Organic Vapor Sampling Group 2 (OVSG-2)
Alcohol Analytes Collected on Synthetic Charcoal Sorbent Tubes

Method number: 5001

Version number: 1.0

Validated analytes:

Analyte	CAS No.
n-Butyl alcohol	71-36-3
sec-Butyl alcohol	78-92-2
Ethyl alcohol	64-17-5
Isobutyl alcohol	78-83-1
Isopropyl alcohol	67-63-0
Methyl alcohol	67-56-1
n-Propyl alcohol	71-23-8

Procedure: Collect air samples by drawing workplace air through two Anasorb 747 sorbent tubes connected in series. Extract samples with 60/40 (v/v) *N*,*N*-dimethylformamide/carbon disulfide (DMF/CS_2) and analyze by gas chromatography (GC) using a flame ionization detector (FID). The analytes listed above are compatible with the sorbent, extraction solvent, and analysis conditions, and may be sampled separately or together, and the single analysis procedure described in Method 5001 may then be used.

Recommended sampling time and sampling rate: 240 min at 50 mL/min (12 L)*

*All except methyl alcohol for which the following should be used:
100 min at 50 mL/min (5 L) if relative humidity is > 50% at 25 °C
60 min at 50 mL/min (3 L) if relative humidity is < 50% at 25 °C

Special requirements: Immediately after sampling, separate the two sampling tubes to prevent post-sampling migration.

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.

March 2019

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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 preparation and analysis of alcohols collected on two Anasorb 747 tubes connected in series. Validation data for each analyte are located in the relevant appendices.

2 Sampling Procedure

Follow all safety practices that apply to the work area being sampled. Attach sampling equipment to the worker in a manner that will not interfere with work performance or safety. Wear eye protection when breaking off ends of flame-sealed glass sampling tubes.

2.1 Apparatus

Two single section 8-mm x 110-mm glass sampling tubes packed with Anasorb 747 sorbent are connected in series with a 1-inch length of ¼ -inch i.d. silicone tubing. The front tube contains 400 mg and the back tube contains 200 mg of Anasorb 747. The sorbent is held in place with glass wool on the inlet side and a foam plug on the outlet side. Commercially prepared tube sets may be purchased from SKC Inc. (catalog no. 226-82).

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

A personal sampling pump calibrated to within ±5% of the recommended flow rate used with a representative sampling device in-line.

2.2 Reagents

None Required

2.3 Technique

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

Attach the tube holder (with the adsorbent tubes) to the sampling pump so that the adsorbent tube is in the worker's breathing zone during sampling. Position the sampling pump, tube holder, and tubing so they do not impede work performance or safety. 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 methyl alcohol. For methyl alcohol sample at 50 mL/min for 100 min (5 L) when the relative humidity is above 50%, and for 60 min (3 L) when the relative humidity is below 50%. The recommended air sample volume for methyl alcohol must be reduced at lower relative humidities because sampler capacity is reduced. Fifty-percent relative humidity at 25 °C (11.5 mg of water per liter of air) was selected as the point at which to reduce the recommended air volume, as this will provide a sufficient margin of safety against sampler saturation. It is anticipated that most samples will be collected at relative humidities greater than 50% at 25 °C. See Section 2.6 of OSHA Method 91[1] for more details on sampling methyl alcohol.

[1] Hendricks, W. Methyl Alcohol (OSHA Method 91), 1991. United States Department of Labor, Occupational Safety & Health Administration.

After sampling for the appropriate time, separate the two samplers and 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 blank sample with each set of samples. Handle the 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 the samples to the laboratory for analysis as soon as possible after sampling. If delay is unavoidable, store the samples in a refrigerator as a precaution.

3 Analytical Procedure

3.1 Apparatus

- Mechanical vial rotator
- One liter amber glass solvent dispenser capable of dispensing 2.0 mL
- Syringes (10 and 50-µL)
- Class A volumetric flasks (2 and 500-mL)
- Amber glass vials with PTFE-lined screw caps (2 and 4-mL)
- GC instrument with FID

3.2 Reagents

- *n*-Butyl alcohol (>99% purity, analytical grade)
- *sec*-Butyl alcohol (>99% purity, analytical grade)
- Ethyl alcohol (>99% purity, analytical grade)
- Isobutyl alcohol (>99% purity, analytical grade)
- Isopropyl alcohol (>99% purity, analytical grade)
- Methyl alcohol (>99% purity, analytical grade)
- *n*-Propyl alcohol (>99% purity, analytical grade)
- Carbon disulfide (CS_2, reagent grade or better)
- *N,N*-Dimethylformamide (DMF, reagent grade or better)
- 1-Octanol (> 99% purity, analytical grade)

3.3 Reagent Preparation

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

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 which contains the ISTD. Fill to the mark with extraction solvent, mix, and transfer to 2-mL amber glass autosampler vials. Multiple analytes in one calibration standard can significantly 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.

3.5 Sample Preparation

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

Add 2.0 mL of extraction solvent containing ISTD to each vial and immediately seal with PTFE-lined caps.

Extract the samples by rotating for 1 hour.

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

3.6 Analysis

Analyze samples using a GC-FID instrument and the analytical conditions described below. Use an ISTD calibration method. For each analyte construct a least-squares linear regression curve by plotting ISTD-corrected response of standard injections versus micrograms of analyte per sample. A weighted least-squares linear regression, using a $1/x$ weight, can also be used. Confirm the presence of analytes when an OSHA Permissible Exposure Limit (PEL) value has been exceeded, as described in Section 3.8. See Figure 1 below for an example of a chromatogram obtained from a standard containing analyte concentrations equivalent to sampling for the recommended time for each analyte at its respective OSHA TWA PEL value.

<u>GC conditions</u>

column:	Agilent J&W DB-WAX capillary column, 60-m × 0.32-mm i.d., df = 0.5-µm, or equivalent
inlet liner:	Restek Topaz 4.0-mm ID Precision Inlet Liner w/wool (Restek catalog no. 23305, or equivalent)
carrier:	hydrogen, 2 mL/min, constant flow mode
septum purge:	hydrogen, 3.0 mL/min
injection:	1.0 µL, split injection (150:1 ratio)
inlet temperature:	235 °C
oven temperature:	40 °C (hold 4 min), ramp to 70 °C at 5 °C/min (hold 0 min), ramp to 205 °C at 15 °C/min (hold 0 min), ramp to 240 °C at 35 °C/min (hold 0 min)
run time:	20 min
retention times:	4.72 min - CS_2 7.88 min - methyl alcohol 8.76 min - isopropyl alcohol 8.95 min - ethyl alcohol 11.39 min - *sec*-butyl alcohol 11.71 min - *n*-propyl alcohol 12.80 min - isobutyl alcohol 13.78 min - *n*-butyl alcohol 16.63 min - DMF 18.53 min - ISTD

FID conditions

detector temperature:	240 °C
hydrogen flow:	40 mL/min
air flow:	450 mL/min
nitrogen make up flow:	45 mL/min

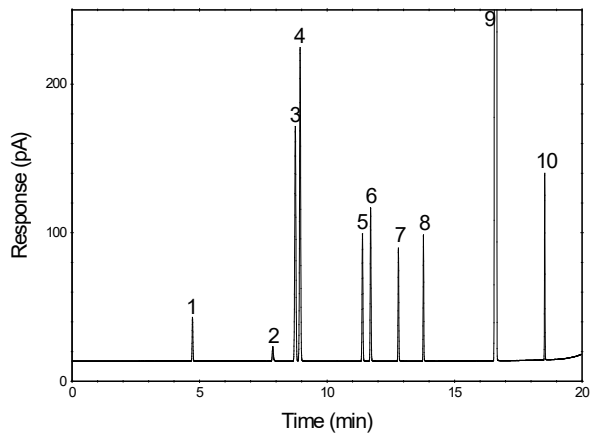

Figure 1. Example chromatogram. Peak labels: (1) CS_2, (2) methyl alcohol, (3) isopropyl alcohol, (4) ethyl alcohol, (5) *sec*-butyl alcohol, (6) *n*-propyl alcohol, (7) isobutyl alcohol, (8) *n*-butyl alcohol, (9) DMF, (10) ISTD.

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 in 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 5001 analytes.

	n-butyl alcohol	*sec*-butyl alcohol	ethyl alcohol	isobutyl alcohol	isopropyl alcohol	methyl alcohol	*n*-propyl alcohol
M (g/mol)	74.12	74.12	46.07	74.12	60.09	32.04	60.09
E_E	1.015	1.025	1.009	1.022	1.024	0.988	1.017
IMIS	0460	0461	1060	1536	1560	1660	2170

3.8 Qualitative Analysis

When necessary, the identity of an analyte peak can be confirmed by gas chromatography – mass spectrometry (GC-MS) using the analytical conditions described below. Confirm the presence of an analyte by matching the retention time and fragmentation pattern of a standard at a similar concentration. See Figure 2 below for an example of a total ion current (TIC) chromatogram obtained from a standard containing analyte concentrations equivalent to sampling for the recommended time for each analyte at its respective OSHA TWA PEL value.

<u>GC conditions</u>

column:	Agilent J&W DB-WAX capillary column, 60-m × 0.32-mm i.d., df = 0.5-µm, or equivalent
inlet liner:	Restek Topaz 4.0-mm ID Precision Inlet Liner w/wool (Restek catalog no. 23305, or equivalent)
carrier:	helium, 1.6 mL/min, constant flow mode
septum purge:	helium, 3.0 mL/min
injection:	1.0 µL, split injection (150:1 ratio)
Inlet temperature	235 °C
oven temperature:	40 °C (hold 4.15 min), ramp to 70 °C at 4.7 °C/min (hold 0 min), ramp to 205 °C at 13 °C/min (hold 0 min), ramp to 240 °C at 35 °C/min (hold 0 min)
run time:	21.9 min
retention times:	7.75 min - methyl alcohol 8.65 min - isopropyl alcohol 8.86 min - ethyl alcohol 11.57 min - *sec*-butyl alcohol 11.97 min - *n*-propyl alcohol 13.25 min - isobutyl alcohol 14.44 min - *n*-butyl alcohol 20.14 min – ISTD

mass spectrometer conditions

mode:	electron ionization (EI)
acquisition mode:	scan, *m/z* 20 – 150
solvent delay:	6 min
timed events:	17.8 – 18.20 min MS Off
EMV mode:	gain factor (1)
temperatures:	250 °C (source), 200 °C (quadrupole assembly), 250 °C (transfer line)

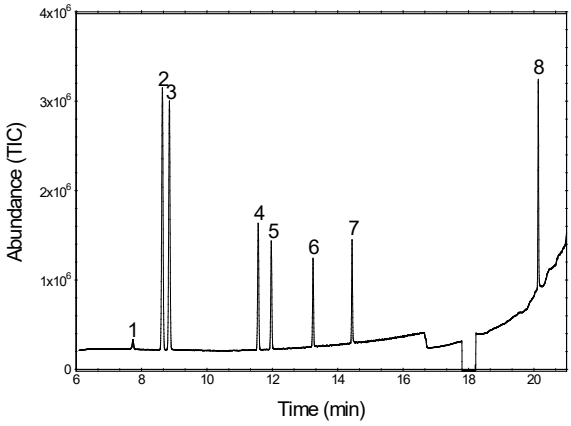

Figure 2. Example TIC GC-MS chromatogram. Peak labels: (1) methyl alcohol, (2) isopropyl alcohol, (3) ethyl alcohol, (4) *sec*-butyl alcohol, (5) *n*-propyl alcohol; (6) isobutyl alcohol, (7) *n*-butyl alcohol, (8) ISTD.

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OSHA 5001, Appendix A
Methyl Alcohol

Version:	1.0
OSHA PEL:	200 ppm (260 mg/m^3) TWA
ACGIH TLV:	200 ppm (262 mg/m^3) TWA, 250 ppm (328 mg/m^3) STEL
Recommended sampling time and sampling rate:	100 min at 50 mL/min (5 L) if relative humidity is > 50% at 25 °C 60 min at 50 mL/min (3 L) if relative humidity is < 50% at 25 °C
Reliable quantitation limit:	1.1 ppm (1.4 mg/m^3)
Standard error of estimate:	5.24%
Status:	Fully validated. Method 5001 has been subjected to the established validation procedures of the Method Development Team for sampling and analysis of methyl alcohol.

October 1991 (OSHA Method 91) Warren Hendricks
March 2019 Michael Simmons

1 Introduction

1.1 Previous Methods used by OSHA for Sampling and Analysis of Methyl Alcohol

Prior to OSHA Method 91[1], OSHA used an in-house modification of a National Institute for Occupational Safety and Health (NIOSH) method for the sampling and analysis of methyl alcohol. The NIOSH method requires sample collection on silica gel, desorption with water, and analysis by gas chromatography (GC) using a flame ionization detector (FID). Two samplers are recommended in the NIOSH method; one is a 2-section sampling tube containing 100/50-mg sections of silica gel and the other is a 3-section sampling tube containing 750/150/150-mg sections of silica gel. The 3-section tube is to be used when either high relative humidity or high levels of methyl alcohol are anticipated.[2] The OSHA in-house modification of the NIOSH method consisted of sample collection using a 2-section sampling tube containing 520/260-mg sections of silica gel, and desorption with dilute sulfuric acid.[3]

When completing an ambient temperature storage stability test using these 520/260-mg silica gel sampling tubes, extensive migration of methyl alcohol from the 520-mg to the 260-mg sections was observed. These results, together with a desire to find a more versatile collection medium, provided motivation to examine different sorbents. Several were screened, but only carbon molecular sieves (SKC) and Anasorb 747 (SKC, a carbon-based adsorbent produced from pitch) had sufficient capacity for methyl alcohol under potential conditions of use. Both sorbents performed poorly in collecting methyl alcohol at low relative humidity compared to high relative humidity, and this was thought to be caused by the affinity of methyl alcohol for simultaneously collected water. The capacity of carbon molecular sieves was more affected at low humidity than Anasorb 747; therefore, Anasorb 747 was selected for further evaluation. Anasorb 747 was also a logical choice for further evaluation due to the likelihood that other analytes, which may have been collected while sampling for methyl alcohol could also be sampled and analyzed using this sorbent.

[1] Hendricks, W. Methyl Alcohol (OSHA Method 91), 1991. United States Department of Labor, Occupational Safety & Health Administration.
[2] "NIOSH Manual of Analytical Methods", 3rd ed. Vol. 2; U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Division of Physical Sciences and Engineering; Cincinnati, OH, 1984, Method 2000, DHHS (NIOSH).
[3] OSHA Computerized Information System Database, SLCAL Chemical Sampling Information, Methyl Alcohol, REV 900508.

Two separate sampling tubes are specified by OSHA Method 91[1] with one serving analogously to a front section and the other as a back section. The tubes are to be connected in series before sampling, and separated after sampling. The desorption solvent specified by OSHA Method 91[1] is 50/50 *N*,*N*-dimethylformamide/carbon disulfide (DMF/CS_2), with the high percentage of DMF used to eliminate or minimize the potential for a 2-phase (water/solvent) sample extract. Due to the effect of low humidity on sampler capacity for methyl alcohol the recommended air sample volume for methyl alcohol collected on Anasorb 747 is reduced at lower relative humidity. Fifty-percent relative humidity at 25 °C (11.5 mg of water per liter of air) was selected as the point at which to reduce the recommended air volume, as this provides an adequate margin of safety against sampler saturation. Most samples will likely be collected at higher relative humidity.

1.2 Changes to the Previously Used Method

This appendix represents an update of OSHA Method 91, which was fully validated at the time it was published based on the validation guidelines in effect at the time. Changes to analytical conditions, internal standard, extraction solvent, and extraction solvent volume have been made to allow standardized collection of methyl alcohol with the other analytes found in the Organic Vapor Sampling Group 2, described in Method 5001. Due to the analytical changes compared to OSHA Method 91, the detection limit of the analytical procedure (DLAP), detection limit of the overall procedure (DLOP), reliable quantitation limit (RQL), instrument response to methyl alcohol, extraction efficiency (E_E), and stability of extracted samples were all reevaluated.

1.3 Validation Parameters

The procedures used to update 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 analyte concentration equivalent to sampling for the recommended time at the OSHA TWA permissible exposure limit (PEL) for methyl alcohol.

2 Detection and Quantification

2.1 Detection Limit of the Analytical Procedure

The DLAP is the analyte mass introduced onto the chromatographic column that produces a response significantly greater than a reagent blank. Ten analytical standards were prepared with approximately equal descending increments of analyte, such that the highest standard concentration would produce a peak approximately 10 times the response of a blank at or near the chromatographic retention time of the analyte. These standards and a reagent blank were analyzed with the analytical parameters. The data obtained were used to determine the required parameters (standard error of estimate ($S_{y/x}$) and slope) for the calculation of the DLAP. Results obtained for the blank and each standard are listed below in Table A-1 and are plotted in Figure A-1.

[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 A-1. DLAP data for methyl alcohol.

concentration (µg/mL)	mass on column (pg)	area counts (µV·s)
0.00	0.00	0.000
0.52	3.43	0.021
1.03	6.87	0.029
1.54	10.3	0.092
2.06	13.7	0.080
2.57	17.1	0.120
3.08	20.6	0.153
3.60	24.0	0.164
4.12	27.4	0.194
4.63	30.9	0.211
5.15	34.3	0.232

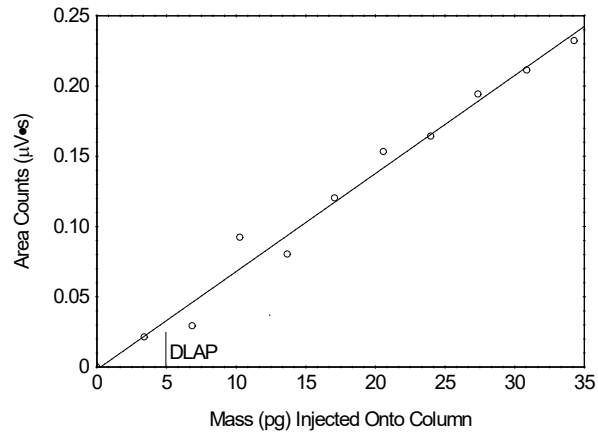

Figure A-1. Plot of data used to determine the DLAP for methyl alcohol ($y = 0.0070x - 0.0018$, $S_{y/x}$ = 0.0114, DLAP = 4.9 pg).

2.2 Detection Limit of the Overall Procedure and Reliable Quantitation Limit

The DLOP is the analyte mass per sample that produces a response significantly different than a sample blank. The RQL is the lowest level of analyte mass per sample for precise quantitative measurements and expressed as an air concentration based on the recommended sampling parameters. Ten samplers were spiked with approximately equal descending increments of analyte, such that the highest loading would produce a peak approximately 10 times the response of a sample blank at or near the chromatographic retention time of the analyte. These spiked samplers and a sample blank were analyzed with the analytical parameters. The data obtained were used to calculate the required parameters ($S_{y/x}$ and the slope) for the calculation of the DLOP and RQL. Results obtained for the sample blank and the ten spiked samplers are listed below in Table A-2 and plotted in Figure A-2.

