mass. The standards were prepared in such a way that the highest standard concentration would produce a peak approximately 10 times the response of a reagent blank at or near the chromatographic retention time of the analyte. The standards and a reagent blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLAP $S_{y/x}$ and slope values for DLAP determination. Results obtained for these analyses are listed in Table N-1, and plotted in Figure N-1.

Table N-1. DLAP data for *sec*-butyl acetate.

concentration (μg/mL)	mass on column (pg)	area counts (μV·s)
0.00	0.00	0.00
0.692	4.61	0.0856
1.38	9.20	0.1318
2.08	13.9	0.2106
2.77	18.5	0.2732
3.46	23.1	0.3025
4.15	27.7	0.3312
4.84	32.3	0.4034
5.54	36.9	0.4656
6.23	41.5	0.4802
6.92	46.1	0.5807

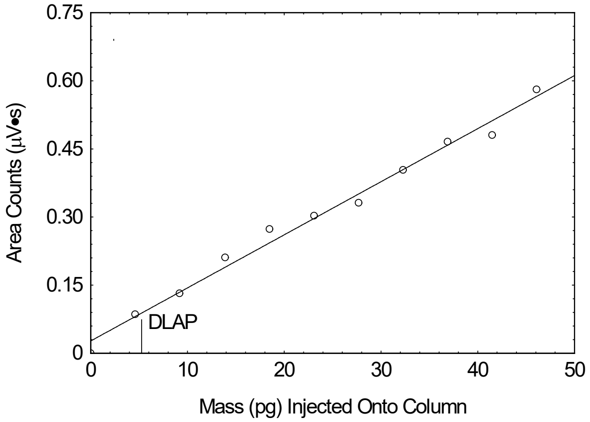

Figure N-1. Plot of data used to determine the DLAP for *sec*-butyl acetate ($y = 0.0117x + 0.0271$, DLAP $S_{y/x}$ = 0.0206, DLAP = 5.28 pg).

2.2 Detection Limit of the Overall Procedure (DLOP) and Reliable Quantitation Limit (RQL)

The DLOP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLOP $S_{y/x}$) divided by the slope of the line produced from analyses of ten samples prepared from sorbent tubes spiked with equally spaced increments of analyte mass. 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 RQL is expressed as an air concentration that will provide sufficient analyte mass per sample that produces a response greater than 10× DLOP $S_{y/x}$ divided by the slope of the line described above. The spiked samplers and a sample blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLOP $S_{y/x}$ and the slope values for DLOP and RQL determinations. Results obtained from this analysis are listed in Table N-2, and plotted in Figure N-2.

Table N-2. DLOP and RQL data for *sec*-butyl acetate.

mass per sample (µg/sample)	area counts (µV·s)
0.00	0.00
0.692	0.0535
1.38	0.1371
2.08	0.1965
2.77	0.2597
3.46	0.3088
4.15	0.3501
4.84	0.3923
5.54	0.3980
6.23	0.4876
6.92	0.5647

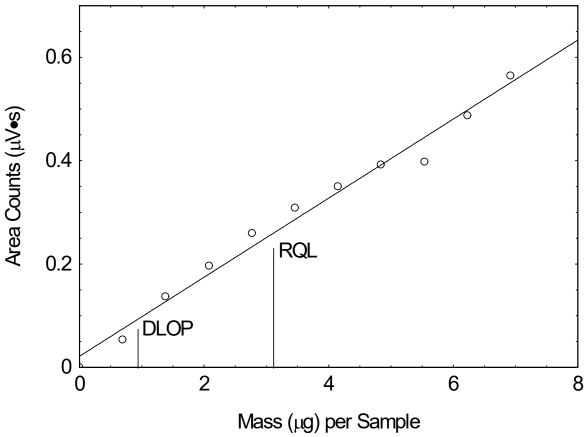

Figure N-2. Plot of data used to determine the DLOP and RQL for *sec*-butyl acetate ($y = 0.0765x + 0.0215$, DLOP $S_{y/x}$ = 0.0239, DLOP = 0.937 µg/sample, RQL = 3.12 µg/sample or 0.055 ppm).

3 Analytical Precision Across the Calibration Range

Fifteen analytical standards over a range of 0.1 to 2 times the analyte concentration in solvent that would be obtained from sampling for the recommended time at the target concentration were analyzed with the recommended analytical parameters described in OSHA Method 5000. An ordinary least-squares linear regression curve was created by plotting the analyte mass per sample versus the corresponding ratio of analyte peak area to internal standard (ISTD) peak area. The resulting data provided the standard error of estimate (Calibration $S_{y/x}$) value across the calibration range, which provides an indication of the imprecision attributable to the instrumental analysis of the target analyte. Results from these analyses are listed in Table N-3, and plotted in Figure N-3.

Table N-3. Analytical precision data for *sec*-butyl acetate.

× target	0.1×	0.5×	1.0×	1.5×	2.0×
concn (µg/sample)	1730	5190	10,380	15,570	20,760
area ratio	3.507	10.71	20.85	31.02	41.64
	3.745	10.79	20.90	31.01	41.05
	3.360	10.43	20.68	30.84	41.01

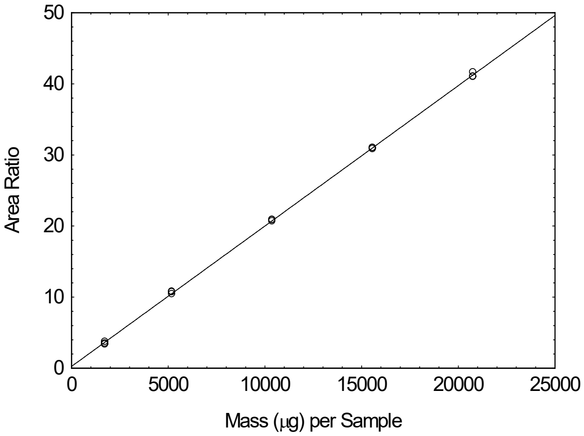

Figure N-3. Plot of data used to determine the precision of the analytical method for *sec*-butyl acetate ($y = 0.00197x + 0.254$, Calibration $S_{y/x}$ = 0.210)

4 Sampler Storage Stability

Pre-existing data from OSHA Method 1009[1] are presented in this section.

Storage stability test samples for *sec*-butyl acetate were prepared by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13. Sampling from this system followed the recommended sampling parameters published in OSHA Method 1009. The nominal concentration of *sec*-butyl acetate for both ambient and refrigerated storage testing was the target concentration (calculated to be 201 ppm). The relative humidity and temperature of the air sampled were 80% and 23 °C for both tests. For each test, eighteen samples were prepared and three of these were analyzed on the same day that samples were created. The remaining fifteen refrigerated storage test samples were stored at reduced temperature (4 °C), while the remaining fifteen ambient storage test samples were kept in a closed drawer at ambient temperature (about 22 °C). For each storage condition, three samples were selected and analyzed from those remaining at 3-4 day intervals. The results of these analyses (uncorrected for extraction efficiency) are provided in Table N-4 and plotted in Figures N-4 through N-5.

The recovery of *sec*-butyl acetate calculated from the regression line generated for the 17-day ambient storage test was 98.3%.

Table N-4. Sampler storage stability data *sec*-butyl acetate.

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	100.0	99.6	100.1	100.0	99.6	100.1
3	99.8	99.9	100.0	100.1	99.7	100.0
7	98.6	99.3	98.9	99.2	99.0	99.4
10	98.9	98.4	98.8	98.6	99.1	99.0
14	98.8	99.1	98.6	99.4	99.0	98.9
17	97.6	98.9	98.3	98.2	99.1	98.5

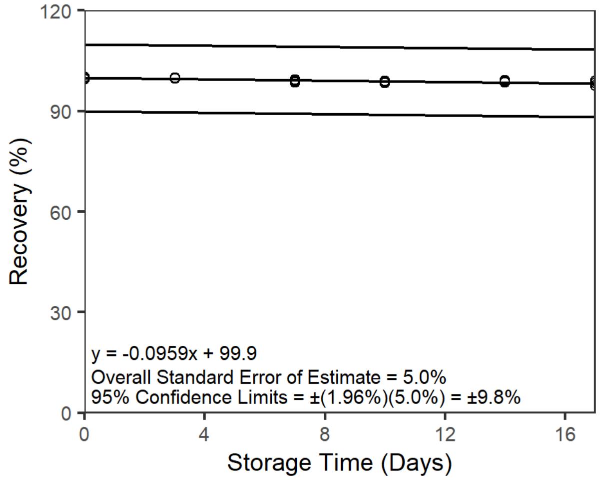

Figure N-4. Plot of ambient storage stability data for *sec*-butyl acetate.

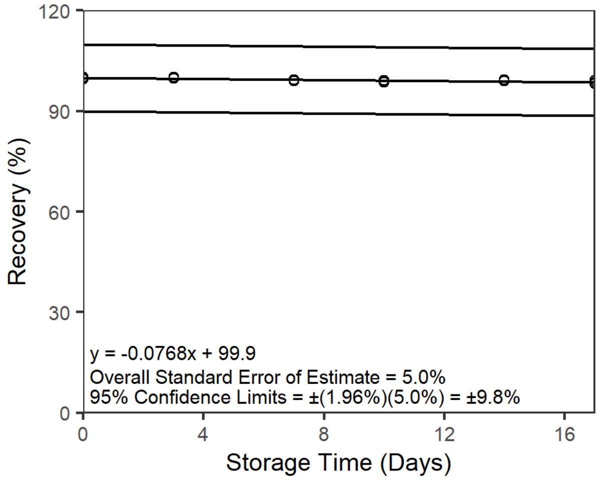

Figure N-5. Plot of refrigerated storage stability data for *sec*-butyl acetate.

5 Precision of the Overall Procedure

Pre-existing data from OSHA Method 1009[1] are presented in this section.

The overall standard error of estimate obtained from the ambient storage test analyses described in Section 4 and sampling pump variability were used to determine the precision of the overall procedure, where all aspects of sampling and analysis (sampling, sorbent tube handling and solvent extraction, and instrumental analysis) are considered. This value was obtained by taking the square root of the squared ambient storage stability standard error of estimate (Storage $S_{y/x}^2$) added to the squared sampling pump variability value (V_{SP}^2). The resulting precision of the overall procedure at the 95% confidence level for the ambient 17-day storage test (at the target concentration) for *sec*-butyl acetate was determined to be ±9.8% based on the observed ambient Storage $S_{y/x}$ value of 5.0% and V_{SP} value of 5.0%.

6 Recovery and Stability of Prepared Samples

Quantitative extraction is affected by the extraction solvent, the ISTD, the sampling medium, and the technique used to extract samples. The data presented demonstrate validity for extraction solvent, ISTD, sampling medium, and extraction technique described in OSHA Method 5000. 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.

A value for extraction efficiency (E_E) was determined by liquid-spiking four replicate sorbent tubes across a range of analyte mass values that would be obtained from sampling at 0.1 to 2 times the target concentration value for 240 min. Four sorbent tubes were also spiked in this fashion at the target concentration after drawing humid air (80.2% relative humidity at 20.9 °C) through these tubes at 50 mL/min for 4 hours. All of the samples described above were analyzed the following day after being kept overnight at ambient temperature. The E_E value at the RQL was 97.2%, while that of the working range samples (excluding the samples through which humid air had been drawn) was 98.7%. The data are shown in Table N-5. Pre-loading sorbent tubes with moisture ("wet" designation in the table) did not have an unacceptable effect on E_E.

Table N-5. Extraction efficiency data for *sec*-butyl acetate.

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.1	1730	97.4	97.9	96.2	96.3	97.0
0.25	3460	101.1	101.9	100.6	100.1	100.9
0.5	5190	95.8	95.9	96.7	98.7	96.8
1.0	10,380	98.0	99.2	100.4	98.3	99.0
1.5	15,570	99.9	98.3	97.9	100.1	99.1
2.0	20,760	99.4	98.9	99.4	99.2	99.2
RQL	4.16	97.4	98.1	105.1	88.2	97.2
1.0 (wet)	10,380	96.2	95.2	95.0	95.8	95.6

The stability of sample extracts prepared according to OSHA Method 5000 was examined by retaining the sample solvent extracts for the target concentration samples described immediately above. Two of the four vials were immediately recapped with new septa following the initial analyses, and again following each re-analysis event. The other two vials retained the original punctured septa throughout. All four vials were re-analyzed at 24, 48, and 72 hours after the initial analyses, with all the vials remaining in an autosampler tray kept at 22 °C. Freshly prepared standards were used with each analysis event and each septum (whether new or previously used) was punctured four times for each injection. The resulting data are shown in Table N-6.

Table N-6. Extracted sample stability data for *sec*-butyl acetate.

	punctured septa replaced recovery (%)		punctured septa retained recovery (%)	
time (days)	1	2	1	2
0	99.4	98.3	99.8	98.7
1	97.7	97.2	97.2	96.3
2	98.8	99.2	97.3	96.6
3	98.3	99.2	96.9	95.7

7 Sampler Capacity

Pre-existing data from OSHA Method 1009[1] are presented in this section.

