

OSHA Method 5004, Organic Vapor Sampling Group 4 (OVSG-4) Ketone Analytes Collected on Silica Gel Sorbent Tubes

Organic Vapor Sampling Group 4 (OVSG-4) Ketone Analytes Collected on Silica Gel Sorbent Tubes

Validated analytes:	<u>Analyte</u>	<u>CAS No.</u>
	Acetone	67-64-1
	2-Butanone (Methyl ethyl ketone)	78-93-3
	Hexone (Methyl isobutyl ketone)	108-10-1

Procedure: Collect samples by drawing workplace air containing specified ketone vapors through two silica gel sorbent tubes connected in series. Extract samples with 190 proof (95%) ethyl alcohol and analyze by gas chromatography (GC) using a flame ionization detector (FID). The analytes listed above are compatible with the sorbent, extraction solvent, and analytical parameters of Method 5004, and may be sampled separately or together.

Recommended sampling time and sampling rate: *180 min at 50 mL/min (9 L)
*exceptions:
acetone 120 min at 50 mL/min (6 L)

Special requirements: Immediately after sampling, separate and cap the two sampling tubes to prevent post-sampling migration. If additional analyses of extracted samples are required, recap sample vials within two days of the initial analysis to avoid sample loss.

Author: Michael Simmons

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

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1 Introduction

This method harmonizes the sampling, sample preparation and analysis of ketone analytes collected on two silica gel tubes connected in series that are extracted with 190 proof (95%) ethyl alcohol. Validation data for each analyte are described in the relevant appendices.

2 Sampling Procedure

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

2.1 Apparatus

Two single section 7-mm x 110-mm glass sampling tubes packed with 20/40 mesh silica gel sorbent are required for sampling. The front and back tube both contain 600 mg. Connect the tube in series with a 1-inch length of ¼ -inch i.d. silicone tubing. The sorbent is held in place with glass wool and a glass fiber filter on the inlet side, and glass wool on the outlet side. Commercially available tube sets were purchased from SKC Inc. (catalog no. 226-183) for method development. Sorbent tubes are provided to OSHA field activities through official sampling media procurement channels, and sorbent tubes are labeled with expiration dates. Store unused sorbent tubes at room temperature prior to use, and discard sorbent tubes when expiration dates are exceeded.

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

A personal sampling pump calibrated to within $\pm 5.0\%$ of the recommended flow rate with a representative sampling device in-line is used to draw air through a sampling tube. When possible, sample over the duration specified for the specific target analyte. If sampling for multiple target analytes, sample no longer than the shortest duration specified for each of those analytes.

2.2 Reagents

None Required

2.3 Technique

Immediately before sampling, break off the ends of the flame-sealed tubes to provide an opening approximately half the internal diameter of the tube. Connect the outlet end of the front 600-mg tube to the inlet end of the back 600-mg tube with a 1-inch length of ¼-inch i.d. silicone tubing. Place tubes into a sampling tube holder to minimize the hazard to the worker from the broken ends of the tubes. All tubes submitted for analysis (including field blanks) should be from the same lot.

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

Sample at 50 mL/min for 180 min (9 L) for all analytes except as specified under "recommended sampling time and sampling rate" on page 1 of this method and as explained in the respective method appendices.

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

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

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

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

3 Analytical Procedure

3.1 Apparatus

- Mechanical vial rotator
- One-liter amber glass solvent dispenser capable of dispensing 2.00 mL
- Syringe (25 and 50- μ L)
- Class A volumetric pipettes (4 and 6-mL)
- Class A volumetric flasks (2, 10, and 500-mL)
- Mechanical pipette capable of dispensing 1.25 mL
- Amber glass vials with polytetrafluoroethylene (PTFE)-lined screw caps (2 and 4-mL)
- GC instrument with FID