Table A-2. DLOP and RQL data for methyl alcohol.

mass per sample (µg)	area counts (µV·s)
0.00	0.000
1.03	0.000
2.06	0.054
3.09	0.088
4.11	0.145
5.14	0.141
6.17	0.172
7.20	0.180
8.23	0.216
9.26	0.220
10.3	0.266

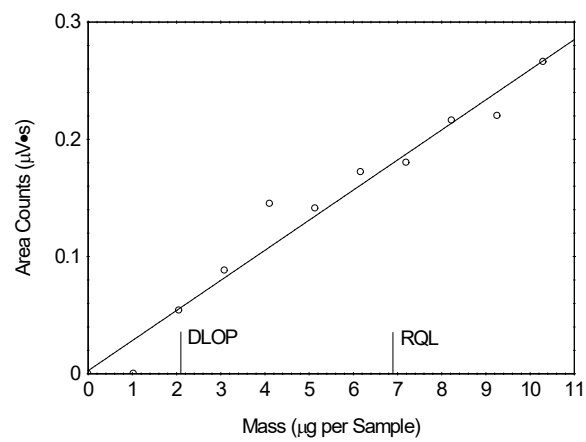

Figure A-2. Plot of data used to determine the DLOP and RQL for methyl alcohol ($y = 0.026x + 0.003$, $S_{y/x}$ = 0.018, DLOP = 2.1 µg/sample, RQL = 6.9 µg/sample (1.1 ppm)).

3 Analytical Calibration

Fifteen analytical standards over a range of 0.1 to 2.0× the target concentration were prepared and analyzed with the analytical parameters. A least-squares linear regression curve was constructed by plotting the analyte mass per sample versus the ratio of analyte peak area to internal standard (ISTD) peak area. The data obtained was used to calculate the analytical calibration precision ($S_{y/x}$). Results are listed below in Table A-3 and plotted in Figure A-3.

Table A-3. Analytical precision data for methyl alcohol.

× target concn (µg/sample)	0.1× 134.5	0.5× 672.5	1.0× 1345	1.5× 2018	2.0× 2690
area ratio	0.0144	0.0791	0.1672	0.2445	0.3306
	0.0151	0.0810	0.1642	0.2463	0.3266
	0.0149	0.0830	0.1652	0.2494	0.3333

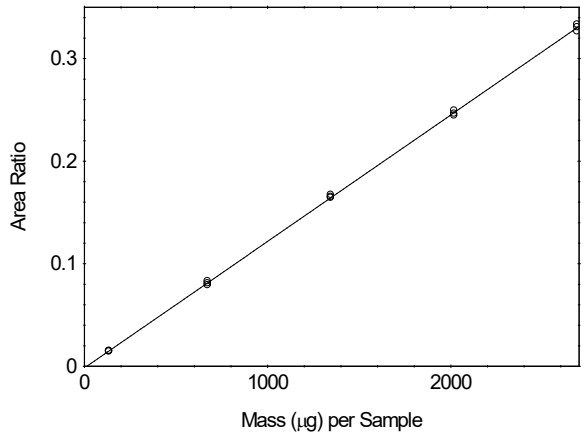

Figure A-3. Plot of data used to estimate precision of the analytical method for methyl alcohol ($y = 0.00012x$ - 0.00158, $S_{y/x} = 0.0020$).

4 Sampler Storage Stability

Pre-existing data from OSHA Method 91[1] are presented in this section.

Thirty-six samples were collected by sampling a test atmosphere containing 526 mg/m^3 methyl alcohol for about 50 min at 0.05 L/min. Storage samples are usually collected by sampling a test atmosphere at the target concentration for the recommended time at the recommended sampling rate. However, the concentration of the test atmosphere was doubled and the sampling time was halved for the generation of storage samples used in this study. This was done so that both ambient and refrigerated storage samples could be collected on the same day. The relative humidity of the atmosphere was 60% at 27 °C. Eighteen of the samples were stored at -2 °C, and the other eighteen were stored in the dark at ambient temperature (about 24 °C). Three samples were selected from each of the two storage sets and analyzed at the intervals noted in Table A-4. Sample results were not corrected for extraction efficiency. Results obtained for the ambient and refrigerated storage test are listed below in Table A-4. Results are plotted in Figure A-4 and Figure A-5.

Table A-4. Sampler storage stability data for methyl alcohol.

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	94.7	91.2	94.6	94.8	91.9	95.4
0	94.8	91.9	95.4	94.7	91.2	94.6
4	91.3	89.2	90.5	93.3	93.8	93.8
8	89.5	91.3	90.6	93.4	91.3	93.1
11	93.1	90.3	91.2	96.7	94.4	96.3
14	90.5	88.7	91.0	94.4	93.1	92.9
18	88.7	89.0	87.0	81.0	90.8	91.4

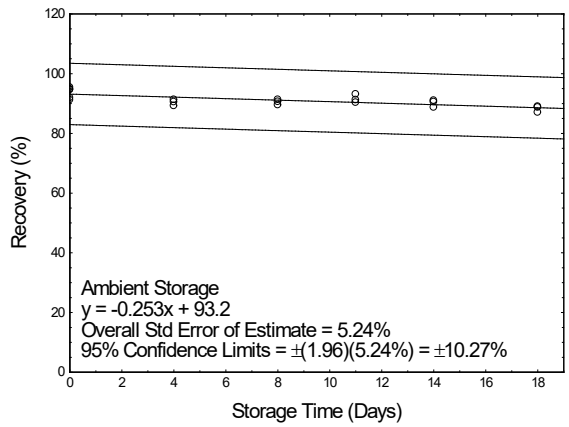

Figure A-4. Plot of the ambient storage stability data for methyl alcohol.

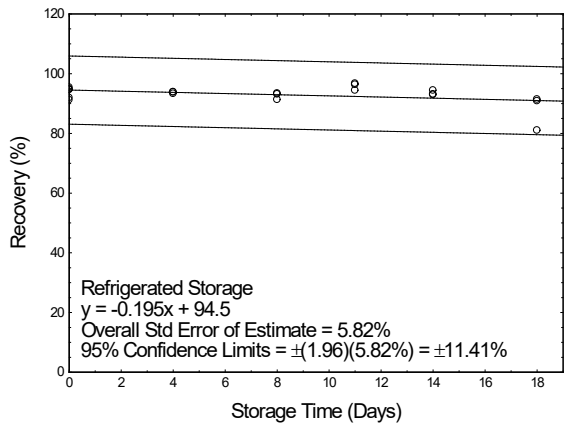

Figure A-5. Plot of refrigerated storage stability data for methyl alcohol.

5 Precision

Pre-existing data from OSHA Method 91[1] are presented in this section.

The precision of the overall procedure at the 95% confidence level is obtained by multiplying the overall standard error of estimate by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). This provides ninety-five percent confidence intervals which are drawn about the regression lines in the storage stability figures shown in Section 4.

The precision of the overall procedure at the 95% confidence level for the ambient temperature (about 22 °C) 18-day storage test (at the target concentration) is ±10.27%. It was obtained from the overall standard error of estimate (5.24%) derived from the data shown in Figure A-4, with an additional 5% added for sampling pump error.

The recovery of methyl alcohol from samples used in the 18-day storage test was 88.6% when the samples were stored at ambient temperature.

6 Recovery and Stability of Prepared Samples

Quantitative extraction is affected by the extraction solvent, the internal standard, the sampling medium, and the technique used to extract the samples. For the use of reagents and techniques other than those described here, testing specified in current OSHA validation guidelines must be completed.

A value for E_E was determined by liquid-spiking four sorbent tubes at a range of 0.1 to 2.0× the target concentration. For a single set of sorbent tubes spiked with analyte equivalent to sampling at the 1.0× target concentration value for 100 min, humid air (80% relative humidity at 21 °C) was passed through the sorbent tubes for 360 min at 50 mL/min prior to spiking. Another set of sorbent tubes was spiked at the RQL level. The spiked samples were stored overnight at ambient temperature and then analyzed. An overall mean E_E value of 98.77% was obtained across the analyte concentration range studied, and the E_E value at the RQL was 96.24%. The results of these tests are provided in Table A-5, and they demonstrate that the presence of water in the sorbent material had no significant effect on E_E. The E_E values for the RQL and wet sampler testing were not included in the overall mean.

Table A-5. Extraction efficiency data for methyl alcohol.

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.1	134.5	100.6	98.25	97.23	98.52	98.65
0.25	322.8	100.6	98.89	100.1	98.03	99.40
0.5	672.5	97.78	98.61	98.72	98.86	98.49
1.0	1345	100.0	98.48	98.83	98.72	99.01
1.5	2018	98.73	97.60	97.59	98.74	98.17
2.0	2690	98.92	98.16	98.83	99.67	98.90
RQL	6.96	91.84	97.18	95.45	100.5	96.24
1.0 (wet)	1345	99.42	99.03	100.2	99.40	99.51

The stability of extracted samples was examined by reanalyzing the 1.0× target concentration samples 24, 48, and 72 hours after the initial analysis. The septum of a vial was punctured four times for each injection (three syringe rinses and 1 syringe fill that was injected for analysis). After the original analysis was performed, two vials were recapped with new septa which were replaced after each reanalysis. The remaining two vials retained their sequentially-punctured septa throughout the test. All samples were allowed to stand at room temperature in the autosampler tray used. Freshly prepared standards were used for each reanalysis event. Results obtained are listed in Table A-6.

Table A-6. Extracted sample stability data for methyl alcohol.

	punctured septa replaced recovery (%)		punctured septa retained recovery (%)	
time (days)	1	2	1	2
0	100.0	98.48	98.83	98.72
1	99.18	98.35	97.51	97.70
2	99.03	98.33	97.11	96.22
3	98.59	98.31	94.51	94.06

7 Sampler Capacity

Pre-existing data from OSHA Method 91[1] are presented in this section.

Sampler capacity was evaluated by sampling controlled test atmospheres with a single front sampling tube (400-mg tube) and several back sampling tubes (200-mg tubes) to monitor the effluent from the front sampling tube. A back sampling tube was connected to a front tube during sampling, with sampling halted at specified intervals to remove a back tube and replace it with a fresh tube, followed by continued sampling. The methyl alcohol concentration in the effluent was determined based on the mass of analyte recovered from a back tube and the air volume sampled during each interval. Percent breakthrough was calculated by dividing the concentration in the effluent by the concentration of the test atmosphere and then multiplying the result by 100. Five-percent breakthrough from the front tube was used as evidence that sampling capacity had been exceeded. Three sampler capacity experiments were performed at different relative humidities as shown in Table A-7. The average concentration of the test atmospheres was 420 ppm and sampling was performed at 0.05 L/min. Results obtained are listed in Table A-7. Cumulative air volumes were used and these were calculated based on the midpoint of each measured time interval. The resulting capacity test data are also presented graphically in Figure A-6. The five-percent breakthrough volumes for each capacity test are listed in Table A-8.

Table A-7. Sampler capacity data for methyl alcohol.[a]

79% RH, 22 °C		41% RH, 25 °C		13% RH, 22 °C	
air vol (L)	BT (%)	air vol (L)	BT (%)	air vol (L)	BT (%)
4.05	0.0	4.49	0.1	2.97	0.0
4.30	0.2	4.74	2.6	3.51	1.0
4.82	0.3	5.25	5.8	4.05	7.7
5.32	0.4	5.75	10.9	4.59	23.2
5.84	0.4	6.25	17.2		
6.34	1.3	6.76	24.9		
6.86	2.3				
7.36	3.1				
7.88	5.7				
8.38	13.0				
8.92	21.7				

[a]RH is relative humidity and BT is breakthrough.

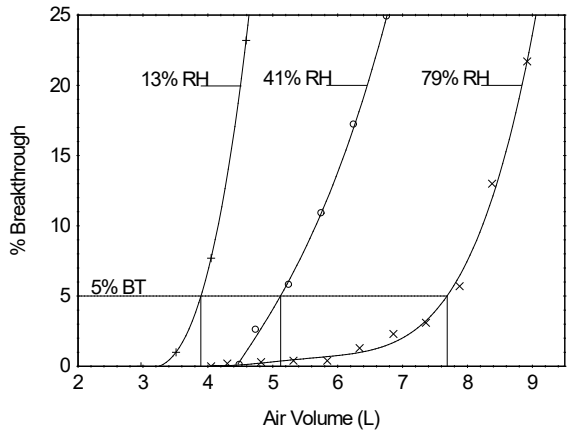

Figure A-6. Plot of data used to determine sampler capacity for methyl alcohol. RH is relative humidity and BT is breakthrough.

Table A-8. Sampler capacity results for methyl alcohol.

relative humidity (%)	temperature (°C)	5% breakthrough (L)
79	22	7.6
41	25	5.1
13	22	3.8

8 Low Humidity

A low humidity recovery test was not performed; however, low humidity capacity tests were performed above in Section 7.

9 Chemical Interferences

Pre-existing data from OSHA Method 91[1] are presented in this section.

A sampling interference study was performed by sampling test atmospheres containing methyl alcohol, toluene, and butyl cellosolve, representative of a known workplace solvent mixture which contained 69% methyl alcohol, 26% toluene, and 5% 2-butoxyethanol. The concentrations of the test atmospheres were 408-mg/m^3 methyl alcohol, 154-mg/m^3 toluene, and 29.6-mg/m^3 2-butoxyethanol. Both humid (76% relative humidity at 26 °C) and dry (23% relative humidity at 24 °C) test atmospheres were generated. The air sample volumes collected from the humid atmosphere were 4, 5, and 6 L and those for the dry atmosphere were 2, 3, and 4 L. No excessive breakthrough was observed in any of the samples and the average recoveries were: methyl alcohol, 94%; toluene, 88%; and butyl cellosolve, 91%. Toluene and 2-butoxyethanol recoveries were not corrected for desorption efficiency.

10 Reproducibility

Pre-existing data from OSHA Method 91[1] are presented in this section.

Six samples were prepared by sampling a dynamically generated controlled test atmosphere. The nominal concentration of methyl alcohol in the test atmosphere was 206 ppm, and the relative humidity was 59% at 26 °C. The samples were submitted to the OSHA Salt Lake Technical Center for analysis using OSHA Method 91, which was completed following fourteen days of storage at -2 °C. Sample results were corrected for E_E. No sample result for methyl

alcohol had a deviation greater than the precision of the overall procedure described in Section 5. One sample was lost in analysis. Results obtained are listed in Table A-9.

Table A-9. Reproducibility data for methyl alcohol.

sampled (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
1135.18	1136.43	100.1	0.1
1210.85	1190.55	98.3	-1.7
1148.69	1116.73	97.2	-2.8
1486.54	1429.91	96.2	-3.8
1483.84	1389.21	93.6	-6.4

11 Additional Testing

No testing other than the tests listed above was performed.

12 Estimation of Uncertainty

Estimation of uncertainty was not performed. Instead the overall standard error of estimate was calculated from the ambient storage test as prescribed by the OSHA validation guidelines in use at the time OSHA Method 91[1] was originally evaluated.

13 Sampler Testing Procedure

Specific details regarding test atmosphere generation were not described in the 1991 version of OSHA Method 91.[1] Additional test atmosphere generation was not performed for this update.

OSHA 5001, Appendix B
Ethyl Alcohol

Version:	1.0
OSHA PEL:	1000 ppm (1900 mg/m^3) TWA
ACGIH TLV:	1000 ppm (1880 mg/m^3) STEL
Recommended sampling time and sampling rate:	240 min at 50 mL/min (12 L)
Reliable quantitation limit:	257 ppb (0.48 mg/m^3)
Standard error of estimate:	5.17%
Status:	Fully validated. Method 5001 has been subjected to the established validation procedures of the Method Development Team for sampling and analysis of ethyl alcohol.

April 1993 (OSHA Method 100) Warren Hendricks
March 2019 Michael Simmons

1 Introduction

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

Prior to OSHA Method 100[1], OSHA used a procedure based on the National Institute for Occupational Safety and Health (NIOSH) Method 1400[2] for the sampling and analysis of ethyl alcohol. The NIOSH method requires sample collection on coconut-shell charcoal, refrigerated sample shipment and storage, desorption with 99/1 carbon disulfide (CS_2)/2-butanol, and that analysis be performed as soon as possible. Analysis with the NIOSH method is by gas chromatography (GC) using a flame ionization detector (FID).

When completing an ambient temperature storage stability test using the coconut-shell charcoal sampling tubes, extensive migration of ethyl alcohol from the front to the rear sections was observed. In completing OSHA Method 100, Anasorb 747 was selected for evaluation based on the previous work completed for OSHA Method 91 using this sorbent for sampling and analysis of methyl alcohol.[3] During testing of OSHA Method 100, sampler capacity tests showed that Anasorb 747 had acceptable capacity for ethyl alcohol, however, ethyl alcohol (like methyl alcohol) was found to undergo post-sampling migration from the front to the rear sorbent section.

Two separate sampling tubes are specified by OSHA Method 100 with one serving analogously to a front section and the other as a back section. The tubes are to be connected in series before sampling, and separated after sampling. The desorption solvent specified by OSHA Method 100 is 60/40 *N*,*N*-dimethylformamide/carbon disulfide (DMF/CS_2), with the high percentage of DMF used to eliminate or minimize the potential for a 2-phase (water/solvent) sample extract. The use of the Anasorb 747 sorbent specified by OSHA Method 100 provides better capacity for ethyl alcohol compared to the NIOSH method.

[1] Hendricks, W. Ethyl Alcohol (OSHA Method 100), 1993. United States Department of Labor, Occupational Safety & Health Administration.
[2] *NIOSH Manual of Analytical Methods*, 3rd. ed; Eller, P.M., Ed.; U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Division of Physical Sciences and Engineering: Cincinnati, DHHS (NIOSH) Publication No. 84-100, 1984; Method 1400.
[3] Hendricks, W. Methyl Alcohol (OSHA Method 91), 1991. United States Department of Labor, Occupational Safety & Health Administration.

1.2 Changes to the Previously Used Method

This appendix represents an update of OSHA Method 100, which was fully validated at the time it was published based on the validation guidelines in effect at the time. Changes to analytical conditions, internal standard, and extraction solvent volume have been made to allow standardized collection of ethyl alcohol with the other analytes found in the Organic Vapor Sampling Group 2, described in Method 5001. Due to the analytical changes compared to OSHA Method 100, the detection limit of the analytical procedure (DLAP), detection limit of the overall procedure (DLOP), reliable quantitation limit (RQL), instrument response to ethyl alcohol, extraction efficiency (E_E), and stability of extracted samples were all reevaluated.

1.3 Validation Parameters

The procedures used to update 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 analyte concentration equivalent to sampling for the recommended time at the OSHA TWA permissible exposure limit (PEL) for ethyl alcohol.

2 Detection and Quantification

2.1 Detection Limit of the Analytical Procedure

The DLAP is the analyte mass introduced onto the chromatographic column that produces a response significantly greater than a reagent blank. Ten analytical standards were prepared with approximately equal descending increments of analyte, such that the highest standard concentration would produce a peak approximately 10 times the response of a blank at or near the chromatographic retention time of the analyte. These standards and a reagent blank were analyzed with the analytical parameters. The data obtained were used to determine the required parameters (standard error of estimate ($S_{y/x}$) and slope) for the calculation of the DLAP. Results obtained for the blank and each standard are listed below in Table B-1 and are plotted in Figure B-1.

Table B-1. DLAP data for ethyl alcohol.

concentration (µg/mL)	mass on column (pg)	area counts (µV·s)
0.00	0.00	0.000
0.51	3.40	0.032
1.02	6.80	0.060
1.53	10.2	0.094
2.04	13.6	0.167
2.55	17.0	0.168
3.06	20.4	0.191
3.58	23.9	0.214
4.08	27.2	0.265
4.60	30.7	0.364
5.10	34.0	0.367

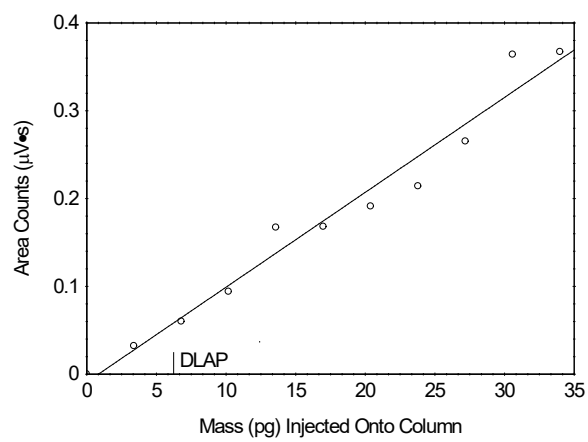

Figure B-1. Plot of data used to determine the DLAP for ethyl alcohol ($y = 0.0108x - 0.0089$, $S_{y/x} = 0.0234$, DLAP = 6.5 pg).