The sampling capacity of the front section of a sorbent tube was tested by sampling from a dynamically generated controlled test atmosphere, using the system described in Section 13, containing *sec*-butyl acetate nominally at two times the target concentration (calculated to be 402 ppm). The relative humidity and temperature of the air sampled were 80% and 23 °C, and the sampling flow rate was 50 mL/min. A sorbent tube testing system was made by placing a complete sampling tube in series behind another tube, which contained only the front sorbent section. The rear tube was changed and analyzed at 120, 180, 240, 270, 300, 330, and 360 min. Data from two sorbent tube testing systems, shown in Table N-7, were used to determine a recommended sampling volume of 12 liters for *sec*-butyl acetate as described in OSHA Method 5000. This volume corresponds to a 240 min sampling period, which is the maximum recommended sampling time regardless of breakthrough. Results are plotted in Figure N-6.

Table N-7. Sampler capacity data for *sec*-butyl acetate.

sample no.	air vol (L)	sampling time (min)	break-through (%)
1	6.46	120	0.00
	9.68	180	0.00
	12.9	240	0.400
	14.5	270	1.0
	16.1	300	3.5
	17.7	330	8.3
	19.4	360	15.4
2	6.89	120	0.00
	10.3	180	0.00
	13.8	240	0.600
	15.5	270	1.2
	17.2	300	4.3
	18.9	330	9.9
	20.7	360	17.4

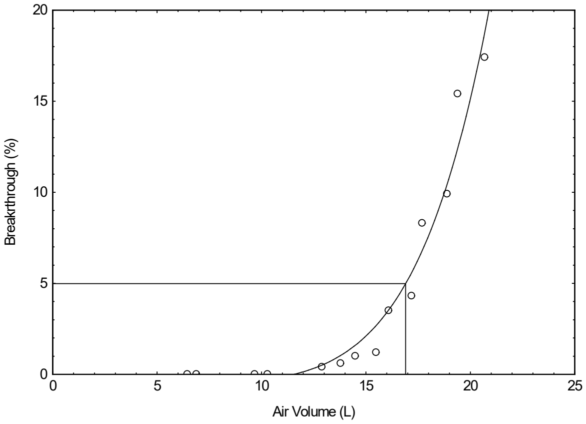

Figure N-6. Plot of data used to determine sampler capacity for *sec*-butyl acetate. The 5% breakthrough volume shown is based on the curve in the figure, which is fit to the data provided in Table N-7.

8 Low Humidity

Pre-existing data from OSHA Method 1009[1] are presented in this section.

The effect of low humidity was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing *sec*-butyl acetate nominally at two times the target concentration (calculated to be 402 ppm). The relative humidity and temperature of the air sampled were 20% and 23 °C, and the sampling flow rate was 50 mL/min. Samples were collected on three sorbent tubes for 240 min. After immediate analysis, results as a percentage of expected recovery were 99.8%, 99.4%, and 98.9%.

9 Chemical Interference

Pre-existing data from OSHA Method 1009[1] are presented in this section.

The effect of potential chemical sampling interference was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing *sec*-butyl acetate nominally at the target concentration (calculated to be 201 ppm). The relative humidity and temperature were 80% and 23 °C, and the sampling flow rate was 50 mL/min. Hexone, *n*-butyl alcohol, and toluene were present as potential interferents, nominally at their 8-hour TWA permissible exposure limits of 100 ppm (calculated to be at 99 ppm, 101 ppm, and 100 ppm). Samples were collected on three sorbent tubes for 240 min. After immediate analysis, results for *n*-butyl acetate as a percentage of expected recovery were 100.8%, 100.1%, and 98.3%.

10 Analytical Method Reproducibility

Pre-existing data from OSHA Method 1009[1] are presented in this section.

Samples were prepared by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing *sec*-butyl acetate nominally at the target concentration (calculated to be 180.7 ppm). The relative humidity and temperature of the air sampled were not reported, 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 Salt Lake Technical Center for analysis using the procedures described in OSHA Method 1009 after storage for 19 days at 4 °C. The analytical results corrected for E_E are provided in Table N-8. No sample result for *sec*-butyl acetate fell outside the permissible bounds set by the precision of the overall procedure determined in Section 5 of this appendix.

Table N-8. Reproducibility data for *sec*-butyl acetate.

sampled (mg/sample)	recovered (mg/sample)	recovery (%)	deviation (%)
10.3	9.98	96.9	-3.1
10.3	9.93	96.4	-3.6
10.3	9.79	95.0	-5.0
10.3	9.92	96.3	-3.7
10.3	9.82	95.3	-4.7
10.3	9.93	96.4	-3.6

11 Effect of Sampling a Low Concentration

Pre-existing data from OSHA Method 1009[1] are presented in this section.

The effect of sampling a low concentration of *sec*-butyl acetate vapor was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing *sec*-butyl acetate nominally at one-tenth the target concentration (calculated to be 20 ppm). The relative humidity and temperature of the air sampled were 80% and 23 °C, and the sampling flow rate was 50 mL/min. Samples were collected on three sorbent for 240 min. After immediate analysis, results for *sec*-butyl acetate as a percentage of expected recovery were 99.9%, 99.2%, and 98.3%.

12 Estimation of Uncertainty

While systematic biases such as analyte storage loss are examined, and limits are placed on these, an estimation of uncertainty that encompasses both potential random and systematic error was not completed. Instead, the overall standard error of estimate was calculated from the random error inherent to the points about the regression line produced by the ambient storage test described in Section 5, as prescribed by the OSHA validation guidelines in use at the time OSHA Method 1009[1] was originally validated. See Section 5 of this appendix for details.

13 Controlled Test Atmosphere Procedure

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 *sec*-butyl acetate 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 *sec*-butyl acetate 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.

OSHA 5000, Appendix O
tert-Butyl Acetate

Version:	1.0
OSHA PEL:	200 ppm (950 mg/m^3) 8-Hour TWA, General Industry, Construction, Shipyard
ACGIH TLV:	50 ppm (238 mg/m^3) 8-Hour TWA; 150 ppm (712 mg/m^3) 15-Minute STEL
Recommended sampling time and sampling rate:	240 min at 50 mL/min (12 L)
Reliable quantitation limit:	0.057 ppm (0.27 mg/m^3)
Standard error of estimate:	5.0%
Status:	Fully validated. Method 5000 has been subjected to the established validation procedures of the Method Development Team for sampling and analysis of *tert*-butyl acetate.

January 2007 (OSHA 1009)	Mary Eide
February 2021 (OSHA 5000)	Chelsea Burke, Daren Pearce

1 Introduction

1.1 Previous Methods used by OSHA for Sampling and Analysis of *tert*-Butyl Acetate

The specific analyte described in this appendix is *tert*-butyl acetate, CAS No. 540-88-5. The methodologies described in this appendix for *tert*-butyl acetate are based on OSHA Method 1009.[1] That method requires the collection of samples using charcoal sorbent tubes, extraction using carbon disulfide, and analysis by gas chromatography using a flame ionization detector.

1.2 Changes to the Previously-Used Method

This appendix represents an update of OSHA Method 1009[1], which was fully validated at the time it was published based on the validation guidelines in effect at that time. Compared to the previous method used this method includes new analytical parameters. Data presented from the previously used method are identified by the statement "Pre-existing data from OSHA Method 1009[1] are presented in this section". The changes were made to allow the standardized collection and analysis of *tert*-butyl acetate with other analytes found in Organic Vapor Sampling Group 1, described in OSHA Method 5000.

1.3 Validation Parameters

The procedures used to develop the method validation data are described in Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis.[2] Air concentrations listed in ppm are referenced to 25 °C and 760 Torr.

---

[1] Eide, M. *n*-butyl acetate, isobutyl acetate, *sec*-butyl acetate, and *tert*-butyl acetate (OSHA Method 1009), 2007. United States Department of Labor, Occupational Safety & Health Administration Web site. https://www.osha.gov/dts/sltc/methods/validated/1009/1009.html (accessed March 2019).

[2] Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration Web site. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed December 2018).

The target concentration for method evaluation was the OSHA 8-hour time-weighted average (TWA) permissible exposure limit (PEL) for *tert*-butyl acetate.

2 Detection and Quantification

2.1 Detection limit of the analytical procedure (DLAP)

The DLAP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLAP $S_{y/x}$) divided by the slope of the line produced from analyses of ten analytical standards prepared with equally spaced increments of analyte mass. The standards were prepared in such a way that the highest standard concentration would produce a peak approximately 10 times the response of a reagent blank at or near the chromatographic retention time of the analyte. The standards and a reagent blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLAP $S_{y/x}$ and slope values for DLAP determination. Results obtained for these analyses are listed in Table O-1, and plotted in Figure O-1.

Table O-1. DLAP data for *tert*-butyl acetate.

concentration (µg/mL)	mass on column (pg)	area counts (µV·s)
0.00	0.00	0.00
0.693	4.62	0.0038
1.39	9.27	0.1389
2.08	13.9	0.1868
2.77	18.5	0.2258
3.47	23.1	0.2764
4.16	27.7	0.3547
4.85	32.3	0.4098
5.55	37.0	0.4342
6.24	41.6	0.5611
6.93	46.2	0.5878

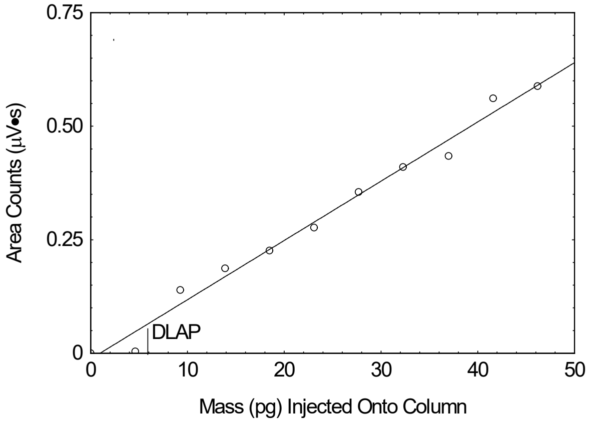

Figure O-1. Plot of data used to determine the DLAP for *tert*-butyl acetate ($y = 0.0130x - 0.0125$, $S_{y/x}$ = 0.0254, DLAP = 5.86 pg).

2.2 Detection Limit of the Overall Procedure (DLOP) and Reliable Quantitation Limit (RQL)

The DLOP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLOP $S_{y/x}$) divided by the slope of the line produced from analyses of ten samples prepared from sorbent tubes spiked with equally spaced increments of analyte mass. 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 RQL is expressed as an air concentration that will provide sufficient analyte mass per sample that produces a response greater than 10× DLOP $S_{y/x}$ divided by the slope of the line described above. The spiked samplers and a sample blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLOP $S_{y/x}$ and the slope values for DLOP and RQL determinations. Results obtained from this analysis are listed below in Table O-2, and plotted in Figure O-2.

Table O-2. DLOP and RQL data for *tert*-butyl acetate.

mass per sample (µg/sample)	area counts (µV·s)
0.00	0.0000
2.08	0.1997
2.77	0.2264
3.47	0.2970
4.16	0.3416
4.85	0.4189
5.55	0.4401
6.24	0.4792
6.93	0.5656
7.63	0.5754
8.32	0.7175

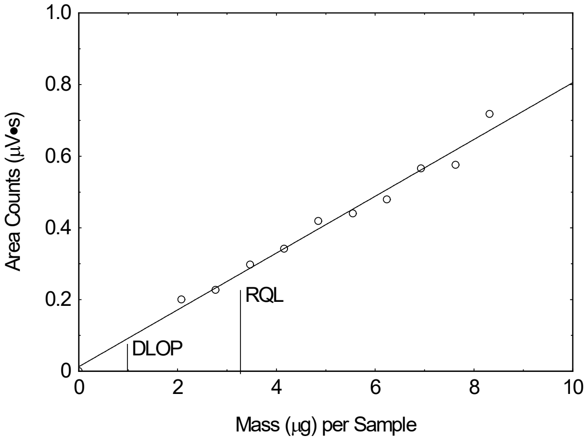

Figure O-2. Plot of data used to determine the DLOP and RQL for *tert*-butyl acetate ($y = 0.0793x + 0.0127$, DLOP $S_{y/x}$ = 0.0259, DLOP = 0.980 µg/sample, RQL = 3.27 µg/sample or 0.057 ppm).

3 Analytical Precision Across the Calibration Range

Fifteen analytical standards over a range of 0.1 to 2 times the analyte concentration in solvent that would be obtained from sampling for the recommended time at the target concentration were analyzed with the recommended analytical parameters described in OSHA Method 5000. An ordinary least-squares linear regression curve was created by plotting the analyte mass per sample versus the corresponding ratio of analyte peak area to internal standard (ISTD) peak area. The resulting data provided the standard error of estimate (Calibration $S_{y/x}$) value across the calibration range, which provides an indication of the imprecision attributable to the instrumental analysis of the target analyte. Results from these analyses are listed in Table O-3, and plotted in Figure O-3.

Table O-3. Analytical precision data for *tert*-butyl acetate.