3.2 Reagents

- Acetone ($\geq 99\%$, analytical grade)
- 2-Butanone (methyl ethyl ketone, $\geq 99\%$, analytical grade)
- Hexone (methyl isobutyl ketone, $\geq 99\%$, analytical grade)
- Ethyl alcohol (190 proof (95%), spectrophotometric grade)
- 1,5-Pentanediol ($> 96\%$)

3.3 Reagent Preparation

Extraction solvent (190 proof (95%) ethyl alcohol with 2.50 μ L/mL 1,5-pentanediol as an internal standard (ISTD)): To a 500-mL volumetric flask add approximately 450 mL of ethyl alcohol and exactly 1.25 mL of 1,5-pentanediol, then add ethyl alcohol to the mark. Immediately mix the solution and transfer to an amber glass solvent dispenser.

3.4 Standard Preparation

Acetone

Prepare calibration standard levels 2-5 by injecting 10.0, 20.0, 30.0, and 40.0 μ L of acetone into 2-mL volumetric flasks containing approximately 1 mL of extraction solvent. Fill flask to the mark with extraction solvent and mix. Prepare calibration standard level 1 by injecting 5.0 μ L of calibration standard level 5 into a 2-mL volumetric flask containing approximately 1 mL of extraction solvent. Fill to the mark with extraction solvent and mix. Transfer the five calibration standards to 2-mL amber glass autosampler vials. The calibration standard concentrations are listed in Table 1 for

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acetone. If sample concentrations are greater than calibration standard level 5, dilute sample with extraction solvent and reanalyze the diluted samples.

Table 1. Calibration standard preparation procedure for acetone.^a

calibration standard level	working standard	working standard concn (µg/µL)	aliquot of working std (µL)	acetone cal std concn (µg/sample)
cal std 1	cal std 5	15.68	5.0	78.40
cal std 2	acetone	783.9	10.0	7839
cal std 3	acetone	783.9	20.0	15,678
cal std 4	acetone	783.9	30.0	23,517
cal std 5	acetone	783.9	40.0	31,356

^a Calculations based on a purity of 99.99% and a density of 784 µg/µL for neat acetone.

2-Butanone (methyl ethyl ketone) and hexone (methyl isobutyl ketone)

Prepare a working standard (WS) by adding 6.00 mL of 2-butanone (methyl ethyl ketone) and 4.00 mL of hexone (methyl isobutyl ketone) to a 10-mL volumetric flask and then mix. Prepare calibration standard levels 2-5 by injecting 6.0, 8.0, 12.0, 18.0, and 25.0 µL of the WS into 2-mL volumetric flasks containing approximately 1 mL of extraction solvent. Fill flask to the mark with extraction solvent and mix. Prepare calibration standard level 1 by injecting 8.0 µL of calibration standard level 5 into a 2-mL volumetric flask containing approximately 1 mL of extraction solvent. Fill to the mark with extraction solvent and mix. Transfer the five calibration standards to 2-mL amber glass autosampler vials. The calibration standard concentrations are listed in Table 2 for 2-butanone (methyl ethyl ketone) and Table 3 for hexone (methyl isobutyl ketone). If sample concentrations are greater than calibration standard level 5, dilute sample with extraction solvent and reanalyze the diluted samples.

Table 2. Calibration standard preparation procedure for 2-butanone (methyl ethyl ketone).^b

calibration standard level	working standard	working standard concn (µg/µL)	aliquot of working std (µL)	2-butanone cal std concn (µg/sample)
cal std 1	cal std 5	6.039	8.0	48.31
cal std 2	WS	483.1	6.0	2899
cal std 3	WS	483.1	12.0	5797
cal std 4	WS	483.1	18.0	8696
cal std 5	WS	483.1	25.0	12,078

^b Calculations based on a purity of 99.9% and a density of 806 µg/µL for neat 2-butanone (methyl ethyl ketone).