[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).

2.2 Detection Limit of the Overall Procedure and Reliable Quantitation Limit

The DLOP is the analyte mass per sample that produces a response significantly different than a sample blank. The RQL is the lowest level of analyte mass per sample for precise quantitative measurements and expressed as an air concentration based on the recommended sampling parameters. Ten samplers were spiked with approximately equal descending increments of analyte, such that the highest loading would produce a peak approximately 10 times the response of a sample blank at or near the chromatographic retention time of the analyte. These spiked samplers and a sample blank were analyzed with the analytical parameters. The data obtained were used to calculate the required parameters ($S_{y/x}$ and the slope) for the calculation of the DLOP and RQL. Results obtained for the sample blank and the ten spiked samplers are listed below in Table B-2 and plotted in Figure B-2.

Table B-2. DLOP and RQL data for ethyl alcohol.

mass per sample (µg)	area counts (µV·s)
0.00	0.000
1.02	0.033
2.04	0.100
3.06	0.080
4.08	0.141
5.10	0.175
6.13	0.190
7.15	0.265
8.17	0.265
9.19	0.282
10.2	0.317

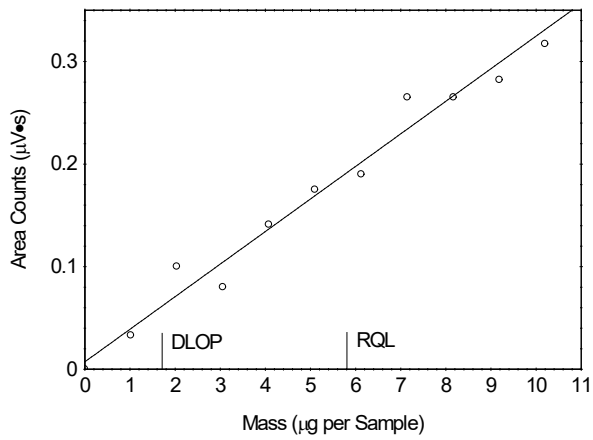

Figure B-2. Plot of data used to determine the DLOP and RQL for ethyl alcohol ($y = 0.031x + 0.009$, $S_{y/x} = 0.018$, DLOP = 1.7 µg/sample, RQL = 5.8 µg/sample (257 ppb)).

3 Analytical Calibration

Fifteen analytical standards over a range of 0.1 to 2.0× the target concentration were prepared and analyzed with the analytical parameters. A least-squares linear regression curve was constructed by plotting the analyte mass per sample versus the ratio of analyte peak area to internal standard (ISTD) peak area. The data obtained was used to calculate the analytical calibration precision ($S_{y/x}$). Results are listed below in Table B-3 and plotted in Figure B-3.

Table B-3. Analytical precision data for ethyl alcohol.

× target concn (µg/sample)	0.1×	0.5×	1.0×	1.5×	2.0×
	2356.1	11780	22775	35340	47121
area ratio	0.3763	1.920	3.786	5.724	7.700
	0.3730	1.934	3.754	5.801	7.616
	0.3708	1.956	3.740	5.824	7.792

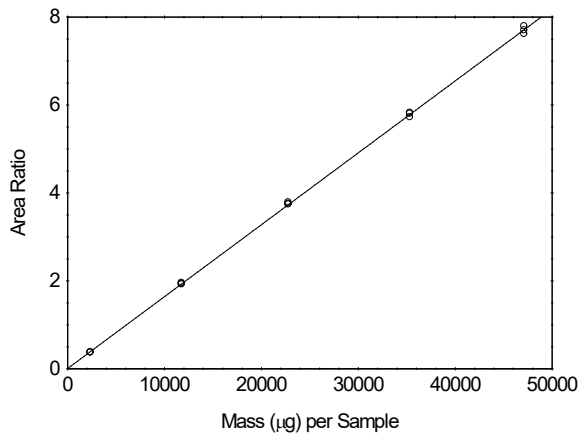

Figure B-3. Plot of the data used to estimate precision of the analytical method for ethyl alcohol ($y = 0.00016x + 0.00571$, $S_{y/x} = 0.0453$).

4 Sampler Storage Stability

Pre-existing data from OSHA Method 100[1] are presented in this section.

Thirty-six samples were collected by sampling a test atmosphere containing 1979 ppm ethyl alcohol for 2 hours at 0.05 L/min. Storage samples are usually collected by sampling a test atmosphere at the target concentration for the recommended time at the recommended sampling rate. However, the concentration of the test atmosphere was doubled and the sampling time was halved for the generation of storage samples used in this study. This was done so that both ambient and refrigerated storage samples could be collected on the same day. The relative humidity of the atmosphere was 75% at 26 °C. Fifteen of the samples were stored in a refrigerator at 5 °C, and another fifteen were stored in the dark at ambient temperature (about 23 °C). Three samples were selected from each of the two storage sets and analyzed at the intervals noted in Table B-4. Sample results were not corrected for extraction efficiency. Results obtained for the ambient and refrigerated storage test are listed below in Table B-4. Results are plotted in Figure B-4 and Figure B-5.

Table B-4. Sampler storage stability data for ethyl alcohol.

time (days)	ambient storage recovery (%)			time (days)	refrigerated storage recovery (%)		
0	105.0	105.4	102.4	0	102.6	104.4	100.3
3	104.2	105.4	103.3	2	104.3	105.7	102.9
7	103.4	101.6	100.7	6	102.5	105.5	102.5
10	104.2	102.9	103.4	9	104.8	103.3	100.4
14	101.3	102.7	101.6	13	106.0	104.9	103.6
16	104.6	102.3	101.7	15	103.4	106.9	102.9

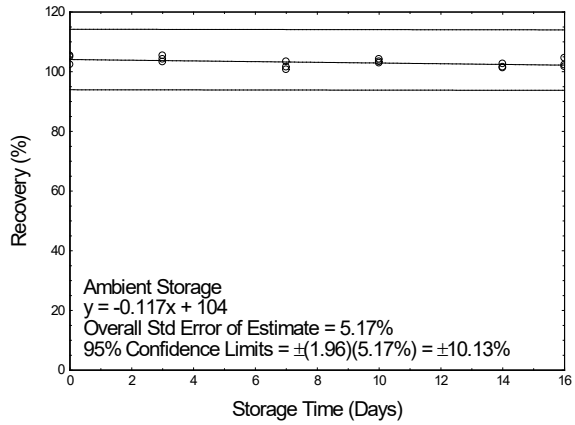

Figure B-4. Plot of ambient storage stability data for ethyl alcohol.

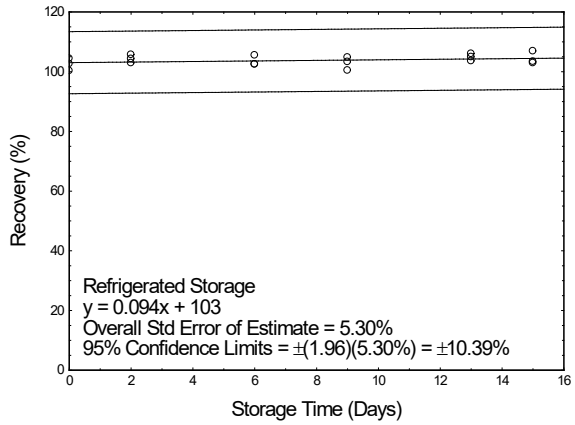

Figure B-5. Plot of refrigerated storage stability data for ethyl alcohol.

5 Precision

Pre-existing data from OSHA Method 100[1] are presented in this section.

The precision of the overall procedure at the 95% confidence level is obtained by multiplying the overall standard error of estimate by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). This provides ninety-five percent confidence intervals which are drawn about the regression lines in the storage stability figures shown in Section 4.

The precision of the overall procedure at the 95% confidence level for the ambient temperature (about 23 °C) 16-day storage test (at the target concentration) is ±10.13%. It was obtained from the overall standard error of estimate (5.17%) derived from the data shown in Figure B-4, with an additional 5% added for sampling pump error.

The recovery of ethyl alcohol from samples used in the 16-day storage test was 102.1% when the samples were stored at ambient temperature.

6 Recovery and Stability of Prepared Samples

Quantitative extraction is affected by the extraction solvent, the internal standard, the sampling medium, and the technique used to extract the samples. For the use of reagents and techniques other than those described here, testing specified in current OSHA validation guidelines must be completed.

A value for E_E was determined by liquid-spiking four sorbent tubes at a range of 0.1 to 2.0× the target concentration. For a single set of sorbent tubes spiked with analyte equivalent to sampling at the target concentration value for 4 hours, humid air (80% relative humidity at 21 °C) was passed through the sorbent tubes for 360 min at 50 mL/min prior to spiking. Another set of sorbent tubes was spiked at the RQL level. The spiked samples were stored overnight at ambient temperature and then analyzed. An overall mean E_E value of 100.9% was obtained across the analyte concentration range studied, and the E_E value at the RQL was 99.95%. The results of these tests are provided in Table B-5, and they demonstrate that the presence of water in the sorbent material had no significant effect on E_E. The E_E values for the RQL and wet sampler testing were not included in the overall mean.

Table B-5. Extraction efficiency data for ethyl alcohol.

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.1	2356	99.84	99.82	98.27	99.18	99.28
0.25	6283	100.4	100.6	100.6	100.5	100.5
0.5	11780	101.5	101.6	101.4	101.8	101.6
1.0	22775	102.5	101.8	101.5	101.8	101.9
1.5	35341	101.6	100.9	100.6	102.1	101.3
2.0	47121	100.7	101.0	101.1	101.0	101.0
RQL	5.89	98.9	103.2	97.9	99.8	99.95
1.0 (wet)	22775	102.1	101.6	102.2	102.4	102.1

The stability of extracted samples was examined by reanalyzing the 1.0× target concentration samples 24, 48, and 72 hours after the initial analysis. The septum of a vial was punctured four times for each injection (three syringe rinses and 1 syringe fill that was injected for analysis). After the original analysis was performed, two vials were recapped with new septa which were replaced after each reanalysis. The remaining two vials retained their sequentially-punctured septa throughout the test. All samples were allowed to stand at room temperature in the autosampler tray used. Freshly prepared standards were used for each reanalysis event. Results obtained are listed in Table B-6.

Table B-6. Extracted sample stability data for ethyl alcohol.

	punctured septa replaced recovery (%)		punctured septa retained recovery (%)	
time (days)	1	2	1	2
0	102.5	101.8	101.5	101.8
1	102.0	101.5	100.4	101.0
2	102.4	101.7	100.4	100.3
3	102.1	101.8	98.0	99.0

7 Sampler Capacity

Pre-existing data from OSHA Method 100[1] are presented in this section.

Sampler capacity was evaluated by sampling controlled test atmospheres with 400-mg front sampling tubes. The effluent of the sampling tube was monitored with a GC. The GC was calibrated with the test atmosphere. The average ethyl alcohol test atmosphere concentration was 1936 ppm for testing performed at 80% and 90% relative humidity, and 1941 ppm for testing performed at 5.9% and 6.1% relative humidity. Test atmosphere temperatures were about 25 °C and the sampling rate was 0.05 L/min. Five-percent breakthrough from the front tube was used as evidence that sampling capacity had been exceeded. The five-percent breakthrough at high humidity is approximately 15.2 L and at low humidity is approximately 18.9 L. Results obtained are listed in Table B-7. The resulting capacity test data are also presented graphically in Figure B-6.

Table B-7. Sampler capacity data for ethyl alcohol.[a]

80% RH, 25 °C		90% RH, 25 °C		5.9% RH, 25 °C		6.1% RH, 26 °C	
air vol (L)	BT, (%)	air vol (L)	BT, (%)	air vol (L)	BT, (%)	air vol (L)	BT, (%)
11.9	0	5.9	0	13.7	0	7.4	0
12.3	0	8.0	0	14.7	0	8.5	0
12.8	0	9.1	0	15.7	0	9.8	0
13.2	0	10.5	0	16.7	0	14.6	0
13.5	0	12.3	0	17.2	0	15.5	0
13.7	0	13.3	0	17.4	0	16.4	0
14.3	0	14.0	0	17.9	0	16.7	0
14.7	0.1	14.4	0.7	18.4	1.1	17.7	0
15.2	0.8	14.7	2.6	18.9	3.6	17.9	1.3
15.6	3.8	15.2	11.1	19.2	5.9	18.1	1.5
16.1	13.6	15.4	19.1	19.5	8.4	18.6	3.7
16.5	35.1	15.7	29.8	19.7	12.7	18.9	6.5
16.7	44.0	16.2	48.6	19.9	16.0	19.1	8.6
17.4	95.9	17.3	72.3	20.2	21.3	19.6	16.8

[a]RH is relative humidity and BT is breakthrough.

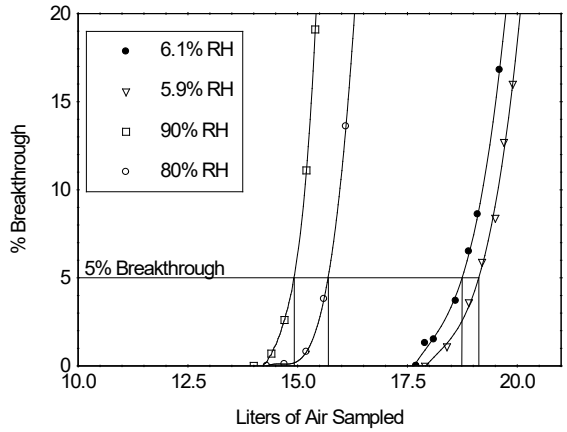

Figure B-6. Plot of data used to determine sampler capacity for ethyl alcohol. RH is relative humidity and BT is breakthrough.

8 Low Humidity

A low humidity recovery test was not performed; however, low humidity capacity tests were performed as described above in Section 7.

9 Chemical Interferences

A sampling interference study was not performed.

10 Reproducibility

Pre-existing data from OSHA Method 100[1] are presented in this section.

Six samples were prepared by sampling a dynamically generated controlled test atmosphere. The nominal concentration of ethyl alcohol in the test atmosphere was 1919 ppm, and the relative humidity was 82% at 26 °C. The samples were submitted to the OSHA Salt Lake Technical Center for analysis using OSHA Method 100, which was

completed following five days of storage at 5 °C. Sample results were corrected for E_E. No sample result for ethyl alcohol had a deviation greater than the precision of the overall procedure described in Section 5. Results obtained are listed in Table B-8.

Table B-8. Reproducibility data for ethyl alcohol.

sampled (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
20636	21492	104.1	4.1
21323	22276	104.5	4.5
22118	23081	104.4	4.4
20708	22106	106.8	6.8
22515	23392	103.9	3.9
20889	21777	104.3	4.3

11 Additional Testing

No testing other than the tests listed above was performed.

12 Estimation of Uncertainty

Estimation of uncertainty was not performed. Instead the overall standard error of estimate was calculated from the ambient storage test as prescribed by the OSHA validation guidelines in use at the time OSHA Method 100[1] was originally evaluated.

13 Sampler Testing Procedure

Specific details regarding test atmosphere generation were not described in the 1993 version of OSHA Method 100. Additional test atmosphere generation was not performed for this update.

OSHA 5001, Appendix C
Isopropyl Alcohol

Version:	1.0
OSHA PEL:	400 ppm (980 mg/m^3) TWA
ACGIH TLV:	200 ppm (491 mg/m^3) TWA, 400 ppm (984 mg/m^3) STEL
Recommended sampling time and sampling rate:	240 min at 50 mL/min (12 L)
Reliable quantitation limit:	170 ppb (0.42 mg/m^3)
Standard error of estimate:	5.15%
Status:	Fully validated. Method 5001 has been subjected to the established validation procedures of the Method Development Team for sampling and analysis of isopropyl alcohol.

October 1997 (OSHA Method 109) Mary Eide
March 2019 Michael Simmons

1 Introduction

1.1 Previous Methods used by OSHA for Sampling and Analysis of Isopropyl Alcohol

Prior to OSHA Method 109[1], OSHA used a procedure based on the National Institute for Occupational Safety and Health (NIOSH) Method 1400[2] for the sampling and analysis of isopropyl alcohol. The NIOSH method requires sample collection on coconut-shell charcoal, refrigerated sample shipment and storage, desorption with 99/1 carbon disulfide (CS_2)/2-butanol, and that analysis be performed as soon as possible. Analysis with the NIOSH method is by gas chromatography (GC) using a flame ionization detector (FID).

A study[3] was completed to evaluate the suitability of coconut-shell charcoal for sampling isopropyl alcohol by spiking charcoal tubes with 6 mg isopropyl alcohol, and drawing 3 L of humid air (80% relative humidity at 22 °C) through the tubes at 0.05 L/min, Recovery was poor whether 99/1 CS_2/2-butanol (77% recovery after extraction efficiency (E_E) correction) or 99/1 CS_2/*N*,*N*-dimethylformamide (DMF) (68% recovery after E_E correction) was used as the desorbing solvent. Poor recovery was likely due to the observed presence of a small water phase in which a portion of the isopropyl alcohol had apparently dissolved. While there was some increase in recovery when a drying agent (200 mg of anhydrous $MgSO_4$) was added (99/1 CS_2/DMF, 88% recovery after E_E correction), increasing the amount of DMF in the desorbing solvent to a 60/40 DMF/CS_2 mixture allowed the water to be dissolved and good recoveries were obtained (99.7% recovery). In completing OSHA Method 109, Anasorb 747 was selected for evaluation based on previous work

[1] Eide, M. Isopropyl Alcohol (OSHA Method 109), 1997. United States Department of Labor, Occupational Safety and Health Administration.
[2] *NIOSH Manual of Analytical Methods*, 3rd. ed; Eller, P.M., Ed.; U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Division of Physical Sciences and Engineering: Cincinnati, DHHS (NIOSH) Publication No. 84-100, 1984; Method 1400.
[3] Eide, M., *A Study of the Desorption, Retention, and Storage Efficiencies of Isopropyl Alcohol from Charcoal tubes Lot 120*, OSHA Salt Lake Technical Center, unpublished, Salt Lake City, UT 84165, October 1996.

on OSHA Methods 91[4] and 100[5] for sampling and analysis of methyl and ethyl alcohol respectively. Isopropyl alcohol (like methyl and ethyl alcohol) was found to undergo post-sampling migration from the front to the rear sorbent section.

Two separate sampling tubes are specified by OSHA Method 109[1] with one serving analogously to a front section and the other as a back section. The tubes are to be connected in series before sampling, and separated after sampling. The desorption solvent specified by OSHA Method 109[1] is 60/40 *N*,*N*-dimethylformamide/carbon disulfide (DMF/CS_2), with the high percentage of DMF used to eliminate or minimize the potential for a 2-phase (water/solvent) sample extract.

1.2 Changes to the Previously Used Method

This appendix represents an update of OSHA Method 109, which was fully validated at the time it was published based on the validation guidelines in effect at the time. Changes to analytical conditions, internal standard, and extraction solvent volume have been made to allow standardized collection of isopropyl alcohol with the other analytes found in the Organic Vapor Sampling Group 2, described in Method 5001. Due to the analytical changes compared to OSHA Method 109, the detection limit of the analytical procedure (DLAP), detection limit of the overall procedure (DLOP), reliable quantitation limit (RQL), instrument response to isopropyl alcohol, E_E, and stability of extracted samples were all reevaluated.