× target	0.1×	0.5×	1.0×	1.5×	2.0×
concn (µg/sample)	1126	6066	12,131	18,197	24,262
area ratio	2.407	13.24	25.97	39.12	51.76
	2.418	13.10	25.85	38.60	51.58
	2.449	13.19	25.94	38.83	51.46

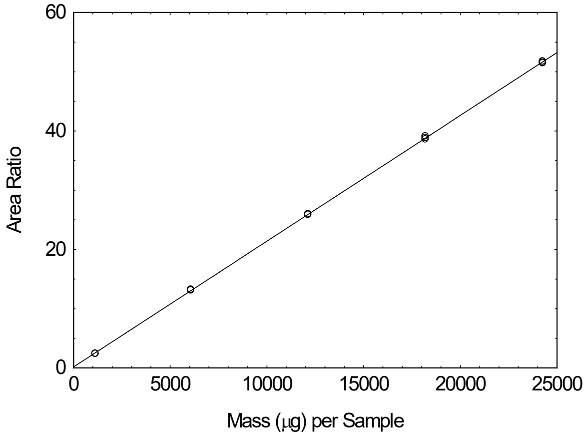

Figure O-3. Plot of data used to determine the precision of the analytical method for *tert*-butyl acetate ($y = 0.00212x + 0.159$, Calibration $S_{y/x}$ = 0.159).

4 Sampler Storage Stability

Pre-existing data from OSHA Method 1009[1] are presented in this section.

Storage stability test samples for *tert*-butyl acetate were prepared by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13. Sampling from this system followed the recommended sampling parameters published in OSHA Method 1009. The nominal concentration of *tert*-butyl acetate for both the ambient and refrigerated storage testing was the target concentration (calculated to be 203 ppm). The relative humidity and temperature of the air sampled were 80% and 23 °C for both tests. For each test, eighteen samples were prepared and three of these were analyzed on the day that samples were created. The remaining fifteen refrigerated storage test samples were stored at reduced temperature (4 °C), while the remaining fifteen ambient storage test samples were kept in a closed drawer at ambient temperature (about 23 °C). For each storage condition, three samples were selected and analyzed from those remaining at 3-4 day intervals. The results of these analyses (uncorrected for extraction efficiency) are provided in Table O-4 and plotted in Figures O-4 through O-5.

The recovery of *tert*-butyl acetate calculated from the regression line generated for the 17-day TWA ambient storage test was 97.8%.

Table O-4. Sampler storage stability data for *tert*-butyl acetate.

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	99.7	99.8	100.3	99.7	99.8	100.3
3	98.7	99.3	98.1	99.3	99.9	100.2
7	99.0	98.7	99.1	99.0	99.3	99.4
10	98.2	98.6	98.9	98.6	99.1	99.3
14	98.8	98.4	98.6	99.2	98.9	98.6
17	96.9	97.3	98.1	98.0	97.4	98.3

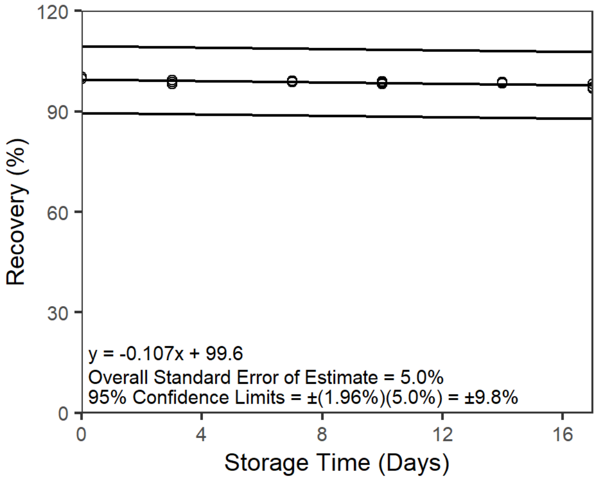

Figure O-4. Plot of ambient storage stability data for *tert*-butyl acetate.

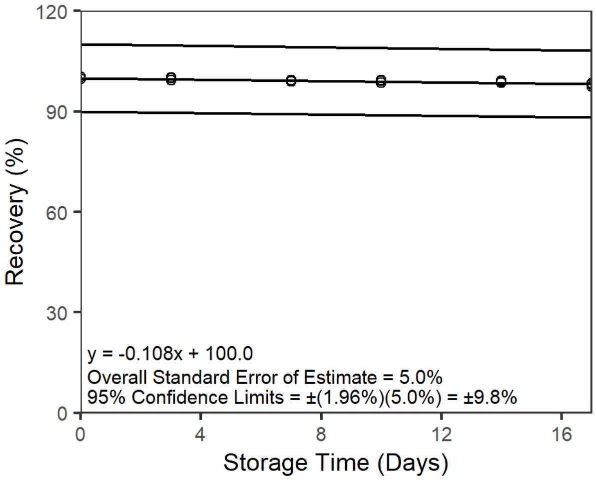

Figure O-5. Plot of refrigerated storage stability data for *tert*-butyl acetate.

5 Precision of the Overall Procedure

Pre-existing data from OSHA Method 1009[1] are presented in this section.

The overall standard error of estimate obtained from the ambient storage test analyses described in Section 4 and sampling pump variability were used to determine the precision of the overall procedure, where all aspects of sampling and analysis (sampling, sorbent tube handling and solvent extraction, and instrumental analysis) are considered. This value was obtained by taking the square root of the squared ambient storage stability standard error of estimate (Storage $S_{y/x}^2$) added to the squared sampling pump variability value (V_{SP}^2). The resulting precision of the overall procedure at the 95% confidence level for the ambient 17-day storage test (at the target concentration) for *tert*-butyl acetate was determined to be ±9.8% based on the observed ambient Storage $S_{y/x}$ value of 5.0% and V_{SP} value of 5.0%.

6 Recovery and Stability of Prepared Samples

Quantitative extraction is affected by the extraction solvent, the ISTD, the sampling medium, and the technique used to extract samples. The data presented demonstrate validity for extraction solvent, ISTD, sampling medium, and extraction technique described in OSHA Method 5000. 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.

A value for extraction efficiency (E_E) was determined by liquid-spiking four replicate sorbent tubes across a range of analyte mass values that would be obtained from sampling at 0.1 to 2 times the target concentration value for 240 min. Four sorbent tubes were also spiked in this fashion at the target concentration after drawing humid air (80.2% relative humidity at 20.9 °C) through these tubes at 50 mL/min for 240 min. All of the samples described above were analyzed the following day after being kept overnight at ambient temperature. The E_E value at the RQL was 103.0%, while that of the working range samples (excluding the samples through which humid air had been drawn) was 99.0%. The data are shown in Table O-5. Pre-loading the sorbent tubes with moisture ("wet" designation in the table) did not have an unacceptable effect on E_E.

Table O-5. Extraction efficiency data for *tert*-butyl acetate.

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.1	1140	99.1	99.6	98.1	98.3	98.8
0.25	2850	100.3	99.1	100.2	99.7	99.8
0.5	5700	95.0	96.8	96.8	94.2	95.7
1.0	11,400	98.2	99.1	98.1	99.1	98.6
1.5	17,100	100.4	100.5	100.1	99.5	100.1
2.0	22,800	102.1	101.0	100.6	101.2	101.2
RQL	5.13	99.3	102.0	97.7	113.1	103.0
1.0 (wet)	11,400	99.4	98.6	98.2	98.0	98.5

The stability of sample extracts prepared according to OSHA Method 5000 was examined by retaining the sample solvent extracts for the target concentration samples described immediately above. Two of the four vials were immediately recapped with new septa following the initial analyses, and again following each re-analysis event. The other two vials retained the original punctured septa throughout. All four vials were re-analyzed at 24, 48, and 72 hours after the initial analyses, with all the vials remaining in an autosampler tray kept at 22 °C. Freshly prepared standards were used with each analysis event and each septum (whether new or previously used) was punctured four times for each injection. The resulting data are shown in Table O-6.

Table O-6. Extracted sample stability data for *tert*-butyl acetate.

	punctured septa replaced recovery (%)		punctured septa retained recovery (%)	
time (days)	1	2	1	2
0	98.8	98.9	98.6	99.8
1	98.2	98.8	97.5	98.8
2	97.2	97.9	94.4	95.2
3	96.4	97.3	90.5	90.2

7 Sampler Capacity

Pre-existing data from OSHA Method 1009[1] are presented in this section.

The sampling capacity of the front section of a sorbent tube was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing *tert*-butyl acetate nominally at two times the target concentration (calculated to be 406 ppm), at 50 mL/min. The relative humidity and temperature of the air sampled were 80% and 23 °C, and the sampling flow rate was 50 mL/min. A sorbent tube testing system was made by placing a complete sorbent tube in series behind another tube, which contained only the front sorbent section. The rear tube was changed and analyzed at 120, 180, 240, 270, 300, 330, and 360 min. Data from three sorbent tube testing systems, shown in Table O-7, were used to determine a recommended sampling volume of 12 liters for *tert*-butyl acetate as described in OSHA Method 5000. This volume corresponds to a 240 min sampling period, which is the maximum recommended sampling time regardless of breakthrough. Results are plotted in Figure O-7.

Table O-7. Sampler capacity data for *tert*-butyl acetate.

sample no.	air vol (L)	sampling time (min)	break-through (%)
1	6.32	120	0.00
	9.49	180	0.00
	12.7	240	0.00
	14.2	270	0.00
	15.8	300	1.5
	17.4	330	3.9
	19.0	360	9.8
2	6.35	120	0.00
	9.52	180	0.00
	12.7	240	0.00
	14.3	270	0.00
	15.9	300	0.80
	17.5	330	2.8
	19.0	360	10.3

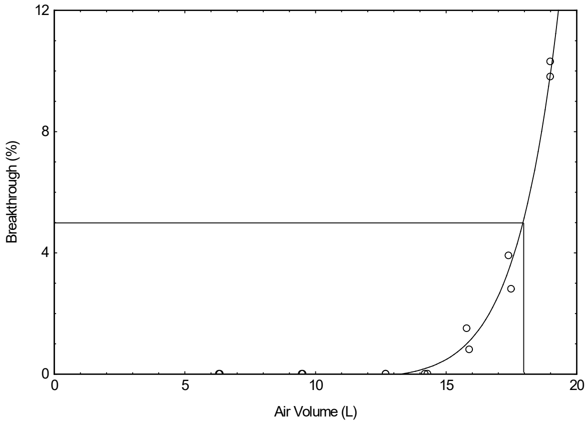

Figure O-6. Plot of data used to determine sampler capacity for *tert*-butyl acetate. The 5% breakthrough volume shown is based on the curve in the figure, which is fit to the data provided in Table O-7.

8 Low Humidity

Pre-existing data from OSHA Method 1009[1] are presented in this section.

The effect of low humidity was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing *tert*-butyl acetate nominally at two times the target concentration (calculated to be 406 ppm). The relative humidity and temperature of the air sampled were 20% and 23 °C, and the sampling flow rate was 50 mL/min. Samples were collected on three sorbent tubes for 240 min. After immediate analysis, results as a percentage of expected recovery were 99.9%, 99.3%, and 99.4%.

9 Chemical Interference

Pre-existing data from OSHA Method 1009[1] are presented in this section.

The effect of potential chemical sampling interference was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing *tert*-butyl acetate nominally at the target concentration (calculated to be 203 ppm). The relative humidity and temperature of the air sampled were 80% and 23 °C, and the sampling flow rate was 50 mL/min. Hexone, *n*-butyl alcohol, and toluene were present as potential interferents, nominally at their permissible exposure limits of 100 ppm (calculated to be 99 ppm, 101 ppm, and 100 ppm respectively). Samples were collected on three sorbent tubes for 240 min. After immediate analysis, results for *tert*-butyl acetate as a percentage of expected recovery were 100.9%, 98.6%, and 98.1%.

10 Analytical Method Reproducibility

Pre-existing data from OSHA Method 1009[1] are presented in this section.

Samples were prepared by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing *tert*-butyl acetate nominally at the target concentration (calculated to be 179.0 ppm). The relative humidity and temperature of the air sampled were not reported, 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 Salt Lake Technical Center for analysis using the procedures described in OSHA Method 1009 after storage for 19 days at 4 °C. The analytical results corrected for E_E are provided in Table O-8. No sample result for *tert*-butyl acetate fell outside the permissible bounds set by the precision of the overall procedure determined in Section 5 of this appendix.

Table O-8. Reproducibility data for *tert*-butyl acetate.

sampled (mg/sample)	recovered (mg/sample)	recovery (%)	deviation (%)
10.2	9.77	95.8	-4.2
10.2	9.73	95.4	-4.6
10.2	9.60	94.1	-5.9
10.2	9.80	96.1	-3.9
10.2	9.57	93.8	-6.2
10.2	9.70	95.1	-4.9

11 Effect of Sampling a Low Concentration

Pre-existing data from OSHA Method 1009[1] are presented in this section.

The effect of low concentration was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing *tert*-butyl acetate nominally at one-tenth the target concentration (calculated to be 20 ppm). The relative humidity and temperature of the air sampled were 80% and 23 °C, and the sampling flow rate was 50 mL/min. Samples were collected on three sorbent tubes for 240 min. After immediate analysis, results for *tert*-butyl acetate as a percentage of expected recovery were 99.8%, 99.4%, and 98.0%.

12 Estimation of Uncertainty

While systematic biases such as analyte storage loss are examined, and limits are placed on these, an estimation of uncertainty that encompasses both potential random and systematic error was not completed. Instead, the overall standard error of estimate was calculated from the random error inherent to the points about the regression line produced by the ambient storage test described in Section 5, as prescribed by the OSHA validation guidelines in use at the time OSHA Method 1009 was originally validated. See Section 5 of this appendix for details

13 Controlled Test Atmosphere Procedure

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 *tert*-butyl acetate 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 *tert*-butyl acetate 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.