Table 3. Calibration standard preparation procedure for hexone (methyl isobutyl ketone).^c

calibration standard level	working standard	working standard concn (µg/µL)	aliquot of working std (µL)	hexone cal std concn (µg/sample)
cal std 1	cal std 5	3.994	8.0	31.95
cal std 2	WS	319.5	6.0	1917
cal std 3	WS	319.5	12.0	3834
cal std 4	WS	319.5	18.0	5751
cal std 5	WS	319.5	25.0	7988

^c Calculations based on a purity of 99.72% and a density of 801 µg/µL for neat hexone (methyl isobutyl ketone).

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3.5 Sample Preparation

Remove the plastic end-caps from the front and back sample tubes. Transfer the 600-mg silica gel from each tube into separate 4-mL vials. Discard the glass fiber filters and glass wool plugs
Add 2.00 mL of extraction solvent to each vial and immediately seal with PTFE-lined caps.

Extract the samples by rotating vials for 1 hour.

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 parameters described below. Use an ISTD calibration method. For each analyte, construct an x^{-1} weighted-least-squares linear regression curve by plotting ISTD-corrected response of standard injections versus micrograms of analyte per sample. Confirm the presence of 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 chromatogram obtained from a standard containing analyte mass concentrations equivalent to sampling for the recommended time with each analyte at its respective OSHA 8-hour time weighted average PEL value.

GC parameters

column:	Agilent J&W DB-WAX capillary column, 60-m × 0.32-mm i.d., $d_f = 0.5\text{-}\mu\text{m}$, or equivalent
inlet liner:	Restek Topaz 4.0-mm ID Precision Inlet Liner w/wool (Catalog no. 23305, or equivalent)
carrier:	hydrogen, constant flow, 2 mL/min
septum purge:	hydrogen, 3.0 mL/min
injection:	1.0 μL , split injection, 150:1 ratio
inlet temperature:	235 °C
oven temperature program:	40 °C (hold 4 min), ramp to 70 °C at 5 °C/min (hold 0 min), ramp to 240 °C at 15 °C/min (hold 1.5 min)
run time:	22.8 min
retention times:	5.78 min - acetone 7.70 min - 2-butanone (methyl ethyl ketone) 8.89 min - ethyl alcohol 10.74 min - hexone (methyl isobutyl ketone) 22.08 min - ISTD

FID parameters

detector temperature:	240 °C
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hydrogen flow: 40 mL/min