1.3 Validation Parameters

The procedures used to update the method validation data are described in Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis.[6] Air concentrations listed in ppm are referenced to 25 °C and 760 Torr. The target concentration for method evaluation was the analyte concentration equivalent to sampling for the recommended time at the OSHA TWA permissible exposure limit (PEL) for isopropyl alcohol.

2 Detection and Quantification

2.1 Detection Limit of the Analytical Procedure

The DLAP is the analyte mass introduced onto the chromatographic column that produces a response significantly greater than a reagent blank. Ten analytical standards were prepared with approximately equal descending increments of analyte, such that the highest standard concentration would produce a peak approximately 10 times the response of a blank at or near the chromatographic retention time of the analyte. These standards and a reagent blank were analyzed with the analytical parameters. The data obtained were used to determine the required parameters (standard error of estimate ($S_{y/x}$) and slope) for the calculation of the DLAP. Results obtained for the blank and each standard are listed below in Table C-1 and are plotted in Figure C-1.

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[4] Hendricks, W. Methyl Alcohol (OSHA Method 91), United States Department of Labor, Occupational Safety and Health Administration.

[5] Hendricks, W. Ethyl Alcohol (OSHA Method 100), United States Department of Labor, Occupational Safety and Health Administration.

[6] 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 C-1. DLAP data for isopropyl alcohol.

concentration (µg/mL)	mass on column (pg)	area counts (µV·s)
0.00	0.00	0.000
0.51	3.40	0.059
1.02	6.80	0.096
1.52	10.1	0.114
2.03	13.5	0.196
2.54	16.9	0.189
3.04	20.3	0.199
3.56	23.7	0.283
4.06	27.1	0.295
4.57	30.5	0.385
5.10	34.0	0.390

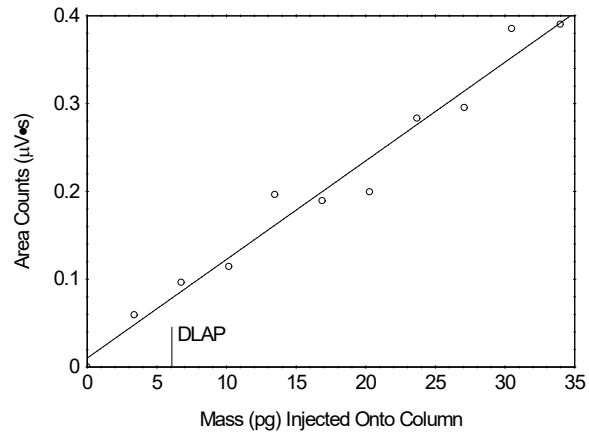

Figure C-1. Plot of data used to determine the DLAP for isopropyl alcohol ($y = 0.0112x + 0.0104$, $S_{y/x} = 0.0228$, DLAP = 6.1 pg).

2.2 Detection Limit of the Overall Procedure and Reliable Quantitation Limit

The DLOP is the analyte mass per sample that produces a response significantly different than a sample blank. The RQL is the lowest level of analyte mass per sample for precise quantitative measurements and expressed as an air concentration based on the recommended sampling parameters. Ten samplers were spiked with approximately equal descending increments of analyte, such that the highest loading would produce a peak approximately 10 times the response of a sample blank at or near the chromatographic retention time of the analyte. These spiked samplers and a sample blank were analyzed with the analytical parameters. The data obtained were used to calculate the required parameters ($S_{y/x}$ and the slope) for the calculation of the DLOP and RQL. Results obtained for the sample blank and the ten spiked samplers are listed below in Table C-2 and plotted in Figure C-2.

Table C-2. DLOP and RQL data for isopropyl alcohol.

mass per sample (µg)	area counts (µV·s)
0.00	0.000
1.02	0.055
2.03	0.118
3.05	0.144
4.06	0.216
5.08	0.235
6.09	0.250
7.11	0.335
8.12	0.324
9.14	0.384
10.2	0.428

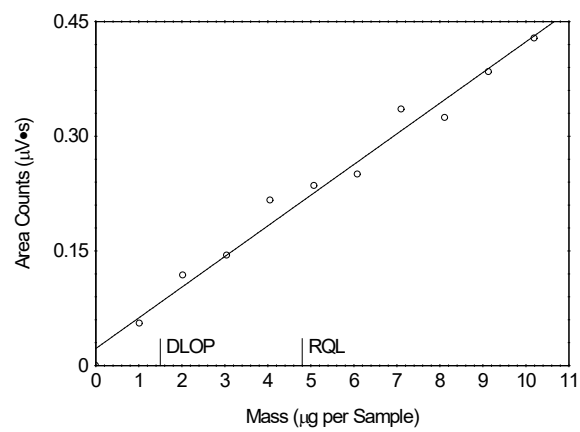

Figure C-2. Plot of data used to determine the DLOP and RQL for isopropyl alcohol ($y = 0.040x + 0.022$, $S_{y/x} = 0.020$, DLOP = 1.5 µg/sample, RQL = 5.0 µg/sample (170 ppb)).

3 Analytical Calibration

Fifteen analytical standards over a range of 0.1 to 2.0× the target concentration were prepared and analyzed with the analytical parameters. A least-squares linear regression curve was constructed by plotting the analyte mass per sample versus the ratio of analyte peak area to internal standard (ISTD) peak area. The data obtained was used to calculate the analytical calibration precision ($S_{y/x}$). Results are listed below in Table C-3 and plotted in Figure C-3.

Table C-3. Analytical precision data for isopropyl alcohol.

× target concn (µg/sample)	0.1×	0.5×	1.0×	1.5×	2.0×
	1562.2	8591.8	17184	25775	34367
area ratio	0.2708	1.485	3.075	4.537	6.121
	0.2610	1.522	3.006	4.586	6.051
	0.2581	1.526	3.042	4.610	6.141

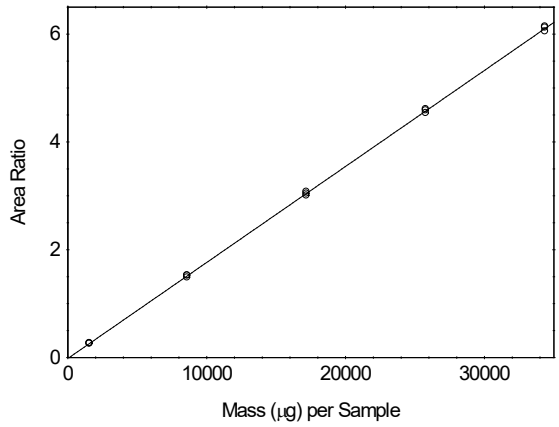

Figure C-3. Plot of the data used to estimate precision of the analytical method for isopropyl alcohol ($y = 0.00018x$-0.01737, $S_{y/x} = 0.0288$).

4 Sampler Storage Stability

Pre-existing data from OSHA Method 109[1] are presented in this section.

Thirty-six samples were collected by sampling a test atmosphere containing 405 ppm isopropyl alcohol for 90 min at 0.2 L/min, to obtain an 18 L air volume sample. Storage samples are usually collected by sampling a test atmosphere at the target concentration for the recommended time at the recommended sampling rate. However, the sampling rate was increased so that both ambient and refrigerated storage samples could be collected on the same day. The relative humidity of the atmosphere was 80% at 22 °C. Eighteen of the samples were stored in a refrigerator at 4 °C, and the other eighteen were stored in the dark at ambient temperature (about 22 °C). Three samples were selected from each of the two storage sets and analyzed at the intervals noted in Table C-4. Results obtained for the ambient and refrigerated storage test are listed below in Table C-4. Results are plotted in Figure C-4 and Figure C-5.

Table C-4. Sampler storage stability data for isopropyl alcohol.

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	103.6	104.6	105.0	103.6	104.6	105.0
0	103.1	104.3	103.2	103.1	104.3	103.2
3	105.8	105.7	104.9	104.0	104.3	103.8
7	103.0	102.3	102.8	107.8	108.5	106.6
10	104.9	105.2	104.6	103.9	104.2	102.0
14	102.4	102.4	102.3	102.5	102.7	103.5
19	102.1	100.3	100.2	100.9	100.3	101.8

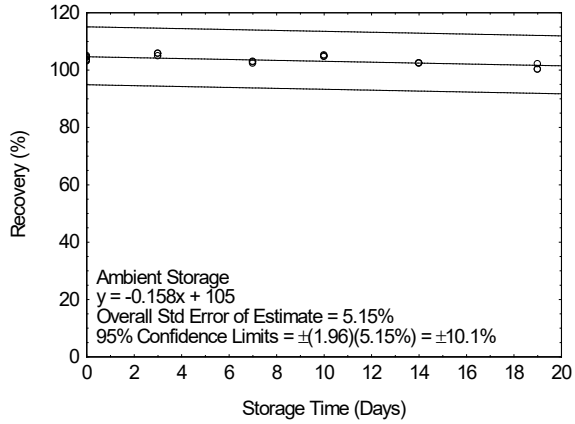

Figure C-4. Plot of ambient storage stability data for isopropyl alcohol.

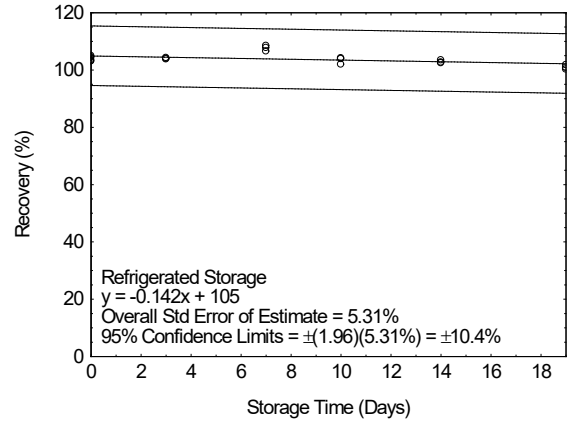

Figure C-5. Plot of refrigerated storage stability data for isopropyl alcohol.

5 Precision

Pre-existing data from OSHA Method 109[1] are presented in this section.

The precision of the overall procedure at the 95% confidence level is obtained by multiplying the overall standard error of estimate by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). This provides ninety-five percent confidence intervals which are drawn about the regression lines in the storage stability figures shown in Section 4.

The precision of the overall procedure at the 95% confidence level for the ambient temperature (about 22 °C) 19-day storage test (at the target concentration) is ±10.1%. It was obtained from the overall standard error of estimate (5.15%) derived from the data shown in Figure C-4, with an additional 5% added for sampling pump error.

The recovery of isopropyl alcohol from samples used in the 19-day storage test was 102.0% when the samples were stored at ambient temperature.

6 Recovery and Stability of Prepared Samples

Quantitative extraction is affected by the extraction solvent, the internal standard, the sampling medium, and the technique used to extract the samples. For the use of reagents and techniques other than those described here, testing specified in current OSHA validation guidelines must be completed.

A value for E_E was determined by liquid-spiking four sorbent tubes at a range of 0.1 to 2.0× the target concentration. For a single set of sorbent tubes spiked with analyte equivalent to sampling at the 1.0× target concentration value for 4 hours, humid air (80% relative humidity at 21 °C) was passed through the sorbent tubes for 360 min at 50 mL/min prior to spiking. Another set of sorbent tubes was spiked at the RQL level. The spiked samples were stored overnight at ambient temperature and then analyzed. An overall mean E_E value of 102.4% was obtained across the analyte concentration range studied, and the E_E value at the RQL was 98.09%. The results of these tests are provided in Table C-5, and they demonstrate that the presence of water in the sorbent material had no significant effect on E_E. The E_E values for the RQL and wet sampler testing were not included in the overall mean.

Table C-5. Extraction efficiency data for isopropyl alcohol.

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.1	1562	101.0	101.1	101.0	100.9	101.0
0.25	4686	103.2	101.6	104.7	104.0	103.4
0.5	8592	102.7	102.6	102.1	102.9	102.6
1.0	17183	103.2	103.0	102.8	102.6	102.9
1.5	25775	102.7	102.0	101.8	102.8	102.3
2.0	34367	102.2	102.0	102.4	102.4	102.2
RQL	4.84	96.25	99.95	98.17	97.98	98.09
1.0 (wet)	17183	102.9	102.0	102.8	103.2	102.7

The stability of extracted samples was examined by reanalyzing the 1.0× target concentration samples 24, 48, and 72 hours after the initial analysis. The septum of a vial was punctured four times for each injection (three syringe rinses and 1 syringe fill that was injected for analysis). After the original analysis was performed two vials were recapped with new septa which were replaced after each reanalysis. The remaining two vials retained their sequentially-punctured septa throughout the test. All samples were allowed to stand at room temperature in the autosampler tray used. Freshly prepared standards were used for each reanalysis event. Results obtained are listed in Table C-6.

Table C-6. Extracted sample stability data for isopropyl alcohol.

	punctured septa replaced recovery (%)		punctured septa retained recovery (%)	
time (days)	1	2	1	2
0	103.2	103.0	102.8	102.6
1	102.8	102.7	101.9	101.8
2	103.1	102.9	102.0	101.4
3	102.9	103.0	100.0	100.6

7 Sampler Capacity

Pre-existing data from OSHA Method 109[1] are presented in this section.

The sampling capacity of the 400-mg Anasorb 747 sampling tube was tested by sampling from a dynamically generated test atmosphere of isopropyl alcohol of 808 ppm. Samples were collected at 0.05 L/min and 0.2 L/min. The relative humidities were approximately 12% and 80% at 22 °C. A GC instrument with a gas sampling valve was placed in-line behind a 400-mg front test section. The valve was rotated to measure the amount of isopropyl alcohol passing through the sampler at the time of rotation. Five-percent breakthrough from the front tube was used as evidence that sampling capacity had been exceeded. Four sampler capacity experiments were performed as shown in Table C-7. The resulting capacity test data are also presented graphically in Figure C-6. The five-percent breakthrough volumes for each capacity test are listed in Table C-8.

Table C-7. Sampler capacity data for isopropyl alcohol.[a]

13% RH at 0.05 L/min		12% RH at 0.20 L/min		84% RH at 0.20 L/min		77% RH at 0.05 L/min	
air vol (L)	BT, (%)	air vol (L)	BT, (%)	air vol (L)	BT, (%)	air vol (L)	BT, (%)
32.11	0.0	29.01	0.0	19.78	0.0	27.39	0.0
34.32	0.44	29.37	2.15	22.08	2.85	28.83	4.23
36.57	1.23	29.76	2.98	22.13	0.58	28.94	4.70
37.18	5.24	29.78	4.13	24.61	19.51	29.53	11.31
38.80	5.44	30.20	6.21	24.74	6.63	30.07	10.40
39.38	14.83	30.55	8.03	26.47	19.84	30.29	21.82
41.26	18.29	30.65	13.47				
		31.01	10.60				
		31.14	22.08				

[a]RH = relative humidity, BT = breakthrough

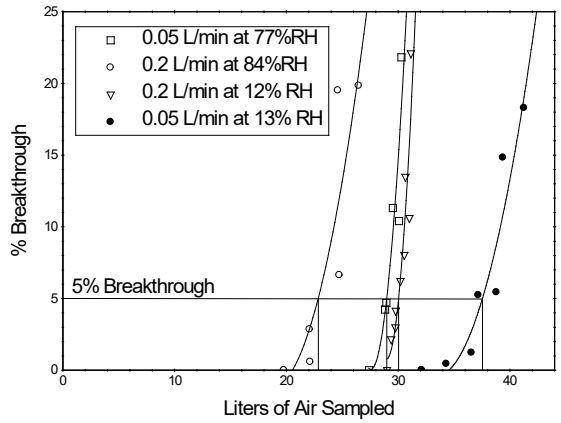

Figure C-6. Plot of data used to determine sampler capacity for isopropyl alcohol. RH is relative humidity.

Table C-8. Sampler capacity results for isopropyl alcohol.

Relative humidity (%)	Sampling rate (L/min)	Temperature (°C)	5% breakthrough (L)
12	0.20	22	29.8
13	0.05	22	37.6
77	0.05	22	29.0
84	0.20	22	22.6

8 Low Humidity

A low humidity recovery test was not performed; however, low humidity capacity tests were performed as described above in Section 7.

9 Chemical Interferences

A sampling interference study was not performed.

10 Reproducibility

Pre-existing data from OSHA Method 109[1] are presented in this section.
Six samples were prepared by sampling a dynamically generated controlled test atmosphere. The nominal concentration of isopropyl alcohol in the test atmosphere was 405 ppm, and the relative humidity was 80% at 22 °C.

The samples were submitted to the OSHA Salt Lake Technical Center for analysis using OSHA Method 109, which was completed following three days of storage at 4 °C. Sample results were corrected for E_E. No sample result for isopropyl alcohol had a deviation greater than the precision of the overall procedure described in Section 5. Results obtained are listed in Table C-9.

Table C-9. Reproducibility data for isopropyl alcohol.

sampled (mg/sample)	recovered (mg/sample)	recovery (%)	deviation (%)
19.47	19.69	101.1	1.1
19.83	20.36	102.7	2.7
19.84	20.15	101.6	1.6
19.81	20.18	101.9	1.9
19.47	20.22	103.9	3.9
19.81	19.85	100.2	0.2

11 Additional Testing

Pre-existing data from OSHA Method 109[1] are presented in this section.

Analyte migration during storage was studied by drawing samples from controlled test atmospheres of 405 ppm isopropyl alcohol at 0.2 L/min for 90 minutes. Samples were collected from atmospheres with a relative humidity of 80% at 22 °C and a relative humidity of 11% at 22 °C. Forty-eight storage samples were prepared at each relative humidity. The front 400 mg and back 200 mg tubes remained connected during storage. For each relative humidity six samples were analyzed immediately after generation, eighteen were stored at reduced temperature (4 °C), and the other eighteen were stored in the dark at ambient temperature (about 22 °C). Three samples were selected from each storage set and analyzed at the intervals noted in Table C-10. Results obtained for the ambient and refrigerated tests are listed below in Table C-10. Results are plotted in Figure C-7 through Figure C-9.

Table C-10. Analyte migration storage data for isopropyl alcohol.

time (days)	11% relative humidity ambient storage recovery (%) front section	11% relative humidity ambient storage recovery (%) back section	11% relative humidity refrigerated storage recovery (%) front section	11% relative humidity refrigerated storage recovery (%) back section	80% relative humidity ambient storage recovery (%) front section	80% relative humidity ambient storage recovery (%) back section	80% relative humidity refrigerated storage recovery (%) front section	80% relative humidity refrigerated storage recovery (%) back section
0	104.5	0.0	104.5	0.0	104.5	0.0	104.5	0.0
0	103.6	0.0	103.6	0.0	103.6	0.0	103.6	0.0
0	103.8	0.0	103.8	0.0	103.8	0.0	103.8	0.0
0	104.6	0.0	104.6	0.0	104.6	0.0	104.6	0.0
0	105.6	0.0	105.6	0.0	105.6	0.0	105.6	0.0
0	104.1	0.0	104.1	0.0	104.1	0.0	104.1	0.0
5	102.1	1.1	103.0	0.0	102.9	0.0	103.5	0.0
5	103.1	0.0	102.8	0.0	102.6	0.0	102.8	0.0
5	102.1	1.2	103.6	0.0	100.3	0.0	103.9	0.0
8	98.1	2.4	105.0	0.0	103.7	0.0	103.4	0.0
8	100.0	3.7	103.6	0.0	104.0	0.0	102.1	0.0
8	101.4	1.0	102.3	0.0	104.0	0.0	102.5	0.0
12	101.5	2.5	103.9	0.5	103.9	0.1	105.3	0.0
12	100.6	4.6	103.3	1.0	102.2	0.0	103.8	0.0
12	98.6	3.7	104.2	1.2	104.2	0.0	103.3	0.0
15	100.4	4.5	103.7	0.2	103.4	0.0	103.1	0.0
15	101.2	3.1	104.8	0.8	104.1	0.0	102.8	0.0
15	101.3	3.1	102.3	0.0	102.2	0.0	103.1	0.0
20	98.7	7.4	104.5	2.2	103.6	0.0	103.9	0.0
20	96.0	9.0	104.3	0.1	101.9	0.3	100.8	0.0
20	95.6	9.3	102.8	3.0	103.6	0.0	101.6	0.0
23	94.7	8.1	104.2	2.2	103.8	0.3	102.2	0.0
23	95.9	10.0	101.4	4.3	101.5	0.2	103.6	0.0
23	94.4	8.1	105.3	0.4	101.8	0.1	103.4	0.0

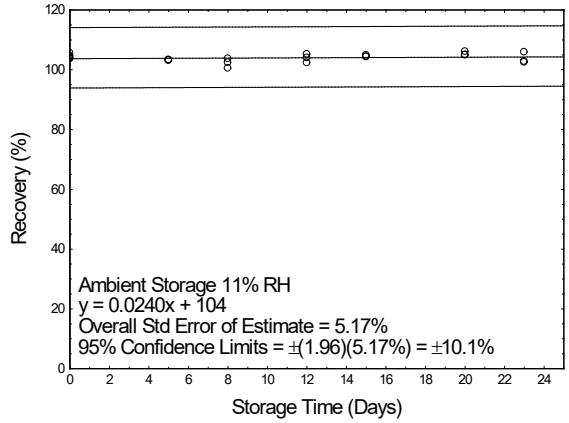

Figure C-7. Plot of the ambient storage migration data for isopropyl alcohol sampled at 11% relative humidity (RH).