OSHA 5000, Appendix P
n-Propyl Acetate

Version:	1.0
OSHA PEL:	200 ppm (840 mg/m^3) 8-Hour TWA, General Industry, Construction, Shipyard
ACGIH TLV:	200 ppm (840 mg/m^3)
Recommended sampling time and sampling rate:	200 min at 50 mL/min (10 L)
Reliable quantitation limit:	0.090 ppm (0.38 mg/m^3)
Standard error of estimate:	5.7%
Status:	Fully validated. Method 5000 has been subjected to the established validation procedures of the Method Development Team for sampling and analysis of *n*-propyl acetate.

May (1979, 2000) (OSHA 7)
February 2021 (OSHA 5000)

Methods Development Team
Chelsea Burke, Carmen Riberas, Daren Pearce

1 Introduction

1.1 Previous Methods used by OSHA for Sampling and Analysis of *n*-Propyl Acetate

The specific analyte described in this appendix is *n*-propyl acetate, CAS No. 109-60-4. The methodologies described in this appendix for *n*-propyl acetate replace OSHA Method 7, Organic Vapors[1], which simply described a modification of NIOSH Method 1450.[2] OSHA Method 7 required collection of samples using charcoal sorbent tubes, extraction using carbon disulfide containing 1% *N,N*-dimethylformamide, and analysis by gas chromatography using a flame ionization detector.

1.2 Changes to the Previously-Used Method

This appendix represents a new method to replace OSHA Method 7, Organic Vapors[1] for sampling and analysis of *n*-propyl acetate. Compared to the previous method used this method includes new analytical parameters, internal standard (ISTD), and sample collection flow rate and collection time. Data presented from the previously used method are identified by the statement "Pre-existing data from NIOSH Method 1450[2] are presented in this section". The changes were made to allow the standardized collection and analysis of *n*-propyl acetate with other analytes found in Organic Vapor Sampling Group 1, described in OSHA Method 5000.

---

[1] OSHA Method 7 Organic Vapors. United States Department of Labor, Occupational Safety & Health Administration Web site. https://www.osha.gov/dts/sltc/methods/archive/org007/org007.pdf (accessed March 2019).

[2] Yoon, Y.; Perkins, J.; Reynolds, J.; Esters I (NIOSH Method 1450, Issue 3), 2003. Center for Disease Control, The National Institute for Occupational Safety and Health (NIOSH) Web site. https://www.cdc.gov/niosh/docs/2003-154/pdfs/1450.pdf (accessed May 2019).

1.3 Validation Parameters

The procedures used to develop the method validation data are described in Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis.[3] Air concentrations listed in ppm are referenced to 25 °C and 760 Torr. The target concentration for method evaluation was the OSHA 8-hour time-weighted average (TWA) permissible exposure limit (PEL) for *n*-propyl acetate.

2 Detection and Quantification

2.1 Detection limit of the analytical procedure (DLAP)

The DLAP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLAP $S_{y/x}$) divided by the slope of the line produced from analyses of ten analytical standards prepared with equally spaced increments of analyte mass. The standards were prepared in such a way that the highest standard concentration would produce a peak approximately 10 times the response of a reagent blank at or near the chromatographic retention time of the analyte. The standards and a reagent blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLAP $S_{y/x}$ and slope values for DLAP determination. Results obtained for these analyses are listed below in Table P-1, and plotted in Figure P-1.

Table P-1. DLAP data for *n*-propyl acetate.

concentration (µg/mL)	mass on column (pg)	area counts (µV·s)
0.00	0.00	0.00
0.402	2.68	0.00
0.804	5.36	0.0157
1.21	8.07	0.0323
1.61	10.7	0.0625
2.01	13.4	0.0797
2.41	16.1	0.1159
2.81	18.7	0.1454
3.22	21.5	0.1484
3.62	24.1	0.1798
4.02	26.8	0.2050

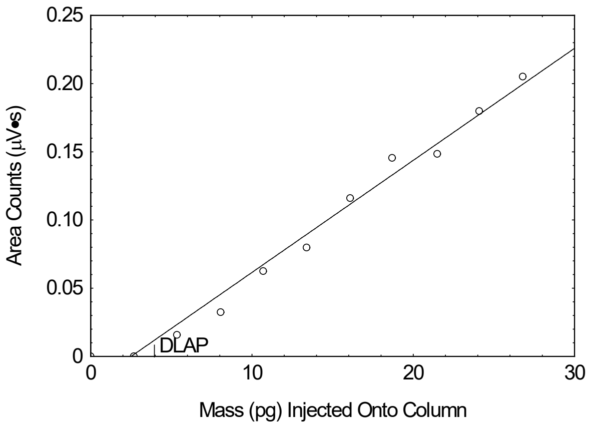

Figure P-1. Plot of data used to determine the DLAP for *n*-propyl acetate ($y = 0.00821x$ - 0.0206, DLAP $S_{y/x}$ = 0.0108, DLAP = 3.95 pg).

2.2 Detection Limit of the Overall Procedure (DLOP) and Reliable Quantitation Limit (RQL)

The DLOP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLOP $S_{y/x}$) divided by the slope of the line produced from analyses of ten samples prepared from sorbent tubes spiked with equally spaced increments of analyte mass. 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 RQL is expressed as an air concentration that will provide sufficient analyte mass per sample that produces a response greater than 10× DLOP $S_{y/x}$ divided by the slope of the line described above. The spiked samplers and a sample blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLOP $S_{y/x}$ and the slope values for DLOP and RQL determinations. Results obtained from these analyses are listed in Table P-2, and plotted in Figure P-2.

---

[3] Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration Web site. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed December 2018).

Table P-2. DLOP and RQL data for *n*-propyl acetate.

mass per sample (µg/sample)	area counts (µV·s)
0.00	0.00
0.402	0.00
0.804	0.0217
1.21	0.0414
1.61	0.0708
2.01	0.0721
2.41	0.1546
2.81	0.1611
3.22	0.1594
3.62	0.1932
4.02	0.1771

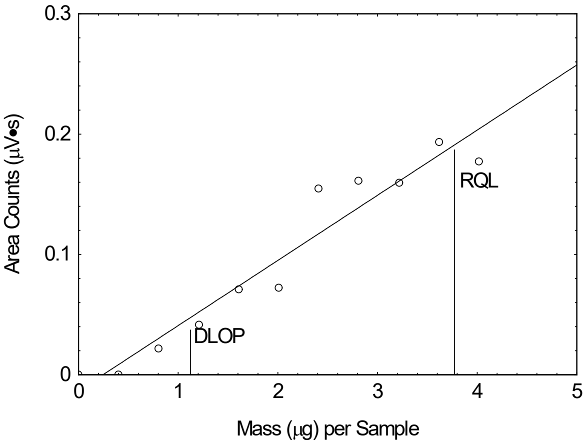

Figure P-2. Plot of data used to determine the DLOP and RQL for *n*-propyl acetate ($y = 0.0541x - 0.0133$, DLOP $S_{y/x}$ = 0.0204, DLOP = 1.13 µg/sample, RQL = 3.77 µg/sample or 0.090 ppm).

3 Analytical Precision Across the Calibration Range

Fifteen analytical standards over a range of 0.1 to 2 times the analyte concentration in solvent that would be obtained from sampling for the recommended time at the target concentration were analyzed with the recommended analytical parameters described in OSHA Method 5000. An ordinary least-squares linear regression curve was created by plotting the analyte mass per sample versus the corresponding ratio of analyte peak area to internal standard (ISTD) peak area. The resulting data provided the standard error of estimate (Calibration $S_{y/x}$) value across the calibration range, which provides an indication of the imprecision attributable to the instrumental analysis of the target analyte. Results from these analyses are listed in Table P-3, and plotted in Figure P-3.

Table P-3. Analytical precision data for *n*-propyl acetate.

× target	0.1×	0.5×	1.0×	1.5×	2.0×
concn (µg/sample)	840	4200	8400	12,600	16,800
area ratio	1.943	9.886	19.51	28.71	38.35
	1.934	9.802	18.86	28.46	37.81
	1.928	9.650	18.78	28.22	37.50

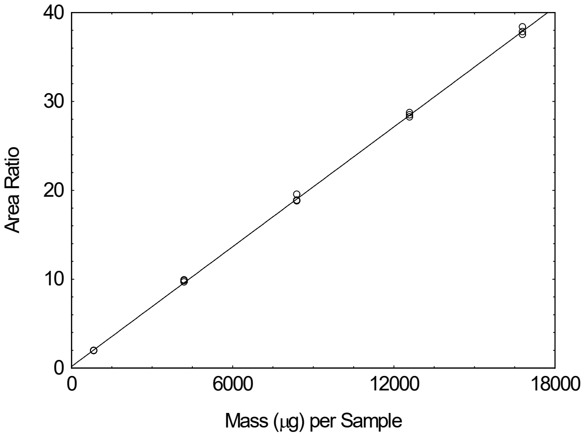

Figure P-3. Plot of data used to determine the precision of the analytical method for *n*-propyl acetate ($y = 0.0022x + 0.179$, Calibration $S_{y/x}$ = 0.27).

4 Sampler Storage Stability

Pre-existing data from NIOSH Method 1450^{2} are presented in this section.

Recovery of *n*-propyl acetate following storage of analyte-laden sorbent tubes for 30 days at 4 °C was determined to be 98%. See NIOSH Method1450 for details. Information regarding migration of n-propyl acetate between sorbent tube sections is not available.

5 Precision of the Overall Procedure

Pre-existing data from NIOSH Method 1450[2] are presented in this section.

Based on the overall precision of NIOSH Method 1450 of 0.0566 as reported by NIOSH researchers, the estimate of precision of the overall procedure was stated to be ±0.162 with 0.05 pump error added.

6 Recovery and Stability of Prepared Samples

Quantitative extraction 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 OSHA Method 5000. 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.

A value for the extraction efficiency (E_E) was determined by liquid-spiking four replicate sorbent tubes across a range of analyte mass values that would be obtained from sampling at 0.1 to 2 times the target concentration value for 240 min. Four sorbent tubes were also spiked in this fashion at the target concentration after drawing humid air (79.6% relative humidity at 22.6 °C) through these tubes at 50 mL/min for 200 min. All of the samples described above were analyzed the following day after being kept overnight at ambient temperature. The E_E value at the RQL was 91.5% while that of the working range samples (excluding the samples through which humid air had been drawn) was 97.5%. The data are shown in Table P-4. Pre-loading sorbent tubes with moisture ("wet" designation in the table) did not have an unacceptable effect on E_E.

Table P-4. Extraction efficiency data for *n*-propyl acetate.

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.1	836	98.4	96.8	96.2	94.5	96.5
0.25	2174	97.3	97.5	96.1	96.8	96.9
0.5	4180	97.3	95.6	96.0	97.1	96.5
1.0	8360	98.4	97.0	99.6	97.1	98.0
1.5	12,540	99.6	98.8	98.3	99.2	99.0
2.0	16,720	97.4	96.9	97.7	99.5	97.9
RQL	3.85	90.0	92.1	89.7	94.0	91.5
1.0 (wet)	8360	95.5	94.9	93.5	93.7	94.4

The stability of sample extracts prepared according to OSHA Method 5000 was examined by retaining the sample solvent extracts for the target concentration samples described immediately above. Two of the four vials were immediately recapped with new septa following the initial analyses, and again following each re-analysis event. The other two vials retained the original punctured septa throughout. All four vials were re-analyzed at 24, 48, and 72 hours after the initial analyses, with all the vials remaining in an autosampler tray kept at 22 °C. Freshly prepared standards were used with each analysis event and each septum (whether new or previously used) was punctured four times for each injection. The resulting data are shown in Table P-5.

Table P-5. Extracted sample stability data for *n*-propyl acetate.

	punctured septa replaced recovery (%)		punctured septa retained recovery (%)	
time (days)	1	2	1	2
0	98.5	97.2	97.4	96.5
1	95.4	96.5	97.0	95.7
2	96.0	96.8	94.3	95.2
3	96.0	96.1	92.7	94.0

7 Sampler capacity

Pre-existing data from NIOSH Method1450[2] and NIOSH Method S48[4] are presented in this section.

Breakthrough (minimum of 5% of front section recovery detected on rear sorbent section) was observed with sampling volume of 17.9-L specified as “dry air.”

8 Low Humidity

A study has not been undertaken to verify that sampling under low humidity conditions for *n*-propyl acetate at the target concentration does not produce anomalous results.

9 Chemical Interference

A study has not been undertaken to verify that sampling another common organic vapor at high concentration concurrently with the sampling of *n*-propyl acetate at the target concentration does not produce anomalous results.

10 Analytical Method Reproducibility

A study has not been undertaken to verify that independent analysis of sorbent tubes used to sample *n*-propyl acetate does not produce results outside the boundaries of the precision of the overall procedure, described in Section 5 of this appendix.

11 Effect of Sampling a Low Concentration

A study has not been undertaken to verify the effect of sampling a low concentration of *n*-propyl acetate vapor.

12 Estimation of Uncertainty

Pre-existing data from NIOSH Method 1450[2] are presented in this section.

Bias of 6.9%, accuracy of 16.2%, and overall precision ($\hat{S}_{rT}$) of 0.0566 were noted for *n*-propyl acetate from studying a range of 384 to 1610 mg/m^3.