air flow: 450 mL/min

nitrogen make up flow: 45 mL/min

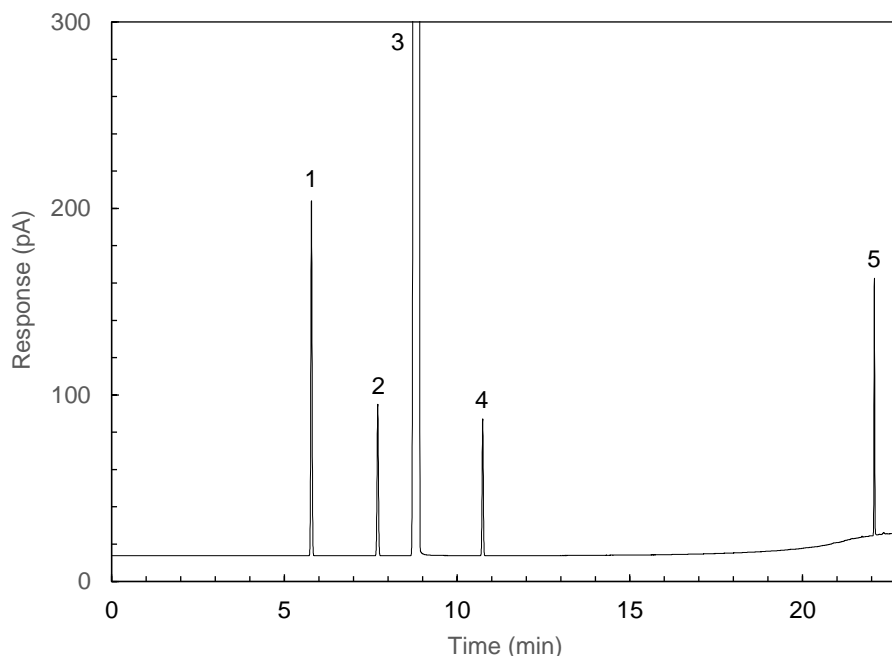


Figure 1. Example chromatogram. Peak labels: (1) acetone, (2) 2-butanone (methyl ethyl ketone), (3) ethyl alcohol, (4) hexone (methyl isobutyl ketone), (5) ISTD.

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 R_A is the extraction efficiency expressed in decimal format.

$$C = \frac{m}{VR_A} \quad (1)$$

The air concentration (C_{ppm}) in terms of parts of analyte vapor per million parts of air (ppm) is obtained using Equation 2, where C is the air concentration with mass per volume units (mg/m^3) calculated using Equation 1, V_M is the molar volume of an ideal gas or vapor at 25 °C and 760 Torr (24.46 L/mol), and M is the analyte molar mass (g/mol).

$$C_{ppm} = \frac{CV_M}{M} \quad (2)$$

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Values for R_A , obtained during validation studies, and M are listed in Table 4 along with the OSHA Integrated Management Information System (IMIS) numbers for each analyte.

Table 4. Molar mass, analytical recovery, and OSHA Integrated Management Information System (IMIS) numbers for Method 5001 analytes.

analyte	M (g/mol)	R_A	IMIS
acetone	58.08	0.9478	0040
2-butanone (methyl ethyl ketone)	72.11	0.9868	0430
hexone (methyl isobutyl ketone)	100.16	1.035	1385

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 parameters described below. Confirm the presence of an analyte by matching the retention time and fragmentation pattern of a standard at a similar concentration. See Figure 2 for an example 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 8-hour time weighted average PEL value.

GC parameters

column:	Agilent J&W DB-WAX capillary column, 60-m × 0.32-mm i.d., d_f = 0.5- μ m, or equivalent
inlet liner: equivalent)	Restek Topaz 4.0-mm ID Precision Inlet Liner w/wool (Catalog no. 23305, or
carrier:	helium, constant flow, 1.6 mL/min
septum purge:	helium, 3.0 mL/min
injection:	1.0 μ L, split injection, 150:1 ratio
inlet temperature:	235 °C
oven temperature program:	40 °C (hold 4.15 min), ramp to 70 °C at 4.7 °C/min (hold 0 min), ramp to 240 °C at 13 °C/min (hold 1.5 min)
run time:	25.11 min
retention times:	6.04 min - acetone 8.10 min - 2-butanone (methyl ethyl ketone) 11.44 min - hexone (methyl isobutyl ketone) 24.91 min - ISTD

mass spectrometer parameters

mode:	70 eV electron ionization
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acquisition mode: scan, m/z 20 - 150

timed events: 8.75 - 9.75 min MS off

EMV mode: gain factor (1)

temperatures: 250 °C (source), 200 °C (quadrupole assembly), 250 °C (transfer line)