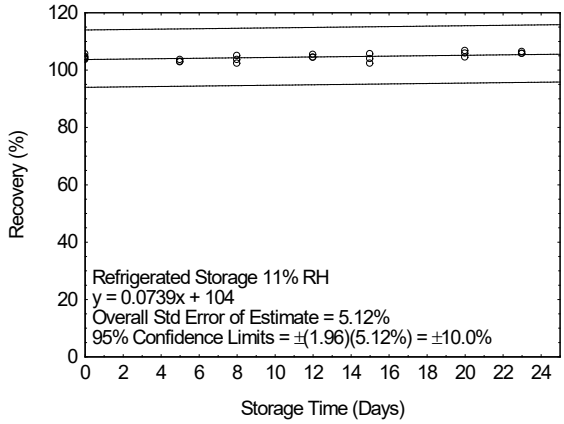

Figure C-8. Plot of the refrigerated storage migration data for isopropyl alcohol sampled at 11% relative humidity (RH).

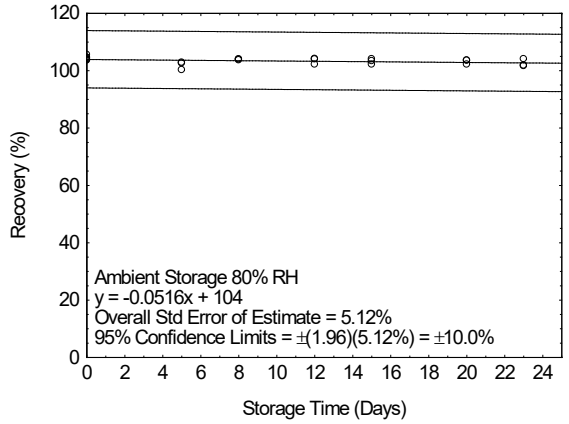

Figure C-8. Plot of the ambient storage migration data for isopropyl alcohol sampled at 80% relative humidity (RH).

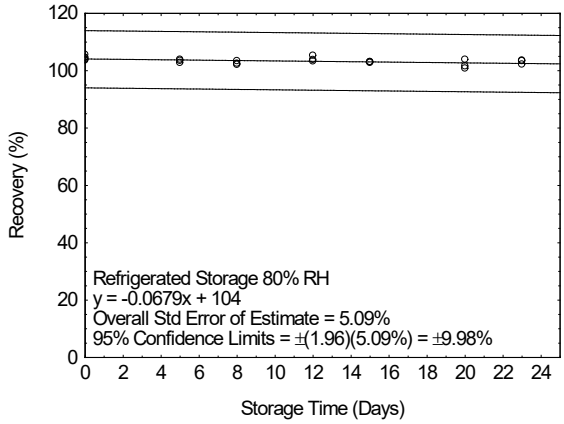

Figure C-9. Plot of the refrigerated storage migration data for isopropyl alcohol sampled at 80% relative humidity (RH).

12 Estimation of Uncertainty

Estimation of uncertainty was not performed. Instead the overall standard error of estimate was calculated from the ambient storage test as prescribed by the OSHA validation guidelines in use at the time OSHA Method 109 was originally evaluated.

13 Sampler Testing Procedure

Specific details regarding test atmosphere generation were not described in the 1997 version of OSHA Method 109. Additional test atmosphere generation was not performed for this update.

OSHA 5001, Appendix D
***n*-Butyl Alcohol**

Version:	1.0
OSHA PEL: ACGIH TLV:	100 ppm (300 mg/m^3) TWA 20 ppm (61 mg/m^3) TWA
Recommended sampling time and sampling rate:	240 min at 50 mL/min (12 L)
Reliable quantitation limit:	80 ppb (0.24 mg/m^3)
Standard error of estimate:	5.22%
Status:	Fully validated. Method 5001 has been subjected to the established validation procedures of the Method Development Team for sampling and analysis of *n*-butyl alcohol.

March 2019 Michael Simmons

1 Introduction

1.1 Previous Methods used by OSHA for Sampling and Analysis of *n*-Butyl Alcohol

Prior to the work described in this appendix, OSHA used a procedure based on the National Institute for Occupational and Health (NIOSH) Method 1401[1] for the sampling and analysis of *n*-butyl alcohol. The NIOSH method requires sample collection on a single dual-bed coconut-shell charcoal sampling tube, and desorption with 99/1 carbon disulfide (CS_2)/2-propanol. Analysis with the NIOSH method is by gas chromatography (GC) using a flame ionization detector (FID).

1.2 Changes to the Previously Used Method

This appendix represents a new method to replace that previously used by OSHA (NIOSH 1401[1]) for sampling and analysis of *n*-butyl alcohol. Compared to the previous method used, new analytical conditions, internal standard, sampling medium, extraction solvent, and extraction solvent volume allow standardized collection of *n*-butyl alcohol with the other analytes found in the Organic Vapor Sampling Group 2, described in Method 5001.

1.3 Validation Parameters

The procedures used to evaluate the method 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 analyte concentration equivalent to sampling for the recommended time at the OSHA TWA permissible exposure limit (PEL) value for *n*-butyl alcohol.

[1] Williamson, G. Alcohols II (NIOSH Method 1401), 1994. Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health web site. https://www.cdc.gov/niosh/docs/2003-154/pdfs/1401.pdf (accessed December 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 significantly greater than a reagent blank. Ten analytical standards were prepared with approximately equal descending increments of analyte, such that the highest standard concentration would produce a peak approximately 10 times the response of a blank at or near the chromatographic retention time of the analyte. These standards and a reagent blank were analyzed with the analytical parameters. The data obtained were used to determine the required parameters (standard error of estimate ($S_{y/x}$) and slope) for the calculation of the DLAP. Results obtained for the blank and each standard are listed below in Table D-1 and are plotted in Figure D-1.

Table D-1. DLAP data for *n*-butyl alcohol.

concentration (µg/mL)	mass on column (pg)	area counts (µV·s)
0.00	0.00	0.000
0.52	3.47	0.060
1.05	7.00	0.092
1.58	10.5	0.172
2.10	14.0	0.166
2.62	17.5	0.247
3.15	21.0	0.277
3.68	24.5	0.346
4.20	28.0	0.382
4.72	31.5	0.489
5.25	35.0	0.448

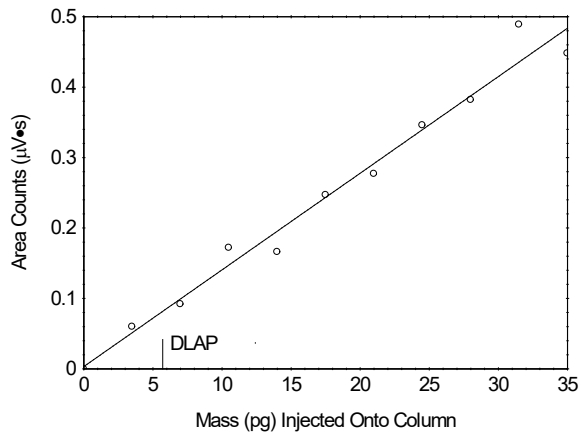

Figure D-1. Plot of data used to determine the DLAP for *n*-butyl alcohol ($y = 0.0137x + 0.0034$, $S_{y/x} = 0.0259$, DLAP = 5.7 pg).

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

The DLOP is the analyte mass per sample that produces a response significantly different than a sample blank. The RQL is the lowest level of analyte mass per sample for precise quantitative measurements and expressed as an air concentration based on the recommended sampling parameters. Ten samplers were spiked with approximately equal descending increments of analyte, such that the highest loading would produce a peak approximately 10 times the response of a sample blank at or near the chromatographic retention time of the analyte. These spiked samplers and a sample blank were analyzed with the analytical parameters. The data obtained were used to calculate the required parameters ($S_{y/x}$ and the slope) for the calculation of the DLOP and RQL. Results obtained for the sample blank and the ten spiked samplers are listed below in Table D-2 and plotted in Figure D-2.

Table D-2. DLOP and RQL data for *n*-butyl alcohol.

mass per sample (µg)	area counts (µV·s)
0.00	0.000
1.05	0.038
2.10	0.070
3.15	0.128
4.20	0.193
5.25	0.219
6.30	0.287
7.35	0.340
8.40	0.399
9.45	0.433
10.5	0.520

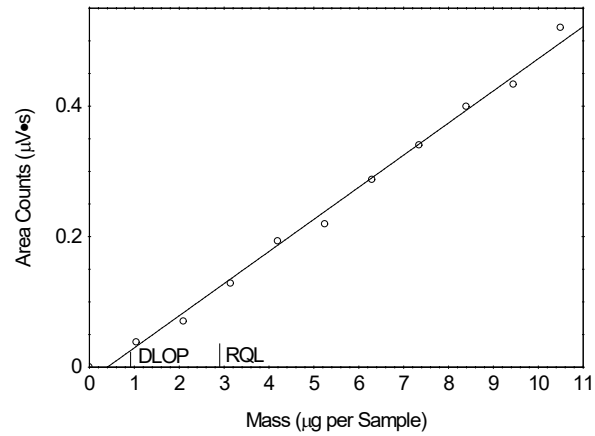

Figure D-2. Plot of data used to determine the DLOP and RQL for *n*-butyl alcohol ($y = 0.049x - 0.020$, $S_{y/x} = 0.014$, DLOP = 0.86 µg/sample, RQL = 2.9 µg/sample (80 ppb)).

3 Analytical Calibration

Fifteen analytical standards over a range of 0.1 to 2.0× the target concentration were prepared and analyzed with the analytical parameters. A least-squares linear regression curve was constructed by plotting the analyte mass per sample versus the ratio of analyte peak area to internal standard (ISTD) peak area. The data obtained was used to calculate the analytical calibration precision ($S_{y/x}$). Results are listed below in Table D-3 and plotted in Figure D-3.

Table D-3. Analytical precision data for *n*-butyl alcohol.

× target concn (µg/sample)	0.1×	0.5×	1.0×	1.5×	2.0×
	368.25	1841.3	3682.5	5523.8	7365.0
area ratio	0.0828	0.4177	0.8307	1.240	1.690
	0.0827	0.4062	0.8548	1.251	1.685
	0.0817	0.4128	0.8259	1.259	1.703

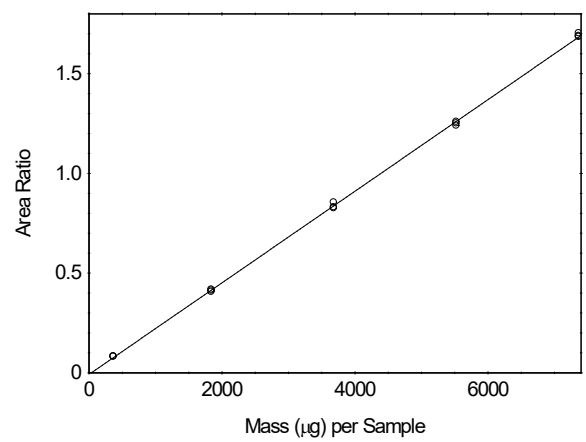

Figure D-3. Plot of the data used to estimate precision of the analytical method for *n*-butyl alcohol ($y = 0.00023x - 0.00774$, $S_{y/x} = 0.0112$).

4 Sampler Storage Stability

Eighteen samples were collected by sampling a test atmosphere containing 92 ppm *n*-butyl alcohol using the recommended sampling parameters. The relative humidity of the test atmosphere was 81% at 21 °C. Three samples were analyzed immediately after sampling. Fifteen of the samples were stored in a drawer at ambient temperature (about 22 °C). Three samples were selected and analyzed at the intervals noted below in Table D-4. Results obtained are listed in Table D-4 and plotted in Figure D-4. Sample results are not corrected for extraction efficiency (E_E).

Table D-4. Sampler storage stability data for *n*-butyl alcohol.

time (days)	ambient storage recovery (%)		
0	98.88	99.94	101.4
3	95.69	97.12	98.11
7	99.14	97.76	99.27
10	98.25	100.3	99.12
13	98.56	100.8	97.07
15	97.35	97.31	99.61

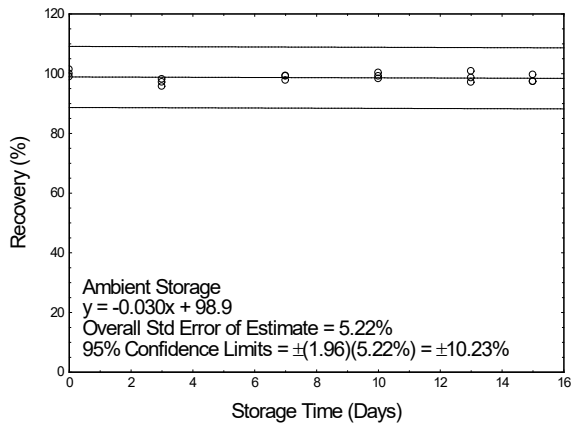

Figure D-4. Plot of storage stability data for *n*-butyl alcohol.

5 Precision

The precision of the overall procedure at the 95% confidence level is obtained by multiplying the overall standard error of estimate by 1.96 (the *z*-statistic from the standard normal distribution at the 95% confidence level). This provides ninety-five percent confidence intervals which are drawn about the regression lines in the storage stability figure shown in Section 4.

The precision of the overall procedure at the 95% confidence level for the ambient temperature (about 22 °C) 15-day storage test (at the target concentration) is ±10.23%. It was obtained from the overall standard error of estimate (5.22%) derived from the data shown in Figure D-4, with an additional 5% added for sampling pump error.

The recovery of *n*-butyl alcohol from samples used in the 15-day storage test was 98.4% when the samples were stored at ambient temperature.

6 Recovery and Stability of Prepared Samples

Quantitative extraction is affected by the extraction solvent, the internal standard, the sampling medium, and the technique used to extract the samples. For the use of reagents and techniques other than those described here, testing specified in current OSHA validation guidelines must be completed.

A value for E_E was determined by liquid-spiking four sorbent tubes at a range of 0.1 to 2.0× the target concentration. For a single set of sorbent tubes spiked with analyte equivalent to sampling at the 1.0× target concentration value for 4 hours, humid air (80% relative humidity at 21 °C) was passed through the sorbent tubes for 360 min at 50 mL/min prior to spiking. Another set of sorbent tubes was spiked at the RQL level. The spiked samples were stored overnight at ambient temperature and then analyzed. An overall mean E_E value of 101.5% was obtained across the analyte concentration range studied, and the E_E value at the RQL was 98.37%. The results of these tests are provided in Table D-5, and they demonstrate that the presence of water in the sorbent material had no significant effect on E_E. The E_E values for the RQL and wet sampler testing were not included in the overall mean.

Table D-5. Extraction efficiency data for *n*-butyl alcohol.

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.1	368.3	100.7	99.45	101.7	100.7	100.6
0.25	920.6	101.5	101.9	101.8	101.2	101.6
0.5	1841	99.94	100.2	101.3	100.6	100.5
1.0	3683	101.8	101.8	102.9	101.9	102.1
1.5	5523	102.3	102.1	102.0	101.8	102.1
2.0	7365	102.6	102.2	102.1	101.6	102.1
RQL	2.83	120.7	94.04	96.73	82.0	98.37
1.0 (wet)	3683	101.5	101.2	101.5	101.9	101.5

The stability of extracted samples was examined by reanalyzing the 1.0× target concentration samples 24, 48, and 72 hours after the initial analysis. The septum of a vial was punctured four times for each injection (three syringe rinses and 1 syringe fill that was injected for analysis). After the original analysis was performed, two vials were recapped with new septa which were replaced after each reanalysis. The remaining two vials retained their sequentially-punctured septa throughout the test. All samples were allowed to stand at room temperature in the autosampler tray used. Freshly prepared standards were used for each reanalysis event. Results obtained are listed in Table D-6.

Table D-6. Extracted sample stability data for *n*-butyl alcohol.

	punctured septa replaced recovery (%)		punctured septa retained recovery (%)	
time (days)	1	2	1	2
0	101.8	101.8	102.9	101.9
1	101.4	101.3	102.5	102.1
2	101.5	101.5	102.2	102.1
3	101.5	101.5	102.2	102.2

7 Sampler Capacity

High humidity sampling capacity of 400-mg Anasorb 747 sampling tubes (front tube) was tested by sampling a dynamically generated controlled test atmosphere containing 179.2 ppm *n*-butyl alcohol with a relative humidity of 79% at 21 °C. Three samples were collected at approximately 50 mL/min. A second 400-mg Anasorb 747 sampling tube was placed in a sampling train behind the first tube. No breakthrough was observed after 480 min of testing, equivalent to an air volume of 24 L.

Low humidity sampling capacity of 400-mg Anasorb 747 sampling tubes (front tube) was tested by sampling a dynamically generated controlled test atmosphere containing 208.7 ppm *n*-butyl alcohol with a relative humidity of 20% at 21 °C. Three samples were collected at approximately 50 mL/min. A second 400-mg Anasorb 747 sampling tube was placed in a sampling train behind the first tube. No breakthrough was observed after 480 min of testing, equivalent to an air volume of 24 L.

8 Low Humidity

The effect of low humidity was tested by sampling a dynamically generated controlled test atmosphere containing 205.5 ppm *n*-butyl alcohol with a relative humidity of 20% at 21 °C. The test atmosphere was sampled with three samplers at 50 mL/min for 240 min. All of the samples were immediately analyzed. Analysis results provided recoveries of 93.25%, 93.23%, and 94.78%.

9 Chemical Interferences

Validation data for the analytes listed in appendices D-G of this method were collected together. All spiking solutions and test atmospheres generated contained *n*-butyl, *sec*-butyl, isobutyl, and *n*-propyl alcohol. The presences of *sec*-butyl, isobutyl, and *n*-propyl alcohol had no effect on the sampling and analysis of *n*-butyl alcohol.

10 Reproducibility

Six samples were prepared by sampling a dynamically generated controlled test atmosphere. The concentration of *n*-butyl alcohol in the test atmosphere was 100.6 ppm, and the relative humidity was 79% at 21 °C. The samples were submitted to the OSHA Salt Lake Technical Center for analysis using OSHA Method 5001, which was completed following eleven days of storage at 4 °C. Sample results were corrected for E_E. No sample result for *n*-butyl alcohol had a deviation greater than the precision of the overall procedure determined in Section 5. Results obtained are listed in Table D-7.