13 Controlled Test Atmosphere Procedure

Controlled test atmospheres were generated for work done to complete NIOSH Method 1450[2], but details sufficient to reproduce the procedures used to create the test atmosphere are not available.

---

[4] *NIOSH Manual of Analytical Methods,* 2nd ed. Vol. 1; U.S. Department of Health, Education and Welfare, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health; Cincinnati, OH, 1977, Method S48 Backup Data Report.

OSHA 5000, Appendix Q
n-Hexane

Version:	1.0
OSHA PEL:	500 ppm (1800 mg/m^3) 8-Hour TWA, General Industry, Construction, Shipyard
ACGIH TLV:	50 ppm (176 mg/m^3) 8-Hour TWA
Recommended sampling time and Sampling rate:	98 min at 50 mL/min (4.9 L)
Reliable quantitation limit:	0.093 ppm (0.33 mg/m^3)
Standard error of estimate at the target concentration:	5.4%
Status:	Fully validated. Method 5000 has been subjected to the established validation procedures of the Method Development Team for sampling and analysis of *n*-hexane.

February 2021 (OSHA 5000)

Daren Pearce

1 Introduction

1.1 Previous Methods used by OSHA for Sampling and Analysis of *n*-Hexane

The specific analyte described in this appendix is *n*-hexane, CAS No. 110-54-3. The methodologies described in this appendix for *n*-hexane replace OSHA Method PV2248.[1] OSHA Method PV2248 required collection of samples using charcoal tubes, extraction using carbon disulfide, and analysis by gas chromatography using a flame ionization detector.

1.2 Changes to the Previously-Used Method

This appendix represents a new method to replace OSHA Method PV2248[1] for sampling and analysis of *n*-hexane. Compared to the previous method used this method includes new analytical parameters, internal standard (ISTD), and sample collection flow rate and collection time. The changes were made to allow the standardized collection and analysis of *n*-hexane with other analytes found in Organic Vapor Sampling Group 1, described in OSHA Method 5000.

1.3 Validation Parameters

The procedures used to develop the method validation data are described in Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis.[2] Air concentrations listed in ppm are referenced to 25 °C and 760 Torr. The target concentration for method evaluation was the OSHA 8-hour time-weighted average (TWA) permissible exposure limit (PEL) for *n*-hexane.

---

[1] Shah, Y. *n*-Hexane (OSHA Method PV2248), 1995. United States Department of Labor, Occupational Safety & Health Administration Web site. https://www.osha.gov/dts/sltc/methods/partial/pv2248/pv2248.pdf (accessed April 2019).

[2] Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration Web site. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed December 2018).

2 Detection and Quantification

2.1 Detection Limit of the Analytical Procedure (DLAP)

The DLAP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLAP $S_{y/x}$) divided by the slope of the line produced from analyses of ten analytical standards prepared with equally spaced increments of analyte mass. The standards were prepared in such a way that the highest standard concentration would produce a peak approximately 10 times the response of a reagent blank at or near the chromatographic retention time of the analyte. The standards and a reagent blank were analyzed with the recommended analytical parameters described in OHSA Method 5000. The resulting data provided the DLAP $S_{y/x}$ and slope values for DLAP determination. Results obtained for these analyses are listed in Table Q-1, and plotted in Figure Q-1.

Table Q-1. DLAP data for *n*-hexane.

concentration (µg/mL)	mass on column (pg)	area counts (µV·s)
0	0.00	0.00
0.529	3.53	0.0750
1.06	7.07	0.141
1.59	10.6	0.226
2.12	14.1	0.280
2.64	17.6	0.384
3.17	21.1	0.407
3.70	24.7	0.474
4.23	28.2	0.531
4.76	31.7	0.597
5.29	35.3	0.644

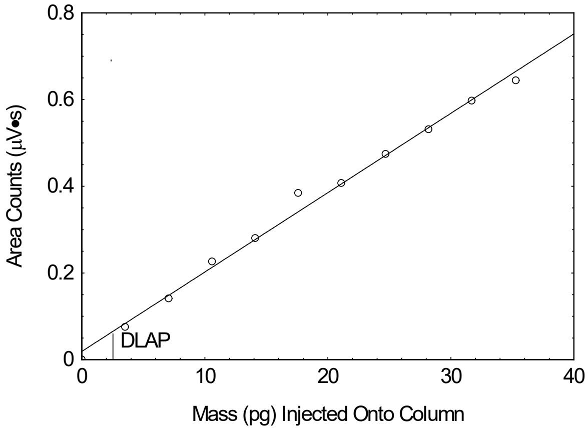

Figure Q-1. Plot of data used to determine the DLAP for n-hexane ($y = 0.0183x + 0.0190$, DLAP $S_{y/x}$ = 0.0182, DLAP = 2.98 pg).

2.2 Detection Limit of the Overall Procedure (DLOP) and Reliable Quantitation Limit (RQL)

The DLOP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLOP $S_{y/x}$) divided by the slope of the line produced from analyses of ten samples prepared from sorbent tubes spiked with equally spaced increments of analyte mass. 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 RQL is expressed as an air concentration that will provide sufficient analyte mass per sample that produces a response greater than 10× DLOP $S_{y/x}$ divided by the slope of the line described above. The spiked samplers and a sample blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLOP $S_{y/x}$ and the slope values for DLOP and RQL determinations. Results obtained from these analyses are listed in Table Q-2, and plotted in Figure Q-2.

Table Q-2. DLOP and RQL data for *n*-hexane.

mass per sample (µg/sample)	area counts (µV·s)
0.00	0.00
0.661	0.0860
1.32	0.171
1.98	0.289
2.64	0.382
3.31	0.487
3.97	0.581
4.63	0.666
5.29	0.740
5.95	0.784
6.61	0.908

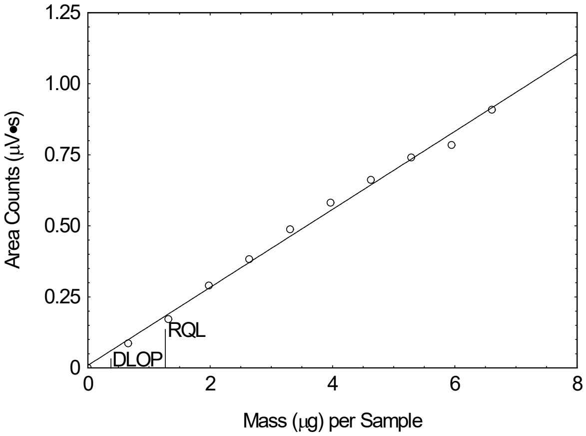

Figure Q-2. Plot of data used to determine the DLOP and RQL for *n*-hexane ($y = 0.137x + 0.00904$, DLOP $S_{y/x}$ = 0.0221, DLOP = 0.484 µg/sample, RQL = 1.61 µg/sample or 0.093 ppm).

3 Analytical Precision Across the Calibration Range

Fifteen analytical standards over a range of 0.1 to 2 times the analyte concentration in solvent that would be obtained from sampling for the recommended time at the target concentration were analyzed with the recommended analytical parameters described in OSHA Method 5000. An ordinary least-squares linear regression curve was created by plotting the analyte mass per sample versus the corresponding ratio of analyte peak area to internal standard (ISTD) peak area. The resulting data provided the standard error of estimate (Calibration $S_{y/x}$) value across the calibration range, which provides an indication of the imprecision attributable to the instrumental analysis of the target analyte. Results from these analyses are listed in Table Q-3, and plotted in Figure Q-3.

Table Q-3. Analytical precision data for *n*-hexane.

× target	0.1×	0.5×	1.0×	1.5×	2.0×
concn (µg/sample)	991.5	4627	8924	13,220	17,847
area ratio	2.550	11.71	22.46	32.22	46.38
	2.487	11.43	21.49	33.12	45.64
	2.575	11.60	22.37	33.06	43.04

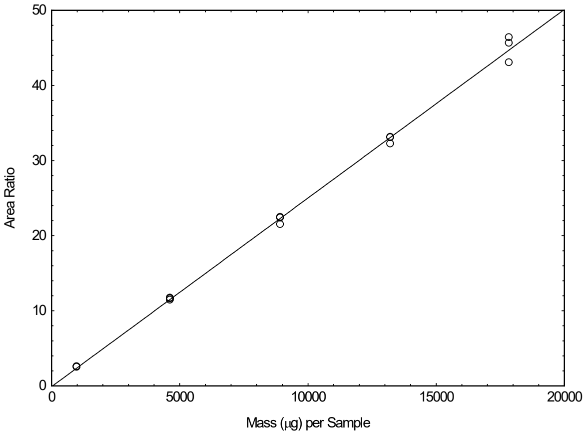

Figure Q-3. Plot of data used to determine the precision of the analytical method for *n*-hexane ($y = 0.00251x - 0.0975$, Calibration $S_{y/x}$ = 0.785).

4 Sampler Storage Stability

Storage stability test samples for *n*-hexane were prepared by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13. Sampling from this system followed the recommended sampling parameters published in OSHA Method 5000. The nominal concentration of *n*-hexane for ambient storage testing was the target concentration (calculated to be 510.8 ppm). The relative humidity and temperature of the air sampled were 80.8% and 21.5 °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 in a closed drawer at ambient temperature (about 22°C). Three samples were selected and analyzed from those remaining at 3-4 day intervals. The results of these analyses (uncorrected for extraction efficiency) are provided in Table Q-4. Results are plotted in Figure Q-4.

The recovery of *n*-hexane calculated from the regression line generated for the 17-day ambient storage test was 99.0%.

Table Q-4. Sampler storage stability data for *n*-hexane.

time (days)	ambient storage recovery (%)		
0	99.9	101.6	101.2
3	98.1	97.9	95.0
7	102.8	101.0	100.2
10	98.8	98.0	97.4
14	98.2	97.8	98.3
17	100.1	102.0	97.9

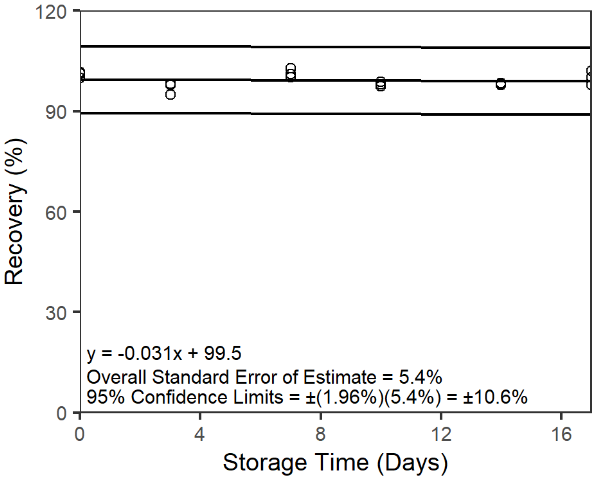

Figure Q-4. Plot of ambient storage stability data for *n*-hexane.

5 Precision of the Overall Procedure

The overall standard error of estimate obtained from the ambient storage test analyses described in Section 4 and sampling pump variability were used to determine the precision of the overall procedure, where all aspects of sampling and analysis (sampling, sorbent tube handling and solvent extraction, and instrumental analysis) are considered. This value was obtained by taking the square root of the squared ambient storage stability standard error of estimate (Storage $S_{y/x}^2$) added to the squared sampling pump variability value (V_{SP}^2). The resulting precision of the overall procedure at the 95% confidence level for the ambient 17-day storage test (at the target concentration) for *n*-hexane was determined to be ±10.6% based on the observed ambient Storage $S_{y/x}$ value of 5.4% and V_{SP} value of 5.0%.

6 Recovery and Stability of Prepared Samples

Quantitative extraction 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 OSHA Method 5000. 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.

A value for extraction efficiency (E_E) was determined by liquid-spiking four replicate sorbent tubes across a range of analyte mass values that would be obtained from sampling at 0.1 to 2 times the target concentration value for 98 min.

Four sorbent tubes were also spiked in this fashion at the target concentration after drawing humid air (80.3% relative humidity at 21.6 °C) through these tubes at 50 mL/min for 98 min. All of the samples described above were analyzed the following day after being kept overnight at ambient temperature. The E_E value at the RQL was 106.5%, while that of the working range samples (excluding the samples through which humid air had been drawn) was 100.6%. The data are shown in Table Q-5. Pre-loading sorbent tubes with moisture ("wet" designation in the table) did not have an unacceptable effect on E_E.

Table Q-5. Extraction efficiency data for *n*-hexane.

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.1	856.7	101.3	100.3	99.5	97.9	99.8
0.25	1983	100.2	101.1	100.1	99.2	100.2
0.5	3966	99.4	99.4	100.4	95.9	98.8
1.0	8593	102.0	102.1	102.9	102.7	102.4
1.5	12,559	96.4	95.6	104.7	105.6	100.6
2.0	17,186	102.2	102.4	101.0	101.6	101.8
RQL	1.59	108.3	115.8	106.8	95.0	106.5
1.0 (wet)	8593	101.1	103.3	103.1	101.8	102.3

The stability of samples extracts prepared according to OSHA Method 5000 was examined by retaining the sample solvent extracts for the target concentration samples described immediately above. Two of the four vials were immediately recapped with new septa following the initial analyses, and again following each re-analysis event. The other two vials retained the original punctured septa throughout. All four vials were re-analyzed at 24, 48, and 72 hours after the initial analyses, with all vials remaining in an autosampler tray kept at 22 °C. Freshly prepared standards were used for each analysis event, and each septum (whether new or previously used) was punctured four times for each injection. The resulting data are shown in Table Q-6, and indicate that vials should be re-capped after analysis due to the loss of analyte when punctured septa are retained.