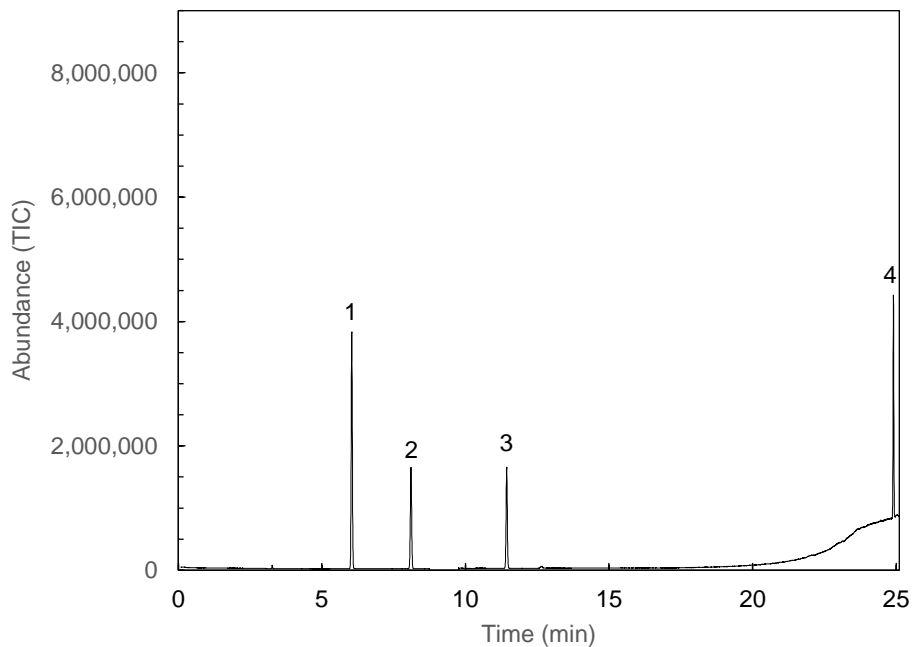


Figure 2. Example TIC GC-MS chromatogram. Peak labels: Peak labels: (1) acetone, (2) 2-butanone (methyl ethyl ketone), (3) hexone (methyl isobutyl ketone), (4) ISTD.

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Appendix A, Acetone

OSHA PEL:	1000 ppm (2400 mg/m ³) 8-Hour TWA, General Industry, Construction, Shipyard
Recommended sampling time and sampling rate:	120 min at 50 mL/min (6 L)
Limit of quantitation:	0.52 ppm (1.2 mg/m ³ , 8-Hour TWA)
Reporting limit:	5.5 ppm (13 mg/m ³ , 8-Hour TWA)
Uncertainty (<i>u</i>):	8.0%
Author:	Michael Simmons

1 Introduction

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

The specific analyte described in this appendix is acetone, CAS No. 67-64-1. The active sampling methodologies described in this appendix for acetone, replaces OSHA's use of OSHA Method 69.¹ That method requires the collection of samples using Carbosieve S-III sorbent tubes with a sampling time and rate of 60 minutes at 50 mL/min, extraction using 99/1 (v/v) carbon disulfide/*N,N*-dimethylformamide, and analysis by gas chromatography (GC) using a flame ionization detector (FID).

1.2 Method Validation

The procedures used to develop the method validation data are described in *Sampling and Analytical Methods*.² Air concentrations listed in ppm are referenced to 25 °C and 760 Torr. The target concentration (T_c) for method evaluation was the OSHA 8-hour TWA PEL. The target mass (T_M) is the equivalent analyte mass per sample collected on a sampler at the T_c using the recommended sampling time and sampling rate.

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

2 Limit of Detection, Limit of Quantitation, and Reporting Limit

The limit of detection (LOD) is the analyte mass introduced onto the chromatographic column that produces a response greater than 3.3x the standard error of estimate ($S_{y/x}$) divided by the slope of the linear regression equation. The linear regression equation is derived from analyses of three spiked samples at five evenly spaced levels, totaling fifteen spiked media samples. Sorbent tubes were spiked such that the highest mass loading produced a peak approximately 10 times greater than that of a sample blank at or near the chromatographic retention time of the analyte. The limit of quantitation (LOQ) is expressed as an air concentration that provides sufficient analyte mass per sample to produce a response greater than $10 \times S_{y/x}$ divided by the slope of the linear regression equation line described above. The spiked

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samplers and three sample blanks were analyzed with the recommended analytical parameters. The resulting data provided the $S_{y/x}$ and the slope values for LOD and LOQ determinations. Results obtained from these analyses are listed in Table A-1 and plotted in Figure A-1.