Table D-7. Reproducibility data for *n*-butyl alcohol.

sampled (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
3672.4	3418.9	93.1	-6.9
3691.7	3360.5	91.0	-9.0
3605.4	3325.6	92.2	-7.8
3609.1	3297.6	91.4	-8.6
3786.5	3548.9	93.7	-6.3
3551.7	3273.1	92.2	-7.8

11 Additional Testing

11.1 Retention

Retention was tested by sampling a dynamically generated controlled test atmosphere containing 201.7 ppm *n*-butyl alcohol with a relative humidity of 80% at 21 °C. The test atmosphere was sampled with six samplers at 50 mL/min for 60 min. Sampling was discontinued and the samplers were separated into two sets of 3 samplers each. The generation system was flushed with contaminant-free air. Contaminant-free air is laboratory conditioned air at known relative humidity and temperature but without any added chemicals except water. One set of samplers was set aside (first set). Sampling was resumed with the second set of three samplers and contaminant-free air at 80% relative humidity and 21 °C at 50 mL/min for 180 min. All six samples were analyzed and the data obtained are listed in Table D-8.

Table D-8. Retention data for *n*-butyl alcohol.

	recovery (%)			
set	1	2	3	mean
first	90.75	91.63	93.98	92.12
second	96.16	97.75	98.95	97.62
second/first				106.0

11.2 Low Concentration

The effect of low concentration was tested by sampling a dynamically generated controlled test atmosphere containing 9.3 ppm *n*-butyl alcohol with a relative humidity of 78% at 21 °C. The test atmosphere was sampled with three samplers at 50 mL/min for 240 min. All of the samples were immediately analyzed. Analysis results provided recoveries of 98.25%, 100.2%, and 97.51%.

11.3 Back Tube Post-Sampling Analyte Migration

High humidity post-sampling analyte migration was studied by sampling a dynamically generated controlled test atmosphere containing 179.3 ppm *n*-butyl alcohol with a relative humidity of 79% at 21 °C. The test atmosphere was sampled with three samplers at 50 mL/min for 240 min. The samples were stored for 14 days at room temperature with the front and back tube connected. No *n*-butyl alcohol was found on the back tube. Front tube analysis results provided recoveries of 90.62%, 93.15%, and 93.96%.

Low humidity post-sampling analyte migration was studied by sampling a dynamically generated controlled test atmosphere containing 205.5 ppm *n*-butyl alcohol with a relative humidity of 20% at 21 °C. The test atmosphere was sampled with three samplers at 50 mL/min for 240 min. The samples were stored for 14 days at room temperature with the front and back tube connected. No *n*-butyl alcohol was found on the back tube. Front tube analysis results provided recoveries of 91.23%, 92.12%, and 93.31%.

12 Estimation of Uncertainty

Estimation of uncertainty was not performed. Instead the overall standard error of estimate was calculated from the ambient storage test as prescribed by the OSHA validation guidelines.

13 Sampler Testing Procedure

A test atmosphere generator was set up in a walk-in hood. Dilution air was regulated using a Miller Nelson Model 401 Flow-Temperature-Humidity Control System. A measured flow of *n*-butyl, *sec*-butyl, isobutyl, and *n*-propyl alcohol was pumped through a 0.53-mm uncoated fused silica capillary tube, using a KD Scientific Legato 100 syringe pump, into a heated vapor generator, and mixed with the dilution air. The generated vapor flowed continually into a glass mixing chamber (10-cm × 30-cm) and then into a glass sampling chamber (10-cm × 68-cm). Samples were collected through sampling ports on the sampling chamber. Temperature and humidity were measured near the exit of the sampling chamber using a Vaisala HUMICAP Hand-Held Humidity and Temperature Meter HM70.

OSHA 5001, Appendix E
***sec*-Butyl Alcohol**

Version:	1.0
OSHA PEL: ACGIH TLV:	150 ppm (450 mg/m^3) TWA 100 ppm (303 mg/m^3) TWA
Recommended sampling time and sampling rate:	240 min at 50 mL/min (12 L)
Reliable quantitation limit:	107 ppb (0.32 mg/m^3)
Standard error of estimate:	5.17%
Status:	Fully validated. Method 5001 has been subjected to the established validation procedures of the Method Development Team for sampling and analysis of *sec*-butyl alcohol.

March 2019 Michael Simmons

1 Introduction

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

Prior to the work described in this appendix, OSHA used a procedure based on the National Institute for Occupational and Health (NIOSH) Method 1401[1] for the sampling and analysis of *sec*-butyl alcohol. The NIOSH method requires sample collection on a single dual-bed coconut-shell charcoal sampling tube, and desorption with 99/1 carbon disulfide (CS_2)/2-propanol. Analysis with the NIOSH method is by gas chromatography (GC) using a flame ionization detector (FID).

1.2 Changes to the Previously Used Method

This appendix represents a new method to replace that previously used by OSHA (NIOSH 1401[1]) for sampling and analysis of *sec*-butyl alcohol. Compared to the previous method used, new analytical conditions, internal standard, sampling medium, extraction solvent, and extraction solvent volume allow standardized collection of *sec*-butyl alcohol with the other analytes found in the Organic Vapor Sampling Group 2, described in Method 5001.

1.3 Validation Parameters

The procedures used to evaluate the method 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 analyte concentration equivalent to sampling for the recommended time at the OSHA TWA permissible exposure limit (PEL) value for *sec*-butyl alcohol.

[1] Williamson, G. Alcohols II (NIOSH Method 1401), 1994. Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health web site. https://www.cdc.gov/niosh/docs/2003-154/pdfs/1401.pdf (accessed December 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 significantly greater than a reagent blank. Ten analytical standards were prepared with approximately equal descending increments of analyte, such that the highest standard concentration would produce a peak approximately 10 times the response of a blank at or near the chromatographic retention time of the analyte. These standards and a reagent blank were analyzed with the analytical parameters. The data obtained were used to determine the required parameters (standard error of estimate ($S_{y/x}$) and slope) for the calculation of the DLAP. Results obtained for the blank and each standard are listed below in Table E-1 and are plotted in Figure E-1.

Table E-1. DLAP data for *sec*-butyl alcohol.

concentration (µg/mL)	mass on column (pg)	area counts (µV·s)
0.00	0.00	0.000
0.52	3.47	0.034
1.04	6.93	0.076
1.57	10.5	0.156
2.09	13.9	0.183
2.62	17.5	0.202
3.14	20.9	0.278
3.66	24.4	0.314
4.18	27.9	0.352
4.70	31.3	0.390
5.25	35.0	0.392

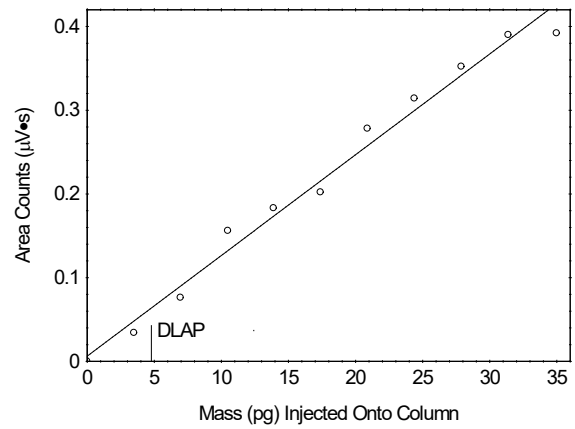

Figure E-1. Plot of data used to determine the DLAP for *sec*-butyl alcohol ($y = 0.0120x + 0.0063$, $S_{y/x} = 0.0191$, DLAP = 4.8 pg).

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

The DLOP is the analyte mass per sample that produces a response significantly different than a sample blank. The RQL is the lowest level of analyte mass per sample for precise quantitative measurements and expressed as an air concentration based on the recommended sampling parameters. Ten samplers were spiked with approximately equal descending increments of analyte, such that the highest loading would produce a peak approximately 10 times the response of a sample blank at or near the chromatographic retention time of the analyte. These spiked samplers and a sample blank were analyzed with the analytical parameters. The data obtained were used to calculate the required parameters ($S_{y/x}$ and the slope) for the calculation of the DLOP and RQL. Results obtained for the sample blank and the ten spiked samplers are listed below in Table E-2 and plotted in Figure E-2.

Table E-2. DLOP and RQL data for *sec*-butyl alcohol.

mass per sample (µg)	area counts (µV·s)
0.00	0.000
1.05	0.068
2.09	0.065
3.14	0.140
4.18	0.161
5.23	0.220
6.27	0.238
7.32	0.294
8.36	0.347
9.41	0.386
10.5	0.453

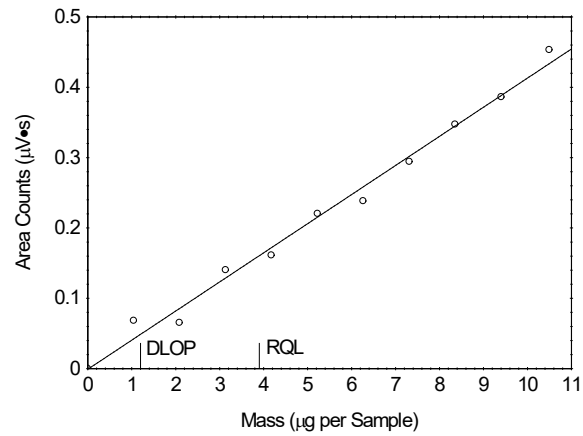

Figure E-2. Plot of data used to determine the DLOP and RQL for *sec*-butyl alcohol ($y = 0.041x - 0.001$, $S_{y/x} = 0.016$, DLOP = 1.2 µg/sample, RQL = 3.9 µg/sample (107 ppb)).

3 Analytical Calibration

Fifteen analytical standards over a range of 0.1 to 2.0× the target concentration were prepared and analyzed with the analytical parameters. A least-squares linear regression curve was constructed by plotting the analyte mass per sample versus the ratio of analyte peak area to internal standard (ISTD) peak area. The data obtained was used to calculate the analytical calibration precision ($S_{y/x}$). Results are listed below in Table E-3 and plotted in Figure E-3.

Table E-3. Analytical precision data for *sec*-butyl alcohol.

× target concn (µg/sample)	0.1×	0.5×	1.0×	1.5×	2.0×
	540.26	2701.3	5402.6	8103.9	10805
area ratio	0.1091	0.5500	1.092	1.638	2.231
	0.1093	0.5340	1.128	1.650	2.228
	0.1077	0.5461	1.090	1.660	2.246

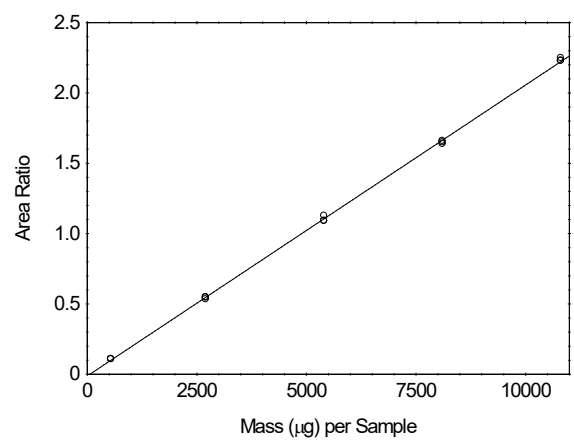

Figure E-3. Plot of the data used to estimate precision of the analytical method for *sec*-butyl alcohol ($y = 0.00021x - 0.01134$, $S_{y/x} = 0.0152$).

4 Sampler Storage Stability

Eighteen samples were collected by sampling a test atmosphere containing 137 ppm *sec*-butyl alcohol using the recommended sampling parameters. The relative humidity of the test atmosphere was 81% at 21 °C. Three samples were analyzed immediately after sampling. Fifteen of the samples were stored in a drawer at ambient temperature (about 22 °C). Three samples were selected and analyzed at the intervals noted below in Table E-4. Results obtained are listed in Table E-4 and plotted in Figure E-4. Sample results are not corrected for extraction efficiency (E_E).

Table E-4. Sampler storage stability data for *sec*-butyl alcohol.

time (days)	ambient storage recovery (%)		
0	101.0	101.3	102.4
3	97.49	99.57	100.0
7	101.1	100.2	101.7
10	100.7	101.9	102.2
13	100.5	102.2	99.88
15	99.49	99.83	102.4

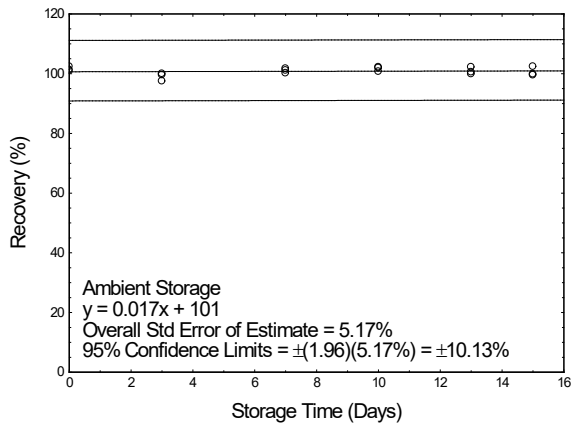

Figure E-4. Plot of storage stability data for *sec*-butyl alcohol.

5 Precision

The precision of the overall procedure at the 95% confidence level is obtained by multiplying the overall standard error of estimate by 1.96 (the *z*-statistic from the standard normal distribution at the 95% confidence level). This provides ninety-five percent confidence intervals which are drawn about the regression lines in the storage stability figure shown in Section 4.

The precision of the overall procedure at the 95% confidence level for the ambient temperature (about 22 °C) 15-day storage test (at the target concentration) is ±10.13%. It was obtained from the overall standard error of estimate (5.17%) derived from the data shown in Figure E-4, with an additional 5% added for sampling pump error.

The recovery of *sec*-butyl alcohol from samples used in the 15-day storage test was 101% when the samples were stored at ambient temperature.

6 Recovery and Stability of Prepared Samples

Quantitative extraction is affected by the extraction solvent, the internal standard, the sampling medium, and the technique used to extract the samples. For the use of reagents and techniques other than those described here, testing specified in current OSHA validation guidelines must be completed.

A value for E_E was determined by liquid-spiking four sorbent tubes at a range of 0.1 to 2.0× the target concentration. For a single set of sorbent tubes spiked with analyte equivalent to sampling at the 1.0× target concentration value for 4 hours, humid air (80% relative humidity at 21 °C) was passed through the sorbent tubes for 360 min at 50 mL/min prior to spiking. Another set of sorbent tubes was spiked at the RQL level. The spiked samples were stored overnight at ambient temperature and then analyzed. An overall mean E_E value of 102.5% was obtained across the analyte concentration range studied, and the E_E value at the RQL was 106.0%. The results of these tests are provided in Table E-5, and they demonstrate that the presence of water in the sorbent material had no significant effect on E_E. The E_E values for the RQL and wet sampler testing were not included in the overall mean.

Table E-5. Extraction efficiency data for *sec*-butyl alcohol.

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.1	540.3	101.9	100.7	102.5	101.6	101.7
0.25	1351	102.5	102.6	102.6	102.4	102.5
0.5	2701	100.8	101.2	102.4	101.5	101.5
1.0	5402	103.0	103.0	104.2	103.1	103.3
1.5	8104	103.2	103.0	103.0	102.7	103.0
2.0	10805	103.6	103.1	103.0	102.4	103.0
RQL	3.7	95.63	109.6	109.3	109.3	106.0
1.0 (wet)	5402	102.4	102.0	102.0	102.6	102.3

The stability of extracted samples was examined by reanalyzing the 1.0× target concentration samples 24, 48, and 72 hours after the initial analysis. The septum of a vial was punctured four times for each injection (three syringe rinses and 1 syringe fill that was injected for analysis). After the original analysis was performed, two vials were recapped with new septa which were replaced after each reanalysis. The remaining two vials retained their sequentially-punctured septa throughout the test. All samples were allowed to stand at room temperature in the autosampler tray used. Freshly prepared standards were used for each reanalysis event. Results obtained are listed in Table E-6.

Table E-6. Extracted sample stability data for *sec*-butyl alcohol.

	punctured septa replaced recovery (%)		punctured septa retained recovery (%)	
time (days)	1	2	1	2
0	103.0	103.0	104.2	103.1
1	102.4	102.3	103.7	103.4
2	102.6	102.8	103.4	103.4
3	102.6	102.8	103.3	103.3

7 Sampler Capacity

High humidity sampling capacity of 400-mg Anasorb 747 sampling tubes (front tube) was tested by sampling a dynamically generated controlled test atmosphere containing 267.7 ppm *sec*-butyl alcohol with a relative humidity of 79% at 21 °C. Three samples were collected at approximately 50 mL/min. A second 400-mg Anasorb 747 sampling tube was placed in a sampling train behind the first tube. No breakthrough was observed after 480 min of testing, equivalent to an air volume of 24 L.

Low humidity sampling capacity of 400-mg Anasorb 747 sampling tubes (front tube) was tested by sampling a dynamically generated controlled test atmosphere containing 311.6 ppm *sec*-butyl alcohol with relative humidity of 20% at 21 °C. Three samples were collected at approximately 50 mL/min. A second 400-mg Anasorb 747 sampling tube was placed in a sampling train behind the first tube. No breakthrough was observed after 480 min of testing, equivalent to an air volume of 24 L.

8 Low Humidity

The effect of low humidity was tested by sampling a dynamically generated controlled test atmosphere containing 306.8 ppm *sec*-butyl alcohol with a relative humidity of 20% at 21 °C. The test atmosphere was sampled with three samplers at 50 mL/min for 240 min. All of the samples were immediately analyzed. Analysis results provided recoveries of 93.57%, 94.48%, and 95.59%.

9 Chemical Interferences

Validation data for the analytes listed in appendices D-G of this method were collected together. All spiking solutions and test atmospheres generated contained *n*-butyl, *sec*-butyl, isobutyl, and *n*-propyl alcohol. The presences of *n*-butyl, isobutyl, and *n*-propyl alcohol had no effect on the sampling and analysis of *sec*-butyl alcohol.

10 Reproducibility

Six samples were prepared by sampling a dynamically generated controlled test atmosphere. The concentration of *sec*-butyl alcohol in the test atmosphere was 150.2 ppm, and the relative humidity was 79% at 21 °C. The samples were submitted to the OSHA Salt Lake Technical Center for analysis using OSHA Method 5001, which was completed following eleven days of storage at 4 °C. Sample results were corrected for E_E. No sample result for *sec*-butyl alcohol had a deviation greater than the precision of the overall procedure determined in Section 5. Results obtained are listed in Table E-7.

Table E-7. Reproducibility data for *sec*-butyl alcohol.

sampled (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
5483.9	5421.4	98.9	-1.1
5512.9	5349.8	97.0	-3.0
5384.0	5290.5	98.3	-1.7
5389.4	5276.7	97.9	-2.1
5654.3	5659.0	100.1	0.1
5303.7	5213.9	98.3	-1.7

11 Additional Testing

11.1 Retention

Retention was tested by sampling a dynamically generated controlled test atmosphere containing 301.2 ppm *sec*-butyl alcohol with a relative humidity of 80% at 21 °C. The test atmosphere was sampled with six samplers at 50 mL/min for 60 min. Sampling was discontinued and the samplers were separated into two sets of 3 samplers each. The generation system was flushed with contaminant-free air. Contaminant-free air is laboratory conditioned air at known relative humidity and temperature but without any added chemicals except water. One set of samplers was set aside (first set). Sampling was resumed with the second set of three samplers and contaminant-free air at 80% relative humidity and 21 °C at 50 mL/min for 180 min. All six samples were analyzed and the data obtained are listed in Table E-8.