Table Q-6. Extracted sample stability data for *n*-hexane.

	punctured septa replaced recovery (%)		punctured septa retained recovery (%)	
time (days)	1	2	1	2
0	98.2	99.5	100.2	101.7
1	100.4	98.7	96.9	98.0
2	98.6	100.7	93.5	96.6
3	100.7	101.6	93.1	96.4

7 Sampler Capacity

The sampling capacity of the front section of a sorbent tube was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing *n*-hexane nominally at two times the target concentration (calculated to be 1028 ppm). The relative humidity and temperature of the air sampled were 78.0% and 22.2 °C, and the sampling flow rate was 50 mL/min. A sorbent tube testing system was made by placing a complete sorbent tube in series behind another complete tube, which contained only the front sorbent section. The rear tube was changed and analyzed at 40, 90, 100, 110, and 120 min. Data from three sorbent tube testing systems, shown in Table Q-7, were used to determine a recommended sampling volume of 4.9 liters for *n*-hexane, as 80% of the volume needed to produce 5% breakthrough. These results provide a recommended sampling time of 98 min as described in OSHA Method 5000. Results are plotted in Figure Q-5.

Table Q-7. Sampler capacity data for *n*-hexane.

sample no.	air vol (L)	sampling time (min)	cumulative downstream concn (mg/m^3)	break-through (%)
1	2.08	40	0.00	0.00
	4.69	90	7.26	0.20
	5.21	100	36.8	1.01
	5.73	110	103	2.84
	6.25	120	221	6.11
2	2.06	40	0.00	0.00
	4.65	90	12.0	0.33
	5.16	100	49.0	1.35
	5.68	110	118	3.25
	6.19	120	233	6.43
3	1.96	40	0.00	0.00
	4.42	90	1.26	0.030
	4.91	100	16.8	0.46
	5.40	110	54.4	1.50
	5.89	120	133	3.67

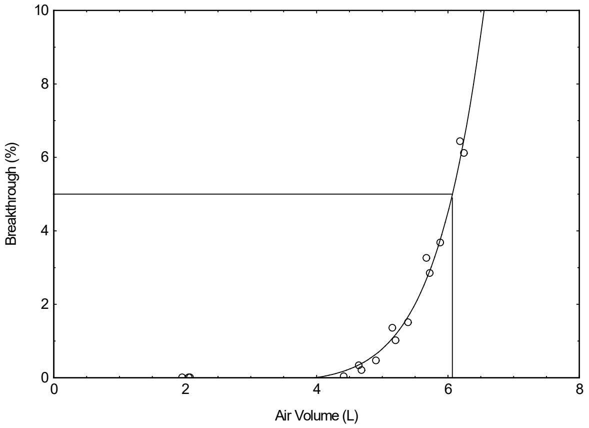

Figure Q-5. Plot of data used to determine sampler capacity for *n*-hexane. The 5% breakthrough volume shown is based on the curve in the figure, which is fit to the data provided in Table Q-7.

8 Low Humidity

The effect of low humidity was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing *n*-hexane nominally at two times the target concentration (calculated to be 1024 ppm). The relative humidity and temperature of the air sampled were 17.6% and 23.2 °C, and the sampling flow rate was 50 mL/min. Samples were collected on three sorbent tubes for 98 min. After immediate analysis, results as a percentage of expected recovery were 101.2%, 101.3%, and 104.9%.

9 Chemical Interference

The effect of potential chemical sampling interference was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing *n*-hexane nominally at two times the target concentration (calculated to be 1,038 ppm). The relative humidity and temperature of the air sampled were 81.9% and 20.7 °C, and the sampling flow rate was 50 mL/min. Cyclohexane was present as a potential interferent, nominally at its permissible exposure limit (calculated to be 310 ppm). Samples were collected on three sorbent tubes for 98 min. After immediate analysis, results for *n*-hexane as a percentage of expected recovery were 101.5%, 97.61%, and 98.38%.

10 Analytical Method Reproducibility

Samples were prepared by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing *n*-hexane nominally at the target concentration (calculated to be 506.7 ppm). The relative humidity and temperature of the air sampled were 80.4% and 20.7 °C, and the sampling flow rate was 50 mL/min. Samples were collected on six sorbent tubes for 98 min. The resulting samples were submitted to the OSHA Salt Lake Technical Center for analysis using the procedures described in OSHA Method 5000 after storage for 15 days at 4 °C. The analytical results corrected E_E are provided in Table Q-8. No sample result for *n*-hexane fell outside the permissible bounds set by the precision of the overall procedure determined in Section 5 of this appendix.

Table Q-8. Reproducibility data from *n*-hexane.

sampled (ppm)	recovered (ppm)	recovery (%)	deviation (%)
506.7	547.9	108.1	+8.1
506.7	522.0	103.0	+3.0
506.7	540.0	106.6	+6.6
506.7	532.2	105.0	+5.0
506.7	512.5	101.1	+1.1
506.7	526.7	103.9	+3.9

11 Effect of Sampling a Low Concentration

The effect of sampling a low concentration of *n*-hexane vapor was tested by sampling a dynamically generated controlled test atmosphere, using the system described in Section 13, containing *n*-hexane nominally at one-tenth the target concentration (calculated to be 44.6 ppm). The relative humidity and temperature of the air sampled were 83.5% and 21.4 °C, and the sampling flow rate was 50 mL/min. Samples were collected on three charcoal tubes for 98 min. After immediate analysis, results for *n*-hexane as percentage of expected recovery were 104.5%, 98.07%, and 97.71%.

12 Estimation of Uncertainty

While systematic biases such as analyte storage loss are examined, and limits are placed on these, an estimation of uncertainty that encompasses both potential random and systematic error was not completed. Instead, the overall standard error of estimate was calculated from the random error inherent to the points about the regression line produced by the ambient storage test described in Section 5, as prescribed by the OSHA validation guidelines in use at the time OSHA Method 5000 was originally validated. See Section 5 of this appendix for details.

13 Controlled Test Atmosphere Procedure

Dynamically generated controlled test atmospheres were created in a walk-in hood. House air was regulated using a Miller Nelson Model 401 flow-temperature-humidity control system. A measured flow of liquid *n*-hexane was introduced with an ISCO model 100DM syringe pump through a short length of 0.53 mm internal diameter 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 *n*-hexane vapor and dilution air flowed into a mixing chamber (76 cm length x 15 cm diameter), and then into a sampling chamber (56 cm length x 9.5 cm diameter). Sampling was completed from sampling ports present on the sampling chamber. Temperature and humidity measurements were obtained near the exit of the sampling chamber using a Vaisala HUMICAP Model HM70 hand-held humidity and temperature meter.

OSHA 5000, Appendix R
Nonane

Version:	1.0
OSHA PEL:	None
ACGIH TLV:	200 ppm (1048 mg/m^3) 8-Hour TWA
Recommended sampling time and sampling rate:	80 min at 50 mL/min (4 L)
Reliable quantitation limit:	0.063 ppm (0.33 mg/m^3)
Standard error of estimate:	5.4%
Status:	Partially validated. Method 5000 has been subjected to the established validation procedures of the Method Development Team for sampling and analysis of nonane.

February 2021 (OSHA 5000) Uyen Bui, Daren Pearce

1 Introduction

1.1 Previous Methods used by OSHA for Sampling and Analysis of Nonane

The specific analyte described in this appendix is nonane, CAS No. 111-84-2. The methodologies described in this appendix for nonane are based on NIOSH Method 1500.[1] That method requires the collection of samples using charcoal sorbent tubes, extraction using carbon disulfide, and analysis by gas chromatography using a flame ionization detector.

1.2 Changes to the Previously-Used Method

This appendix represents a new method to replace NIOSH Method 1500[1] for sampling and analysis of nonane. Compared to the previous method used this method includes new analytical parameters, internal standard (ISTD), and samples collection flow rate and collection time. Data presented from the previously used method are identified by the statement “Pre-existing data from NIOSH Method 1500[1] are presented in this section”. The changes were made to allow the standardized collection and analysis of nonane with other analytes found in Organic Vapor Sampling Group 1, described in OSHA Method 5000.

1.3 Validation Parameters

The procedures used to develop the method validation data are described in Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis.[2] Air concentrations listed in ppm are referenced to 25 °C and 760 Torr. The target concentration for method evaluation was the American Conference of Governmental Industrial Hygienists 8-hour time-weighted average (TWA) Threshold Limit Value for nonane.

---

[1] Pendegrass, S.; May, L. Hydrocarbons, BP 36 ºC-216 ºC (NIOSH Method 1500, Issue 3), 2003. Center for Disease Control, The National Institute for Occupational Safety and Health (NIOSH) Web site. http://www.cdc.gov/niosh/docs/2003-154/pdfs/1500.pdf (accessed October 2018).

[2] Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration Web site. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed December 2018).

2 Detection and Quantification

2.1 Detection limit of the analytical procedure (DLAP)

The DLAP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLAP $S_{y/x}$) divided by the slope of the line produced from analyses of ten analytical standards prepared with equally spaced increments of analyte mass. The standards were prepared in such a way that the highest standard concentration would produce a peak approximately 10 times the response of a reagent blank at or near the chromatographic retention time of the analyte. The standards and a reagent blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLAP $S_{y/x}$ and slope values for DLAP determination. Results obtained for these analyses are listed in Table R-1, and plotted in Figure R-1.

Table R-1. DLAP data for nonane.

concentration (µg/mL)	mass on column (pg)	area counts (µV·s)
0.00	0.00	0.00
0.359	2.39	0.0204
0.718	4.79	0.0827
1.01	6.73	0.1462
1.44	9.60	0.1900
1.80	12.0	0.2195
2.15	14.3	0.2931
2.51	16.7	0.3709
2.87	19.1	0.3881
3.23	21.5	0.4576
3.59	23.9	0.4947

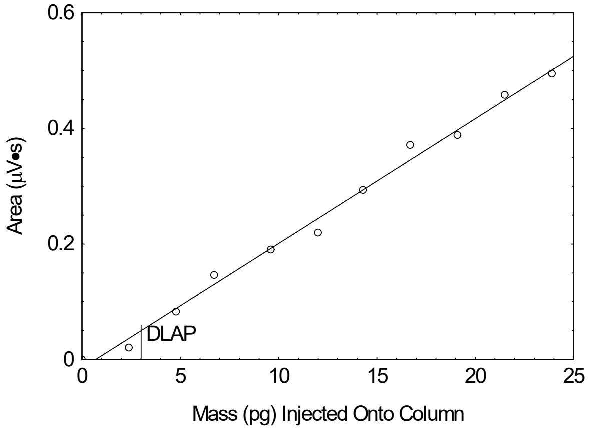

Figure R-1. Plot of data used to determine the DLAP for nonane ($y = 0.0216x - 0.0149$, DLAP $S_{y/x}$ = 0.0157, DLAP = 2.18 pg).

2.2 Detection Limit of the Overall Procedure (DLOP) and Reliable Quantitation Limit (RQL)

The DLOP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLAP $S_{y/x}$) divided by the slope of the line produced from analyses of ten samples prepared from sorbent tubes spiked with equally spaced increments of analyte mass. 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 RQL is expressed as an air concentration that will provide sufficient analyte mass per sample that produces a response greater than 10× DLOP $S_{y/x}$ divided by the slope of the line described above. The spiked samplers and the sample blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLAP $S_{y/x}$ and the slope values for DLOP and RQL determination. Results obtained from this analysis are listed in Table R-2, and plotted in Figure R-2.

Table R-2. DLOP and RQL data for nonane.

mass per sample (µg/sample)	area counts (µV·s)
0.00	0.00
0.359	0.0765
0.718	0.1141
1.08	0.1547
1.44	0.2365
1.80	0.2641
2.15	0.3384
2.51	0.3640
2.87	0.4065
3.32	0.4631
3.59	0.4753

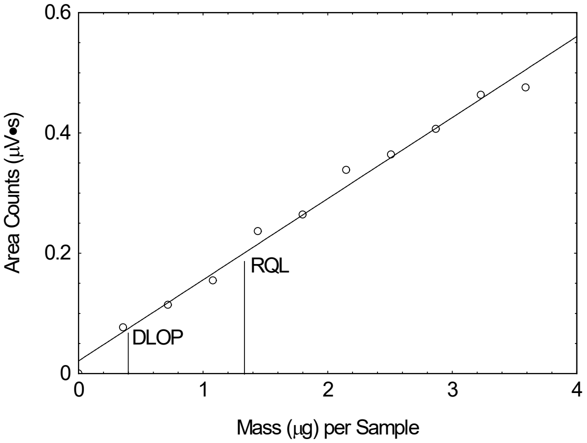

Figure R-2. Plot of data used to determine the DLOP and RQL for nonane ($y = 0.135x + 0.0210$, DLOP $S_{y/x}$ = 0.0177, DLOP = 0.393 µg/sample, RQL = 1.31 µg/sample or 0.0626 ppm).

3 Analytical Precision Across the Calibration Range

Fifteen analytical standards over a range of 0.1 to 2 times the analyte concentration in solvent that would be obtained from sampling for the recommended time at the target concentration were analyzed with the recommended analytical parameters described in OSHA Method 5000. An ordinary least-squares linear regression curve was created by plotting the analyte mass per sample versus the corresponding ratio of analyte peak area to internal standard (ISTD) peak area. The resulting data provided the standard error of estimate (Calibration $S_{y/x}$) value across the calibration range, which provides an indication of the imprecision attributable to the instrumental analysis of the target analyte. Results from these analyses are listed in Table R-3, and plotted in Figure R-3.

Table R-3. Analytical precision data for nonane.

× target concn (µg/sample)	0.1×	0.5×	1.0×	1.5×	2.0×
	430.8	2154	4308	6462	8616
area ratio	1.822	9.049	18.08	27.03	36.08
	1.823	9.066	18.10	26.99	36.13
	1.828	9.069	18.02	26.99	36.17

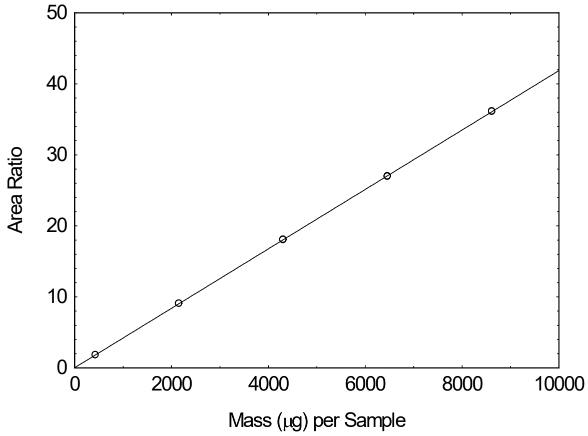

Figure R-3. Plot of data used to determine the precision of the analytical method for nonane ($y = 0.00419x + 0.0255$, Calibration $S_{y/x}$ = 0.0474).

4 Sampler Storage Stability

Storage stability test samples for nonane were prepared by liquid-spiking sorbent tubes. The mass of nonane spiked was equivalent to the mass that would be sampled at the target concentration in air for 80 min at a flow rate of 50 mL/min (calculated to be 205 ppm). Humid air (80.0% relative humidity at 21.1 °C) was drawn through the spiked sorbent tubes at 50 mL/min for 80 min. Twelve storage samples were prepared and three of these were analyzed on the day that samples were created. For ambient storage testing, the remaining nine samples were stored in a closed drawer at ambient temperature (about 22 °C). Three samples were selected and analyzed from those remaining at 4-5 day intervals. The results of these analyses (uncorrected for extraction efficiency) are provided in Table R-4, and in Figures R-4.

The recovery of nonane calculated from the regression line generated for the 14-day ambient storage test was 96.1%.

Table R-4. Sampler storage stability data for nonane.

time (days)	ambient storage recovery (%)		
0	102.1	101.8	98.7
5	98.2	100.0	96.9
9	97.6	98.5	97.5
14	100.3	92.8	95.8

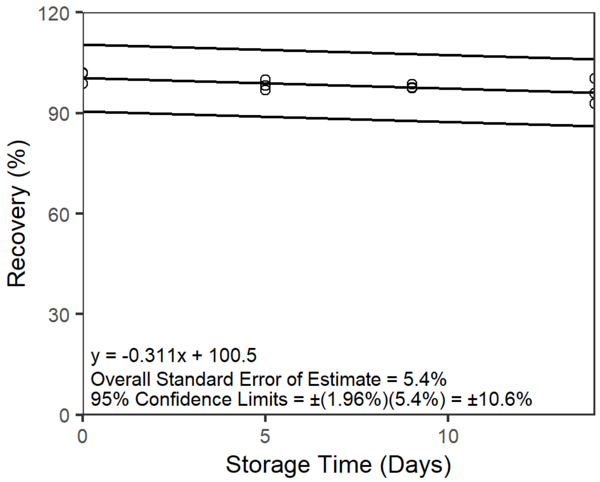

Figure R-4. Plot of ambient storage stability data for nonane.

5 Precision of the Overall Procedure

The overall standard error of estimate obtained from the ambient storage test analyses described in Section 4 and sampling pump variability were used to determine the precision of the overall procedure, where all aspects of sampling and analysis (sampling, sorbent tube handling and solvent extraction, and instrumental analysis) are considered. This value was obtained by taking the square root of the squared ambient storage stability standard error of estimate (Storage $S_{y/x}^2$) added to the squared sampling pump variability value (V_{SP}^2). The resulting precision of the overall procedure at the 95% confidence level for the ambient 14-day storage test (at the target concentration) for nonane was determined to be ±10.6% based on the observed ambient Storage $S_{y/x}$ value of 5.4% and V_{SP} value of 5.0%.

6 Recovery and Stability of Prepared Samples

Quantitative extraction 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 OSHA Method 5000. 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.

A value for extraction efficiency (E_E) was determined by liquid-spiking four replicate sorbent tubes across a range of analyte mass values that would be obtained from sampling at 0.1 to 2 times the target concentration value for 80 min. Four sorbent tubes were also spiked in this fashion at the target concentration after drawing humid air (80.5% relative humidity at 21.4 °C) through these tubes at 50 mL/min for 80 min. All of the samples described above were analyzed the following day after being kept at ambient temperature. The E_E value at the RQL was 105.8%, while that of the working range samples (excluding the samples through which humid air had been drawn) was 102.0%. The data are shown in Table R-5. Pre-loading sorbent tubes with moisture ("wet" designation in the table) did not have an unacceptable effect on E_E.

Table R-5. Extraction efficiency data for nonane.

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.1	430.8	101.8	101.2	101.1	101.4	101.4
0.25	1077	102.2	102.6	102.5	101.2	102.1
0.5	2154	102.0	101.9	104.1	103.7	102.9
1.0	4308	103.9	101.2	101.5	101.5	102.0
1.5	6462	101.5	101.6	101.6	101.7	101.6
2.0	8616	102.0	102.0	101.9	102.0	102.0
RQL	1.36	101.6	97.3	114.7	109.4	105.8
1.0 (wet)	4308	103.7	101.9	102.1	103.4	102.8

The stability of extracted samples extracts prepared according to OSHA Method 5000 was examined by retaining the sample solvent extracts for the target concentration samples described immediately above. Two of the four vials were immediately recapped with new septa following the initial analyses, and again following each re-analysis event. The other two vials retained the original punctured septa throughout. All four vials were re-analyzed at 24, 48, and 72 hours after the initial analyses, with all vials remaining in an autosampler tray kept at 22 °C. Freshly prepared standards were used for each analysis event, and each septum (whether new or previously used) was punctured four times for each injection. The resulting data are shown in Table R-6.

Table R-6. Extracted sample stability data for nonane.

	punctured septa replaced recovery (%)		punctured septa retained recovery (%)	
time (days)	1	2	1	2
0	99.7	101.8	101.2	100.9
1	100.0	101.8	101.0	100.7
2	100.0	101.5	100.9	100.1
3	99.7	101.7	101.0	100.3

7 Sampler capacity

Pre-existing data from NIOSH Method 1500[1] are presented in this section.

Breakthrough (minimum of 5% of front section recovery detected on rear sorbent section) was observed with sampling volume of 5.9-L specified as "dry air."

8 Low Humidity

A study has not been undertaken to verify that sampling under low humidity conditions for nonane at the target concentration does not produce anomalous results.

9 Chemical Interference

A study has not been undertaken to verify that sampling another common organic vapor at high concentration concurrently with the sampling of nonane at the target concentration does not produce anomalous results.

10 Analytical Method Reproducibility

Samples were prepared by liquid-spiking the front sections of six sorbent tubes with nonane. The mass of nonane spiked was equivalent to the mass that would be sampled at the target concentration in air for 80 min at a flow rate of

50 mL/min (calculated to be 205 ppm). Humid air (80.0% relative humidity at 21.0 °C) was drawn through the spiked sorbent tubes at 50 mL/min for 80 min. The resulting samples were submitted to the OSHA Salt Lake Technical Center for analysis using the procedures described in OSHA Method 5000 after refrigerated (4 °C) storage for 15 days. The analytical results corrected for E_E are provided in Table R-7. No sample result for nonane fell outside the permissible bounds set by the precision of the overall procedure determined in Section 5 of this appendix.

Table R-7. Reproducibility data for nonane.

sampled (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
4308	4126	95.8	-4.2
4308	4039	93.8	-6.2
4308	4114	95.5	-4.5
4308	4164	96.7	-3.3
4308	4181	97.0	-3.0
4308	4138	96.0	-4.0

11 Effect of Sampling a Low Concentration

A study has not been undertaken to verify the effect of sampling a low concentration of nonane vapor.

12 Estimation of Uncertainty

While systematic biases such as analyte storage loss are examined, and limits are placed on these, an estimation of uncertainty that encompasses both potential random and systematic error was not completed. Instead, the overall standard error of estimate was calculated from the random error inherent to the points about the regression line produced by the ambient storage test described in Section 5, as prescribed by the OSHA validation guidelines in use at the time OSHA Method 5000 was originally validated. See Section 5 of this appendix for details.

13 Controlled Test Atmosphere Procedure

Controlled test atmospheres were generated for work done to complete NIOSH Method 1500[2], but details sufficient to reproduce the procedures used to create the test atmospheres are not available.

OSHA 5000, Appendix S
Octane

Version:	1.0
OSHA PEL:	500 ppm (2350 mg/m^3) 8-Hour TWA, General Industry; 400 ppm (1900 mg/m^3) 8-Hour TWA, Construction, Shipyard
ACGIH TLV:	300 ppm (1401 mg/m^3) 8-Hour TWA
Recommended sampling time and sampling rate:	80 min at 50 mL/min (4 L)
Reliable quantitation limit:	0.068 ppm (0.32 mg/m^3)
Standard error of estimate:	5.4%
Status:	Partially validated. Method 5000 has been subjected to the established validation procedures of the Method Development Team for sampling and analysis of octane.

March 2004 (PV2138)
February 2021 (OSHA 5000)

Anna Tang
Chelsea Burke, Daren Pearce

1 Introduction

1.1 Previous Methods used by OSHA for Sampling and Analysis of Octane

The specific analyte described in this appendix is octane, CAS No. 111-65-9. The methodologies described in this appendix for octane are based on OSHA Method PV2138[1], which used NIOSH Method 1500[2] and OSHA 48[3] as starting guides. That method requires the collection of samples using charcoal sorbent tubes, extraction using carbon disulfide containing 1% *N,N*-dimethylformamide, and analysis by gas chromatography using a flame ionization detector.

1.2 Changes to the Previously-Used Method

This appendix represents an update to OSHA Method PV2138[1], which was partially validated at the time it was published based on the validation guidelines in effect at that time. Compared to the previous method used this method includes new analytical parameters and extraction solvent. Data presented from the previously used method are identified by the statement "Pre-existing data from OSHA Method PV2138[1] are presented in this section" or "Pre-existing data from NIOSH 1500 are presented in this section". The changes were made to allow the standardized collection and analysis of octane with other analytes found in Organic Vapor Sampling Group 1, described in OSHA Method 5000.

---

[1] Tang, A. n-Octane (OSHA Method PV2138), 2004. United States Department of Labor, Occupational Safety & Health Administration Web site. https://www.osha.gov/dts/sltc/methods/partial/pv2138/pv2138.html (accessed June 2019).

[2] Pendegrass, S.; May, L. Hydrocarbons, BP 36 ºC-216 ºC (NIOSH Method 1500, Issue 3), 2003. Center for Disease Control, The National Institute for Occupational Safety and Health (NIOSH) Web site. http://www.cdc.gov/niosh/docs/2003-154/pdfs/1500.pdf (accessed May 2019).

[3] Shulsky, M. Petroleum Distillate Fraction (OSHA Method 48), 1984. United States Department of Labor, Occupational Safety & Health Administration Web site. https://www.osha.gov/dts/sltc/methods/organic/org048/org048.html (accessed June 2019).

1.3 Validation Parameters

The procedures used to develop the method validation data are described in Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis.[4] Air concentrations listed in ppm are referenced to 25 °C and 760 Torr. The target concentration for method evaluation was the OSHA 8-hour time-weighted average (TWA) General Industry permissible exposure limit (PEL) for octane.

2 Detection and Quantification

2.1 Detection limit of the analytical procedure (DLAP)

The DLAP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLAP $S_{y/x}$) divided by the slope of the line produced from analyses of ten analytical standards prepared with equally spaced increments of analyte mass. The standards were prepared in such a way that the highest standard concentration would produce a peak approximately 10 times the response of a reagent blank at or near the chromatographic retention time of the analyte. The standards and a reagent blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLAP $S_{y/x}$ and slope values for DLAP determination. Results obtained for these analyses are listed in Tables S-1, and plotted in Figure S-1.