Table E-8. Retention data for *sec*-butyl alcohol.

	recovery (%)			
set	1	2	3	mean
first	93.33	95.34	96.78	95.15
second	98.18	100.1	101.0	99.76
second/first				104.8

11.2 Low Concentration

The effect of low concentration was tested by sampling a dynamically generated controlled test atmosphere containing 13.5 ppm *sec*-butyl alcohol with a relative humidity of 78% at 21 °C. The test atmosphere was sampled with three samplers at 50 mL/min for 240 min. All of the samples were immediately analyzed. Analysis results provided recoveries of 100.9%, 102.6%, and 100.9%.

11.3 Back Tube Post-Sampling Analyte Migration

High humidity post-sampling analyte migration was studied by sampling a dynamically generated controlled test atmosphere containing 267.7 ppm *sec*-butyl alcohol with a relative humidity of 79% at 21 °C. The test atmosphere was sampled with three samplers at 50 mL/min for 240 min. The samples were stored for 14 days at room temperature with the front and back tube connected. No *sec*-butyl alcohol was found on the back tube. Front tube analysis results provided recoveries of 93.78%, 97.16%, and 97.52%.

Low humidity post-sampling analyte migration was studied by sampling a dynamically generated controlled test atmosphere containing 306.8 ppm *sec*-butyl alcohol with a relative humidity of 20% at 21 °C. The test atmosphere was sampled with three samplers at 50 mL/min for 240 min. The samples were stored for 14 days at room temperature with the front and back tube connected. No *sec*-butyl alcohol was found on the back tube. Front tube analysis results provided recoveries of 94.46%, 95.42%, and 96.29%.

12 Estimation of Uncertainty

Estimation of uncertainty was not performed. Instead the overall standard error of estimate was calculated from the ambient storage test as prescribed by the OSHA validation guidelines.

13 Sampler Testing Procedure

A test atmosphere generator was set up in a walk-in hood. Dilution air was regulated using a Miller Nelson Model 401 Flow-Temperature-Humidity Control System. A measured flow of *n*-butyl, *sec*-butyl, isobutyl, and *n*-propyl alcohol was pumped through a 0.53-mm uncoated fused silica capillary tube, using a KD Scientific Legato 100 syringe pump, into a heated vapor generator, and mixed with the dilution air. The generated vapor flowed continually into a glass mixing chamber (10-cm × 30-cm) and then into a glass sampling chamber (10-cm × 68-cm). Samples were collected through sampling ports on the sampling chamber. Temperature and humidity were measured near the exit of the sampling chamber using a Vaisala HUMICAP Hand-Held Humidity and Temperature Meter HM70.

OSHA 5001, Appendix F
Isobutyl Alcohol

Version:	1.0
OSHA PEL: ACGIH TLV:	100 ppm (300 mg/m^3) TWA 50 ppm (152 mg/m^3) TWA
Recommended sampling time and sampling rate:	240 min at 50 mL/min (12 L)
Reliable quantitation limit:	74 ppb (0.22 mg/m^3)
Standard error of estimate:	5.19%
Status:	Fully validated. Method 5001 has been subjected to the established validation procedures of the Method Development Team for sampling and analysis of isobutyl alcohol.

March 2019 Michael Simmons

1 Introduction

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

Prior to the work described in this appendix, OSHA used a procedures based on the National Institute for Occupational and Health (NIOSH) Method 1401[1] for the sampling and analysis of isobutyl alcohol. The NIOSH method requires sample collection on a single dual-bed coconut-shell charcoal sampling tube, and desorption with 99/1 carbon disulfide (CS_2)/2-propanol. Analysis with the NIOSH method is by gas chromatography (GC) using a flame ionization detector (FID).

1.2 Changes to the Previously Used Method

This appendix represents a new method to replace that previously used by OSHA (NIOSH 1401[1]) for sampling and analysis of isobutyl alcohol. Compared to the previous method used, new analytical conditions, internal standard, sampling medium, extraction solvent, and extraction solvent volume allow standardized collection of isobutyl alcohol with the other analytes found in the Organic Vapor Sampling Group 2, described in Method 5001.

1.3 Validation Parameters

The procedures used to evaluate the method 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 analyte concentration equivalent to sampling for the recommended time at the OSHA TWA permissible exposure limit (PEL) value for isobutyl alcohol.

[1] Williamson, G. Alcohols II (NIOSH Method 1401), 1994. Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health web site. https://www.cdc.gov/niosh/docs/2003-154/pdfs/1401.pdf (accessed December 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 measured as the mass of analyte introduced onto the chromatographic column. Ten analytical standards were prepared with approximately equal descending increments of analyte, such that the highest standard concentration would produce a peak approximately 10 times the response of a blank at or near the chromatographic retention time of the analyte. These standards and a reagent blank were analyzed with the analytical parameters. The data obtained were used to determine the required parameters (standard error of estimate ($S_{y/x}$) and slope) for the calculation of the DLAP. Results obtained for the blank and each standard are listed below in Table F-1 and are plotted in Figure F-1.

Table F-1. DLAP data for isobutyl alcohol.

concentration (µg/mL)	mass on column (pg)	area counts (µV·s)
0.00	0.00	0.000
0.52	3.47	0.039
1.04	6.93	0.131
1.55	10.3	0.133
2.06	13.7	0.209
2.58	17.2	0.248
3.10	20.7	0.302
3.62	24.1	0.340
4.14	27.6	0.405
4.65	31.0	0.451
5.15	34.3	0.454

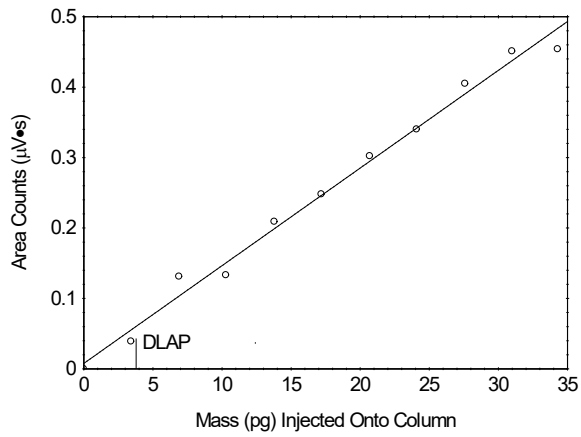

Figure F-1. Plot of data used to determine the DLAP for isobutyl alcohol ($y = 0.0139x + 0.0077$, $S_{y/x} = 0.0177$, DLAP = 3.8 pg).

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

The DLOP is the analyte mass per sample that produces a response significantly different than a sample blank. The RQL is the lowest level of analyte mass per sample for precise quantitative measurements and expressed as an air concentration based on the recommended sampling parameters. Ten samplers were spiked with approximately equal descending increments of analyte, such that the highest loading would produce a peak approximately 10 times the response of a sample blank at or near the chromatographic retention time of the analyte. These spiked samplers and a sample blank were analyzed with the analytical parameters. The data obtained were used to calculate the required parameters ($S_{y/x}$ and the slope) for the calculation of the DLOP and RQL. Results obtained for the sample blank and the ten spiked samplers are listed below in Table F-2 and plotted in Figure F-2.

Table F-2. DLOP and RQL data for isobutyl alcohol.

mass per sample (µg)	area counts (µV·s)
0.00	0.000
1.03	0.033
2.07	0.138
3.10	0.168
4.13	0.213
5.17	0.249
6.20	0.316
7.23	0.372
8.27	0.434
9.30	0.489
10.3	0.533

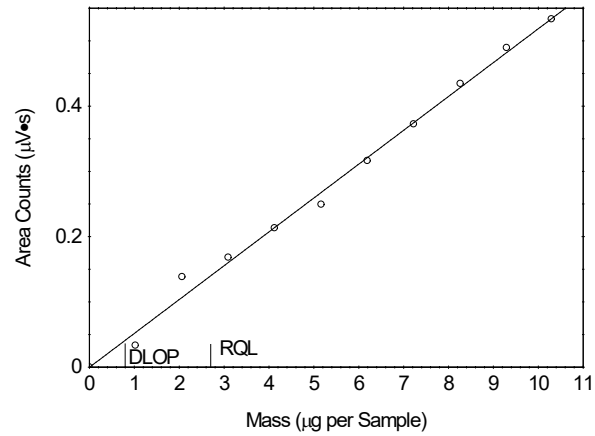

Figure F-2. Plot of data used to determine the DLOP and RQL for isobutyl alcohol ($y = 0.052x - 0.0001$, $S_{y/x} = 0.014$, DLOP = 0.81 µg/sample, RQL = 2.7 µg/sample (74.2 ppb)).

3 Analytical Calibration

Fifteen analytical standards over a range of 0.1 to 2.0× the target concentration were prepared and analyzed with the analytical parameters. A least-squares linear regression curve was constructed by plotting the analyte mass per sample versus the ratio of analyte peak area to internal standard (ISTD) peak area. The data obtained was used to calculate the analytical calibration precision ($S_{y/x}$). Results are listed below in Table F-3 and plotted in Figure F-3.

Table F-3. Analytical precision data for isobutyl alcohol.

× target concn (µg/sample)	0.1×	0.5×	1.0×	1.5×	2.0×
	362.51	1812.5	3625.1	5437.6	7250.1
area ratio	0.0850	0.4284	0.8519	1.274	1.736
	0.0852	0.4165	0.8777	1.285	1.732
	0.0838	0.4250	0.8480	1.292	1.750

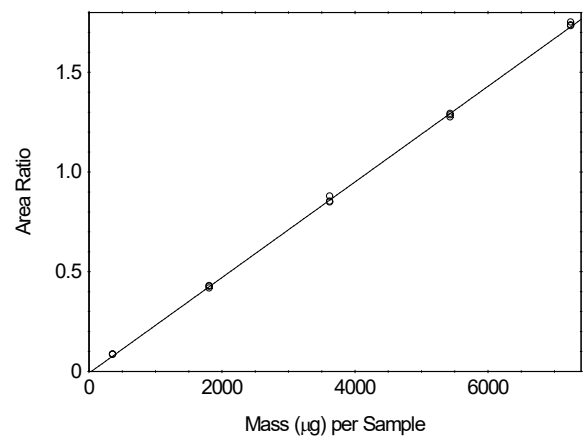

Figure F-3. Plot of the data used to estimate precision of the analytical method for isobutyl alcohol ($y = 0.00024x - 0.00829$, $S_{y/x} = 0.0116$).

4 Sampler Storage Stability

Eighteen samples were collected by sampling a test atmosphere containing 137 ppm isobutyl alcohol using the recommended sampling parameters. The relative humidity of the test atmosphere was 81% at 21 °C. Three samples were analyzed immediately after sampling. Fifteen of the samples were stored in a drawer at ambient temperature (about 22 °C). Three samples were selected and analyzed at the intervals noted below in Table F-4. Results obtained are listed in Table F-4 and plotted in Figure F-4. Sample results are not corrected for extraction efficiency (E_E).

Table F-4. Sampler storage stability data for isobutyl alcohol.

time (days)	ambient storage recovery (%)		
0	101.5	102.0	103.1
3	97.78	99.74	100.3
7	101.1	100.2	101.7
10	100.7	101.9	102.0
13	100.5	102.4	99.77
15	99.37	99.78	102.4

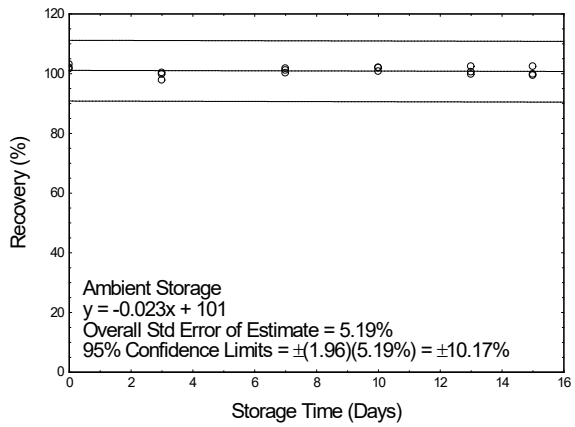

Figure F-4. Plot of storage stability data for isobutyl alcohol.

5 Precision

The precision of the overall procedure at the 95% confidence level is obtained by multiplying the overall standard error of estimate by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). This provides ninety-five percent confidence intervals which are drawn about the regression lines in the storage stability figure shown in Section 4.

The precision of the overall procedure at the 95% confidence level for the ambient temperature (about 22 °C) 15-day storage test (at the target concentration) is ±10.17%. It was obtained from the overall standard error of estimate (5.19%) derived from the data shown in Figure F-4, with an additional 5% added for sampling pump error.

The recovery of isobutyl alcohol from samples used in the 15-day storage test was 101% when the samples were stored at ambient temperature.

6 Recovery and Stability of Prepared Samples

Quantitative extraction is affected by the extraction solvent, the internal standard, the sampling medium, and the technique used to extract the samples. For the use of reagents and techniques other than those described here, testing specified in current OSHA validation guidelines must be completed.

A value for E_E was determined by liquid-spiking four sorbent tubes at a range of 0.1 to 2.0× the target concentration. For a single set of sorbent tubes spiked with analyte equivalent to sampling at the 1.0× target concentration value for 4 hours, humid air (80% relative humidity at 21 °C) was passed through the sorbent tubes for 360 min at 50 mL/min prior to spiking. Another set of sorbent tubes was spiked at the RQL level. The spiked samples were stored overnight at ambient temperature and then analyzed. An overall mean E_E value of 102.2% was obtained across the analyte concentration range studied, and the E_E value at the RQL was 99.59%. The results of these tests are provided in Table F-5, and they demonstrate that the presence of water in the sorbent material had no significant effect on E_E. The E_E values for the RQL and wet sampler testing were not included in the overall mean.

Table F-5. Extraction efficiency data for isobutyl alcohol.

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.1	362.5	101.5	100.2	102.2	100.9	101.2
0.25	906.3	102.2	102.4	102.4	101.8	102.2
0.5	1813	100.7	101.0	102.1	101.4	101.3
1.0	3625	102.8	102.7	103.9	102.8	103.0
1.5	5438	103.0	102.7	102.7	102.5	102.7
2.0	7250	103.3	102.9	102.8	102.2	102.8
RQL	2.78	107.9	96.64	97.85	95.98	99.59
1.0 (wet)	3625	102.4	102.0	102.0	102.6	102.2

The stability of extracted samples was examined by reanalyzing the 1.0× target concentration samples 24, 48, and 72 hours after the initial analysis. The septum of a vial was punctured four times for each injection (three syringe rinses and 1 syringe fill that was injected for analysis). After the original analysis was performed, two vials were recapped with new septa which were replaced after each reanalysis. The remaining two vials retained their sequentially-punctured septa throughout the test. All samples were allowed to stand at room temperature in the autosampler tray used. Freshly prepared standards were used for each reanalysis event. Results obtained are listed in Table F-6.

Table F-6. Extracted sample stability data for isobutyl alcohol.

	punctured septa replaced recovery (%)		punctured septa retained recovery (%)	
time (days)	1	2	1	2
0	102.8	102.7	103.9	103.4
1	102.2	102.2	103.5	103.3
2	102.4	102.5	103.1	103.1
3	102.5	102.5	103.1	103.1

7 Sampler Capacity

High humidity sampling capacity of 400-mg Anasorb 747 sampling tubes (front tube) was tested by sampling a dynamically generated controlled test atmosphere containing 176.5 ppm isobutyl alcohol with a relative humidity of 79% at 21 °C. Three samples were collected at approximately 50 mL/min. A second 400-mg Anasorb 747 sampling tube was placed in a sampling train behind the first tube. No breakthrough was observed after 480 min of testing, equivalent to an air volume of 24 L.

Low humidity sampling capacity of 400-mg Anasorb 747 sampling tubes (front tube) was tested by sampling a dynamically generated controlled test atmosphere containing 205.5 ppm isobutyl alcohol with a relative humidity of 20% at 21 °C. Three samples were collected at approximately 50 mL/min. A second 400-mg Anasorb 747 sampling tube was placed in a sampling train behind the first tube. No breakthrough was observed after 480 min of testing, equivalent to an air volume of 24 L.

8 Low Humidity

The effect of low humidity was tested by sampling a dynamically generated controlled test atmosphere containing 202.3 ppm isobutyl alcohol with a relative humidity of 20% at 21 °C. The test atmosphere was sampled with three samplers at 50 mL/min for 240 min. All of the samples were immediately analyzed. Analysis results provided recoveries of 94.52%, 95.28%, and 96.48%.

9 Chemical Interferences

Validation data for the analytes listed in appendices D-G of this method were collected together. All spiking solutions and test atmospheres generated contained *n*-butyl, *sec*-butyl, isobutyl, and *n*-propyl alcohol. The presences of *sec*-butyl, *n*-butyl, and *n*-propyl alcohol had no effect on the sampling and analysis of isobutyl alcohol.

10 Reproducibility

Six samples were prepared by sampling a dynamically generated controlled test atmosphere. The concentration of isobutyl alcohol in the test atmosphere was 99.0 ppm, and the relative humidity was 79% at 21 °C. The samples were submitted to the OSHA Salt Lake Technical Center for analysis using OSHA Method 5001, which was completed following eleven days of storage at 4 °C. Sample results were corrected for E_E. No sample result for isobutyl alcohol had a deviation greater than the precision of the overall procedure determined in Section 5. Results obtained are listed in Table F-7.

Table F-7. Reproducibility data for isobutyl alcohol.

sampled (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
3615.1	3435.4	95.0	-5.0
3634.2	3395.2	93.4	-6.6
3549.2	3360.2	94.7	-5.3
3552.8	3344.6	94.1	-5.9
3727.4	3592.6	96.4	-3.6
3496.3	3310.1	94.7	-5.3

11 Additional Testing

11.1 Retention

Retention was tested by sampling a dynamically generated controlled test atmosphere containing 198.5 ppm isobutyl alcohol with a relative humidity of 80% at 21 °C. The test atmosphere was sampled with six samplers at 50 mL/min for 60 min. Sampling was discontinued and the samplers were separated into two sets of 3 samplers each. The generation system was flushed with contaminant-free air. Contaminant-free air is laboratory conditioned air at known relative humidity and temperature but without any added chemicals except water. One set of samplers was set aside (first set). Sampling was resumed with the second set of three samplers and contaminant-free air at 80% relative humidity and 21 °C at 50 mL/min for 180 min. All six samples were analyzed and the data obtained are listed in Table F-8.

Table F-8. Retention data for isobutyl alcohol.

	recovery (%)			
set	1	2	3	mean
first	93.47	95.32	96.94	95.24
second	98.47	100.4	101.2	100.0
second/first				105.0

11.2 Low Concentration

The effect of low concentration was tested by sampling a dynamically generated controlled test atmosphere containing 9.2 ppm isobutyl alcohol with a relative humidity of 78% at 21 °C. The test atmosphere was sampled with three samplers at 50 mL/min for 240 min. All of the samples were immediately analyzed. Analysis results provided recoveries of 99.11%, 101.0%, and 99.61%.

11.3 Back Tube Post-Sampling Analyte Migration

High humidity post-sampling analyte migration was studied by sampling a dynamically generated controlled test atmosphere containing 176.5 ppm isobutyl alcohol with a relative humidity of 79% at 21 °C. The test atmosphere was sampled with three samplers at 50 mL/min for 240 min. The samples were stored for 14 days at room temperature with the front and back tube connected. No isobutyl alcohol was found on the back tube. Front tube analysis results provided recoveries of 93.16%, 96.35%, and 96.83%.

Low humidity post-sampling analyte migration was studied by sampling a dynamically generated controlled test atmosphere containing 202.3 ppm isobutyl alcohol with a relative humidity pf 20% at 21 °C. The test atmosphere was sampled with three samplers at 50 mL/min for 240 min. The samples were stored for 14 days at room temperature with the front and back tube connected. No isobutyl alcohol was found on the back tube. Front tube analysis results provided recoveries of 94.19%, 95.17%, and 96.06%.