Table S-1. DLAP data for octane.

concentration (μg/mL)	mass on column (pg)	area counts (μV·s)
0.00	0.00	0.00
0.492	3.28	0.111
0.980	6.53	0.175
1.48	9.90	0.252
1.97	13.1	0.268
2.46	16.4	0.318
2.95	19.7	0.379
3.44	22.9	0.482
3.94	26.3	0.563
4.43	29.5	0.589
4.92	32.8	0.638

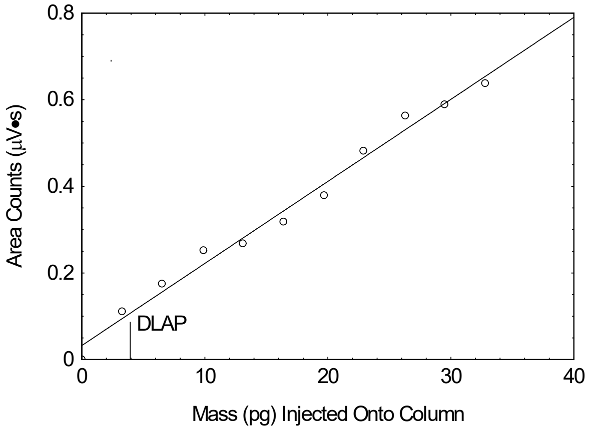

Figure S-1. Plot of data used to determine the DLAP for octane ($y = 0.0190x + 0.0324$, DLAP $S_{y/x}$ = 0.0253, DLAP = 3.99 pg).

2.2 Detection Limit of the Overall Procedure (DLOP) and Reliable Quantitation Limit (RQL)

The DLOP is the analyte mass introduced onto the chromatographic column that produces a response greater than 3× the standard error of estimate (DLOP $S_{y/x}$) divided by the slope of the line produced from analyses of ten samples prepared from sorbent tubes spiked with equally spaced increments of analyte mass. 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 RQL is expressed as an air concentration that will provide sufficient analyte mass per sample that produces a response greater than 10× DLOP $S_{y/x}$ divided by the slope of the line just described. The spiked samplers and a sample blank were analyzed with the recommended analytical parameters described in OSHA Method 5000. The resulting data provided the DLOP $S_{y/x}$ and the slope for DLOP and RQL determinations. Results obtained from these analyses are listed in Table S-2, and plotted in Figure S-2.

---

[4] Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration Web site. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed December 2018).

Table S-2. DLOP and RQL data for octane.

mass per sample (μg/sample)	area counts (μV·s)
0.00	0.00
0.492	0.097
0.984	0.153
1.48	0.224
1.97	0.310
2.46	0.373
2.95	0.402
3.44	0.489
3.94	0.574
4.43	0.637
4.92	0.666

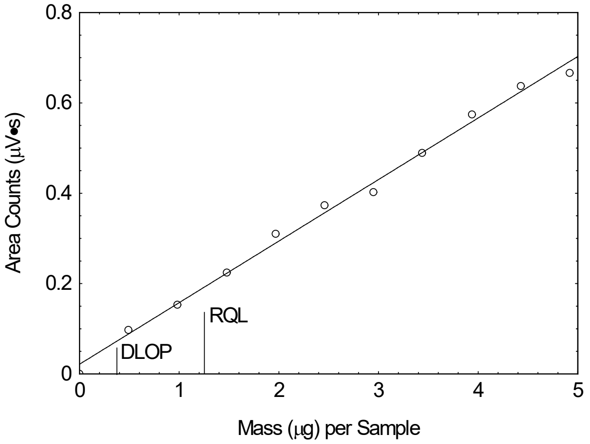

Figure S-2. Plot of data used to determine the DLOP and RQL for octane ($y = 0.136x + 0.0215$, DLOP $S_{y/x}$ = 0.0174, DLOP = 0.384 μg/sample, RQL = 1.28 μg/sample or 0.0685 ppm).

3 Analytical Precision Across the Calibration Range

Fifteen analytical standards over a range of 0.1 to 2 times the analyte concentration in solvent that would be obtained from sampling for the recommended time at the target concentration were analyzed with the recommended analytical parameters described in OSHA Method 5000. An ordinary least-squares linear regression curve was created by plotting the analyte mass per sample versus the corresponding ratio of analyte peak area to internal standard (ISTD) peak area. The resulting data provided the standard error of estimate (Calibration $S_{y/x}$) value across the calibration range, which provides an indication of the imprecision attributable to the instrumental analysis of the target analyte. Results from these analyses are listed in Table S-3, and plotted in Figure S-3.

Table S-3. Analytical precision data for octane.

× target	0.1×	0.5×	1.0×	1.5×	2.0×
concn (μg/sample)	983.9	4920	9839	14,759	19,678
area ratio	4.168	21.02	41.66	62.28	82.10
	4.211	21.47	42.63	62.36	83.31
	4.221	21.32	41.82	61.24	84.29

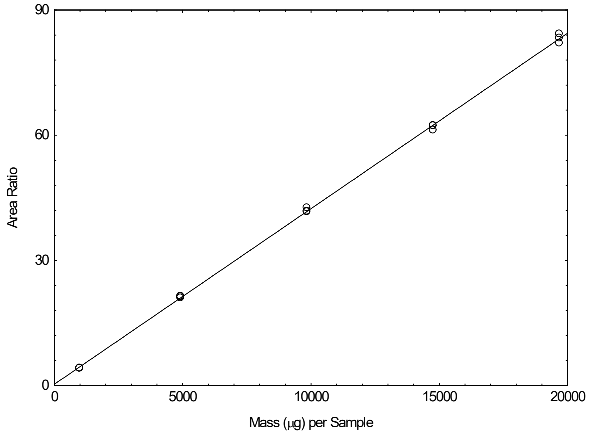

Figure S-3. Plot of data used to determine the precision of the analytical method for octane ($y = 0.00421x + 0.314$, Calibration $S_{y/x}$ = 0.633).

4 Sampler Storage Stability

Pre-existing data from OSHA Method PV2138[1] are presented in this section.

Storage stability test samples for octane were prepared by liquid-spiking sorbent tubes. The mass of octane spiked for ambient storage testing was equivalent to the mass that would be sampled at the target concentration in air (calculated to be 486 ppm) for 80 min at a flow rate of 50 mL/min. Humid air (78.0% relative humidity at 23.0 °C) was drawn through the spiked sorbent tubes at 50 mL/min for 80 min. For each test, twelve samples were prepared and three of these were analyzed on the day that samples were created. The remaining six refrigerated storage test samples were stored at reduced temperature (4 °C), while the remaining six ambient storage test samples were stored in a closed drawer at ambient temperature (about 23 °C). For each storage condition, three samples were selected and analyzed from those remaining at 7-day intervals. The results of these analyses (uncorrected for extraction efficiency) are provided in Table S-4, and in Figures S-4 through S-5.

The recovery of octane calculated from the regression line generated for the 14-day ambient storage test was 99.6%.

Table S-4. Sampler storage stability data for octane.

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	97.5	97.0	96.1	97.5	97.0	96.1
7	94.9	96.3	94.1	98.0	92.7	96.5
14	100.5	100.7	101.3	100.1	101.3	101.1

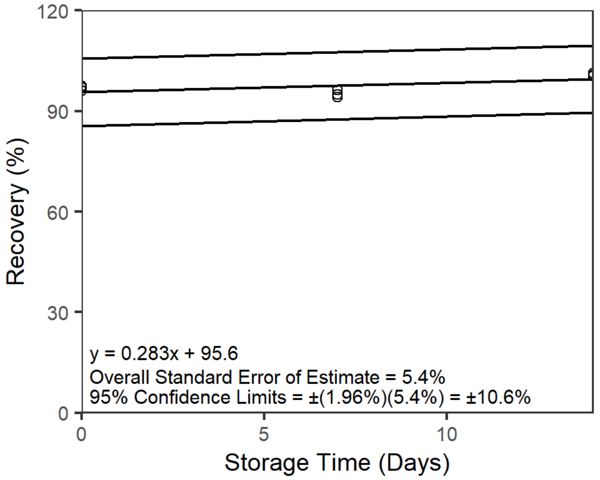

Figure S-4. Plot of ambient storage stability data for octane.

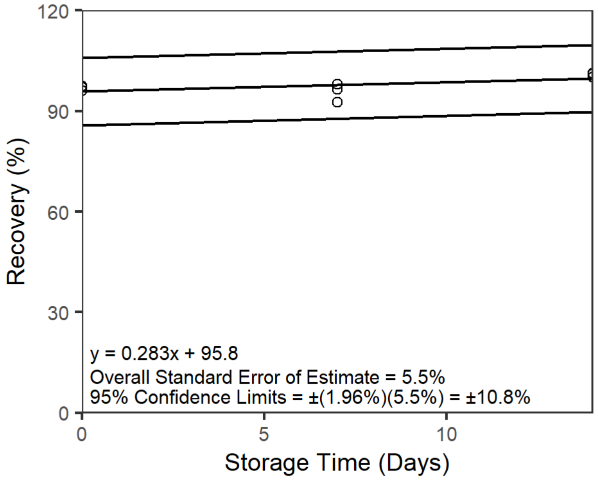

Figure S-5. Plot of refrigerated storage stability data for octane.

5 Precision of the Overall Procedure

The overall standard error of estimate obtained from the ambient storage test analyses described in Section 4 and sampling pump variability were used to determine the precision of the overall procedure, where all aspects of sampling and analysis (sampling, sorbent tube handling and solvent extraction, and instrumental analysis) are considered. This value was obtained by taking the square root of the squared ambient storage stability standard error of estimate (Storage $S_{y/x}^2$) added to the squared sampling pump variability value (V_{SP}^2). The resulting precision of the overall procedure at the 95% confidence level for the ambient 14-day storage test (at the target concentration) for octane was determined to be ±10.6% based on the observed ambient Storage $S_{y/x}$ value of 5.4% and V_{SP} value of 5.0%.

6 Recovery and Stability of Prepared Samples

Quantitative extraction 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 OSHA Method 5000. 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.

A value for extraction efficiency (E_E) was determined by liquid-spiking four replicate sorbent tubes across a range of analyte mass values that would be obtained from sampling at 0.1 to 2 times the target concentration value for 80 min. Four sorbent tubes were also spiked in this fashion at the target concentration after drawing humid air (79.2% relative humidity at 20.0 °C) through these tubes at 50 mL/min for 80 min. All of the samples described above were analyzed the following day after being kept overnight at ambient temperature. The E_E value at the RQL was 92.8%, while that of the working range samples (excluding the samples through which humid air had been drawn) was 101.5%. The data are shown in Table S-5. Pre-loading sorbent tubes with moisture ("wet" designation in the table) did not have an unacceptable effect on E_E.

Table S-5. Extraction efficiency data for octane.

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.1	983.9	101.4	101.5	102.0	100.4	101.3
0.25	2560	102.3	102.9	102.3	102.0	102.4
0.5	4920	99.8	102.0	101.3	99.9	100.7
1.0	9839	102.0	101.5	101.2	101.7	101.6
1.5	14,759	102.3	102.6	102.0	100.9	101.9
2.0	19,678	101.3	101.1	101.3	100.1	101.0
RQL	1.48	87.7	98.1	98.5	86.8	92.8
1.0 (wet)	9839	100.3	101.4	101.2	100.9	100.9

The stability of extracted samples extracts prepared according to OSHA Method 5000 was examined by retaining the sample solvent extracts for the target concentration samples described immediately above. Two of the four vials were immediately recapped with new septa following the initial analyses, and again following each re-analysis event. The other two vials retained the original punctured septa throughout. All four vials were re-analyzed at 24, 48, and 72 hours after the initial analyses, with all vials remaining in an autosampler tray kept at 22 °C. Freshly prepared standards were used for each analysis event, and each septum (whether new or previously used) was punctured four times for each injection. The resulting data are shown in Table S-6.

Table S-6. Extracted sample stability data for octane.

	punctured septa replaced recovery (%)		punctured septa retained recovery (%)	
time (days)	1	2	1	2
0	104.6	104.5	103.1	103.1
1	103.8	103.8	103.0	102.4
2	104.0	104.2	102.7	102.1
3	104.5	104.0	103.1	102.2

7 Sampler Capacity

Pre-existing data from NIOSH Method 1500[2] are presented in this section.

Breakthrough (minimum of 5% of front section recovery detected on rear sorbent section) was observed with sampling volume of 6.1-L specified as “dry air.”

8 Low Humidity

A study has not been undertaken to verify that sampling under low humidity conditions for octane at the target concentration does not produce anomalous results.

9 Chemical Interference

A study has not been undertaken to verify that sampling another common organic vapor at high concentration concurrently with the sampling of octane at the target concentration does not produce anomalous results.

10 Analytical Method Reproducibility

A study has not been undertaken to verify that independent analysis of sorbent tubes used to sample octane does not produce results outside the boundaries of the precision of the overall procedure, described in Section 5 of this appendix.

11 Effect of Sampling a Low Concentration

A study has not been undertaken to verify the effect of sampling a low concentration of octane vapor.

12 Estimation of Uncertainty

While systematic biases such as analyte storage loss are examined, and limits are placed on these, an estimation of uncertainty that encompasses both potential random and systematic error was not completed. Instead, the overall standard error of estimate was calculated from the random error inherent to the points about the regression line produced by the ambient storage test described in Section 5, as prescribed by the OSHA validation guidelines in use at the time OSHA Method 5000 was originally validated. See Section 5 of this appendix for details.

13 Controlled Test Atmosphere Procedure

Controlled test atmospheres were generated for work done to complete NIOSH Method 1500[2], but details sufficient to reproduce the procedures used to create the test atmosphere are not available.