12 Estimation of Uncertainty

Estimation of uncertainty was not performed. Instead the overall standard error of estimate was calculated from the ambient storage test as prescribed by the OSHA validation guidelines.

13 Sampler Testing Procedure

A test atmosphere generator was set up in a walk-in hood. Dilution air was regulated using a Miller Nelson Model 401 Flow-Temperature-Humidity Control System. A measured flow of *n*-butyl, *sec*-butyl, isobutyl, and *n*-propyl alcohol was pumped through a 0.53-mm uncoated fused silica capillary tube, using a KD Scientific Legato 100 syringe pump, into a heated vapor generator, and mixed with the dilution air. The generated vapor flowed continually into a glass mixing chamber (10-cm × 30-cm) and then into a glass sampling chamber (10-cm × 68-cm). Samples were collected through sampling ports on the sampling chamber. Temperature and humidity were measured near the exit of the sampling chamber using a Vaisala HUMICAP Hand-Held Humidity and Temperature Meter HM70.

OSHA 5001, Appendix G
***n*-Propyl Alcohol**

Version:	1.0
OSHA PEL: ACGIH TLV:	200 ppm (500 mg/m^3) TWA 100 ppm (246 mg/m^3) TWA
Recommended sampling time and sampling rate:	240 min at 50 mL/min (12 L)
Reliable quantitation limit:	139 ppb (0.34 mg/m^3)
Standard error of estimate:	5.18%
Status:	Fully validated. Method 5001 has been subjected to the established validation procedures of the Method Development Team for sampling and analysis of *n*-propyl alcohol.

March 2019 Michael Simmons

1 Introduction

1.1 Previous Methods used by OSHA for Sampling and Analysis of *n*-Propyl Alcohol

Prior to the work described in this appendix, OSHA used a procedures based on the National Institute for Occupational and Health (NIOSH) Method 1401[1] for the sampling and analysis of *n*-propyl alcohol. The NIOSH method requires sample collection on a single dual-bed coconut-shell charcoal sampling tube, and desorption with 99/1 carbon disulfide (CS_2)/2-propanol. Analysis with the NIOSH method is by gas chromatography (GC) using a flame ionization detector (FID).

1.2 Changes to the Previously Used Method

This appendix represents a new method to replace that previously used by OSHA (NIOSH 1401[1]) for sampling and analysis of *n*-propyl alcohol. Compared to the previous method used, new analytical conditions, internal standard, sampling medium, extraction solvent, and extraction solvent volume allow standardized collection of *n*-propyl alcohol with the other analytes found in the Organic Vapor Sampling Group 2, described in Method 5001.

1.3 Validation Parameters

The procedures used to evaluate the method 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 analyte concentration equivalent to sampling for the recommended time at the OSHA TWA permissible exposure limit (PEL) value for *n*-propyl alcohol.

[1] Williamson, G. Alcohols II (NIOSH Method 1401), 1994. Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health web site. https://www.cdc.gov/niosh/docs/2003-154/pdfs/1401.pdf (accessed December 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 significantly greater than a reagent blank. Ten analytical standards were prepared with approximately equal descending increments of analyte, such that the highest standard concentration would produce a peak approximately 10 times the response of a blank at or near the chromatographic retention time of the analyte. These standards and a reagent blank were analyzed with the analytical parameters. The data obtained were used to determine the required parameters (standard error of estimate ($S_{y/x}$) and slope) for the calculation of the DLAP. Results obtained for the blank and each standard are listed below in Table G-1 and are plotted in Figure G-1.

Table G-1. DLAP data for *n*-propyl alcohol.

concentration (µg/mL)	mass on column (pg)	area counts (µV·s)
0.00	0.00	0.000
0.52	3.47	0.082
1.04	6.93	0.103
1.56	10.4	0.129
2.09	13.9	0.173
2.61	17.4	0.199
3.13	20.9	0.256
3.65	24.3	0.337
4.18	27.9	0.312
4.70	31.3	0.395
5.20	34.7	0.432

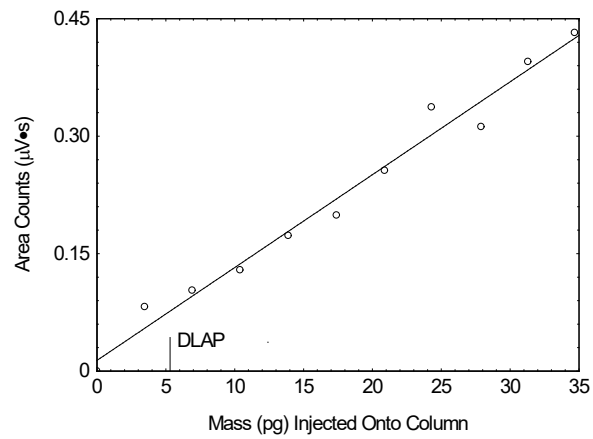

Figure G-1. Plot of data used to determine the DLAP for *n*-propyl alcohol ($y = 0.0119x + 0.0137$, $S_{y/x} = 0.0210$, DLAP = 5.3 pg).

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

The DLOP is the analyte mass per sample that produces a response significantly different than a sample blank. The RQL is the lowest level of analyte mass per sample for precise quantitative measurements and expressed as an air concentration based on the recommended sampling parameters. Ten samplers were spiked with approximately equal descending increments of analyte, such that the highest loading would produce a peak approximately 10 times the response of a sample blank at or near the chromatographic retention time of the analyte. These spiked samplers and a sample blank were analyzed with the analytical parameters. The data obtained were used to calculate the required parameters ($S_{y/x}$ and the slope) for the calculation of the DLOP and RQL. Results obtained for the sample blank and the ten spiked samplers are listed below in Table G-2 and plotted in Figure G-2.

Table G-2. DLOP and RQL data for *n*-propyl alcohol.

mass per sample (µg)	area counts (µV·s)
0.00	0.000
1.04	0.027
2.09	0.074
3.13	0.120
4.18	0.163
5.22	0.232
6.26	0.237
7.31	0.287
8.35	0.389
9.40	0.408
10.4	0.435

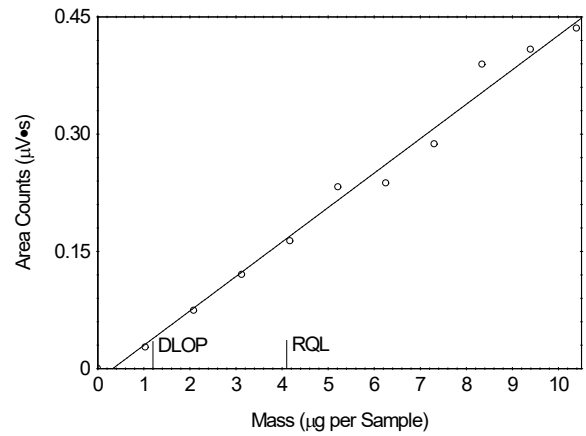

Figure G-2. Plot of data used to determine the DLOP and RQL for *n*-propyl alcohol ($y = 0.044x - 0.014$, $S_{y/x} = 0.018$, DLOP = 1.2 µg/sample, RQL = 4.1 µg/sample (139 ppb)).

3 Analytical Calibration

Fifteen analytical standards over a range of 0.1 to 2.0× the target concentration were prepared and analyzed with the analytical parameters. A least-squares linear regression curve was constructed by plotting the analyte mass per sample versus the ratio of analyte peak area to internal standard (ISTD) peak area. The data obtained was used to calculate the analytical calibration precision ($S_{y/x}$). Results are listed below in Table G-3 and plotted in Figure G-3.

Table G-3. Analytical precision data for *n*-propyl alcohol.

× target concn (µg/sample)	0.1×	0.5×	1.0×	1.5×	2.0×
	587.94	2939.7	5879.4	8819.1	11759
area ratio	0.1160	0.5829	1.157	1.736	2.365
	0.1157	0.5660	1.197	1.750	2.362
	0.1142	0.5788	1.155	1.760	2.385

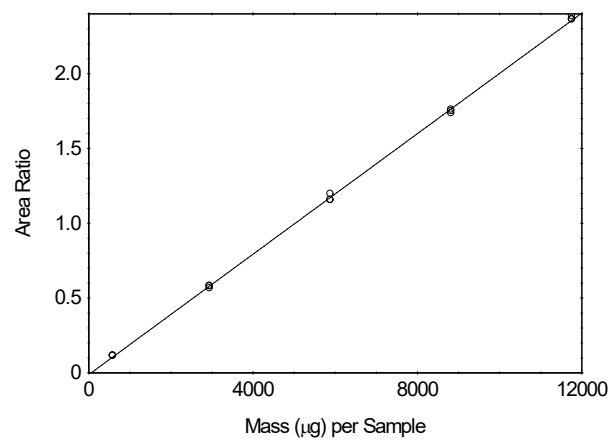

Figure G-3. Plot of the data used to estimate precision of the analytical method for *n*-propyl alcohol ($y = 0.00020x - 0.0121$, $S_{y/x} = 0.0165$).

4 Sampler Storage Stability

Eighteen samples were collected by sampling a test atmosphere containing 169.2 ppm *n*-propyl alcohol using the recommended sampling parameters. The relative humidity of the test atmosphere was 81% at 21 °C. Three samples were analyzed immediately after sampling. Fifteen of the samples were stored in a drawer at ambient temperature (about 22 °C). Three samples were selected and analyzed at the intervals noted below in Table G-4. Results obtained are listed in Table G-4 and plotted in Figure G-4. Sample results are not corrected for extraction efficiency (E_E).

Table G-4. Sampler storage stability data for *n*-propyl alcohol.

time (days)	ambient storage recovery (%)		
0	100.8	101.2	102.1
3	96.83	98.95	99.35
7	99.85	99.24	100.9
10	99.59	100.6	101.2
13	99.17	100.9	99.13
15	98.30	98.72	101.4

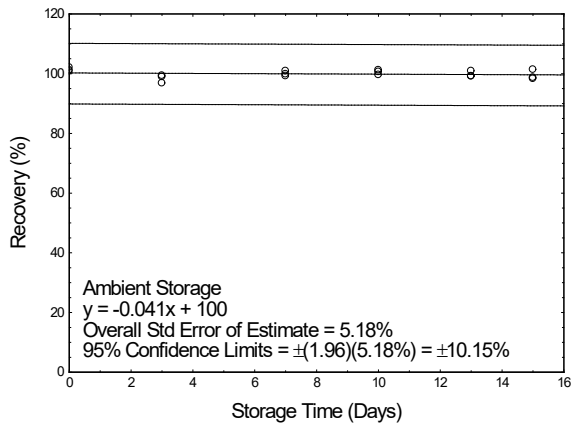

Figure G-4. Plot of storage stability data for *n*-propyl alcohol.

5 Precision

The precision of the overall procedure at the 95% confidence level is obtained by multiplying the overall standard error of estimate by 1.96 (the *z*-statistic from the standard normal distribution at the 95% confidence level). This provides ninety-five percent confidence intervals which are drawn about the regression lines in the storage stability figure shown in Section 4.

The precision of the overall procedure at the 95% confidence level for the ambient temperature (about 22 °C) 15-day storage test (at the target concentration) is ±10.15%. It was obtained from the overall standard error of estimate (5.18%) derived from the data shown in Figure G-4, with an additional 5% added for sampling pump error.

The recovery of *n*-propyl alcohol from samples used in the 15-day storage test was 99.4% when the samples were stored at ambient temperature.

6 Recovery and Stability of Prepared Samples

Quantitative extraction is affected by the extraction solvent, the internal standard, the sampling medium, and the technique used to extract the samples. For the use of reagents and techniques other than those described here, testing specified in current OSHA validation guidelines must be completed.

A value for E_E was determined by liquid-spiking four sorbent tubes at a range of 0.1 to 2.0× the target concentration. For a single set of sorbent tubes spiked with analyte equivalent to sampling at the 1.0× target concentration value for 4 hours, humid air (80% relative humidity at 21 °C) was passed through the sorbent tubes for 360 min at 50 mL/min prior to spiking. Another set of sorbent tubes was spiked at the RQL level. The spiked samples were stored overnight at ambient temperature and then analyzed. An overall mean E_E value of 101.7% was obtained across the analyte concentration range studied, and the E_E value at the RQL was 101.0%. The results of these tests are provided in Table G-5, and they demonstrate that the presence of water in the sorbent material had no significant effect on E_E. The E_E values for the RQL and wet sampler testing were not included in the overall mean.

Table G-5. Extraction efficiency data for *n*-propyl alcohol.

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
0.1	587.9	101.1	99.62	101.8	100.7	100.8
0.25	1470	101.7	101.8	101.8	101.5	101.7
0.5	2940	99.92	100.4	101.5	100.7	100.6
1.0	5879	102.2	102.2	103.4	102.3	102.5
1.5	8819	102.3	102.2	102.2	102.0	102.2
2.0	11759	102.8	102.3	102.2	101.7	102.2
RQL	4.18	100.0	95.00	104.8	104.4	101.0
1.0 (wet)	5879	101.5	101.2	101.3	101.9	101.5

The stability of extracted samples was examined by reanalyzing the 1.0× target concentration samples 24, 48, and 72 hours after the initial analysis. The septum of a vial was punctured four times for each injection (three syringe rinses and 1 syringe fill that was injected for analysis). After the original analysis was performed, two vials were recapped with new septa which were replaced after each reanalysis. The remaining two vials retained their sequentially-punctured septa throughout the test. All samples were allowed to stand at room temperature in the autosampler tray used. Freshly prepared standards were used for each reanalysis event. Results obtained are listed in Table G-6.

Table G-6. Extracted sample stability data for *n*-propyl alcohol.

	punctured septa replaced recovery (%)		punctured septa retained recovery (%)	
time (days)	1	2	1	2
0	102.2	102.2	103.4	102.9
1	101.6	101.4	102.9	102.8
2	101.8	101.8	102.6	102.6
3	101.8	102.0	102.5	102.5

7 Sampler Capacity

High humidity sampling capacity of 400-mg Anasorb 747 sampling tubes (front tube) was tested by sampling a dynamically generated controlled test atmosphere containing 329.8 ppm *n*-propyl alcohol with relative humidity of 79% at 21 °C. Three samples were collected at approximately 50 mL/min. A second 400-mg Anasorb 747 sampling tube was placed in a sampling train behind the first tube. No breakthrough was observed after 480 min of testing, equivalent to an air volume of 24 L.

Low humidity sampling capacity of 400-mg Anasorb 747 sampling tubes (front tube) was tested by sampling a dynamically generated controlled test atmosphere containing 384.0 ppm *n*-propyl alcohol with a relative humidity of 20% at 21 °C. Three samples were collected at approximately 50 mL/min. A second 400-mg Anasorb 747 sampling tube was placed in a sampling train behind the first tube. There was no breakthrough observed after 480 min of testing, equivalent to an air volume of 24 L.

8 Low Humidity

The effect of low humidity was tested by sampling a dynamically generated controlled test atmosphere containing 378.0 ppm *n*-propyl alcohol with a relative humidity of 20% at 21 °C. The test atmosphere was sampled with three samplers at 50 mL/min for 240 min. All of the samples were immediately analyzed. Analysis results provided recoveries of 94.20%, 95.31%, and 96.24%.

9 Chemical Interferences

Validation data for the analytes listed in appendices D-G of this method were collected together. All spiking solutions and test atmospheres generated contained *n*-butyl, *sec*-butyl, isobutyl, and *n*-propyl alcohol. The presences of *sec*-butyl, isobutyl, and *n*-butyl alcohol had no effect on the sampling and analysis of *n*-propyl alcohol.

10 Reproducibility

Six samples were prepared by sampling a dynamically generated controlled test atmosphere. The concentration of *n*-propyl alcohol in the test atmosphere was 185.0 ppm, and the relative humidity was 79% at 21 °C. The samples were submitted to the OSHA Salt Lake Technical Center for analysis using OSHA Method 5001, which was completed following eleven days of storage at 4 °C. Sample results were corrected for E_E. No sample result for *n*-propyl alcohol had a deviation greater than the precision of the overall procedure determined in Section 5. Results obtained are listed in Table G-7.

Table G-7. Reproducibility data for *n*-propyl alcohol.

sampled (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
5478.7	5253.7	95.9	-4.1
5507.6	5205.0	94.5	-5.5
5378.9	5158.4	95.9	-4.1
5384.3	5142.8	95.5	-4.5
5648.9	5516.4	97.7	-2.3
5298.7	5081.6	95.9	-4.1

11 Additional Testing

11.1 Retention

Retention was tested by sampling a dynamically generated controlled test atmosphere containing 371.1 ppm *n*-propyl alcohol with a relative humidity of 80% at 21 °C. The test atmosphere was sampled with six samplers at 50 mL/min for 60 min. Sampling was discontinued and the samplers were separated into two sets of 3 samplers each. The generation system was flushed with contaminant-free air. Contaminant-free air is laboratory conditioned air at known relative humidity and temperature but without any added chemicals except water. One set of samplers was set aside (first set). Sampling was resumed with the second set of three samplers and contaminant-free air at 80% relative humidity and 21 °C at 50 mL/min for 180 min. All six samples were analyzed and the data obtained are listed in Table G-8.

Table G-8. Retention data for *n*-propyl alcohol.

	recovery (%)			
set	1	2	3	mean
first	93.07	95.23	96.75	95.02
second	97.87	99.83	100.4	99.37
second/first				104.6

11.2 Low Concentration

The effect of low concentration was tested by sampling a dynamically generated controlled test atmosphere containing 17.2 ppm *n*-propyl alcohol with a relative humidity of 78% at 21 °C. The test atmosphere was sampled with three samplers at 50 mL/min for 240 min. All of the samples were immediately analyzed. Analysis results provided recoveries of 101.0%, 102.7%, and 102.2%.

11.3 Back Tube Post-Sampling Analyte Migration

High humidity post-sampling analyte migration was studied by sampling a dynamically generated controlled test atmosphere containing 329.8 ppm *n*-propyl alcohol at 79% relative humidity and 21 °C. The test atmosphere was sampled with three samplers at 50 mL/min for 240 min. The samples were stored for 14 days at room temperature with the front and back tube connected. No *n*-propyl alcohol was found on the back tube. Front tube analysis results provided recoveries of 92.40%, 96.22%, and 96.24%.

Low humidity post-sampling analyte migration was studied by sampling a dynamically generated controlled test atmosphere containing 378.1 ppm *n*-propyl alcohol at 20% relative humidity and 21 °C. The test atmosphere was sampled with three samplers at 50 mL/min for 240 min. The samples were stored for 14 days at room temperature with the front and back tube connected. No *n*-propyl alcohol was found on the back tube. Front tube analysis results provided recoveries of 92.82%, 93.75%, and 94.41%.

12 Estimation of Uncertainty

Estimation of uncertainty was not performed. Instead the overall standard error of estimate was calculated from the ambient storage test as prescribed by the OSHA validation guidelines.

13 Sampler Testing Procedure

A test atmosphere generator was set up in a walk-in hood. Dilution air was regulated using a Miller Nelson Model 401 Flow-Temperature-Humidity Control System. A measured flow of *n*-butyl, *sec*-butyl, isobutyl, and *n*-propyl alcohol was pumped through a 0.53-mm uncoated fused silica capillary tube, using a KD Scientific Legato 100 syringe pump, into a heated vapor generator, and mixed with the dilution air. The generated vapor flowed continually into a glass mixing chamber (10-cm × 30-cm) and then into a glass sampling chamber (10-cm × 68-cm). Samples were collected through sampling ports on the sampling chamber. Temperature and humidity were measured near the exit of the sampling chamber using a Vaisala HUMICAP Hand-Held Humidity and Temperature Meter HM70.