Table A-1. LOD and LOQ data for acetone.

$\mu\text{g}/\text{sample}$	0.00	3.45	6.90	10.4	13.8	17.2
	0.00	8.81×10^{-4}	1.37×10^{-3}	1.91×10^{-3}	2.40×10^{-3}	3.20×10^{-3}
area ratio	0.00	7.98×10^{-4}	1.50×10^{-3}	2.05×10^{-3}	2.61×10^{-3}	2.93×10^{-3}
	0.00	9.36×10^{-4}	1.26×10^{-3}	1.91×10^{-3}	2.37×10^{-3}	3.10×10^{-3}

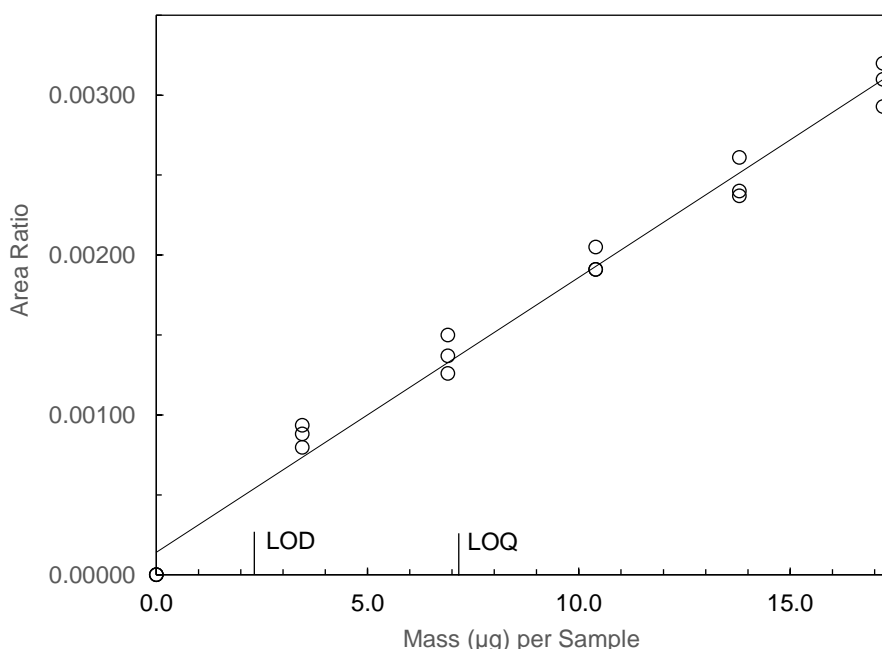


Figure A-1. Plot of data used to determine the LOD and LOQ for acetone ($y = 1.72 \times 10^{-4}x + 1.40 \times 10^{-4}$, $S_{y/x} = 1.27 \times 10^{-4}$, LOD = 2.44 $\mu\text{g}/\text{sample}$, LOQ = 7.40 $\mu\text{g}/\text{sample}$ or 0.519 ppm at the 8-hour TWA).

The reporting limit (RL) is expressed as an air concentration at the equivalent mass per sample at the lowest analytical calibration standard providing the recovery is within $\pm 25\%$. Six replicate sorbent tubes were liquid-spiked with 78.39 μg of acetone. After one hour of storage at ambient temperature the samples were analyzed using the analytical calibration procedure described in OSHA Method 5004. After analysis, results for acetone as a percentage of expected recovery were 103.7%, 102.9%, 102.4%, 100.8%, 100.8%, and 96.7%. The mean percentage of expected recovery was 101.2%. The reporting limit is 5.50 ppm at the 8-hour TWA.

3 Analytical Calibration

Thirty analytical standards over a range of 0.0055 to 2.2 times the 8-hour TWA T_M were analyzed with the recommended analytical parameters described in OSHA Method 5004. Graphical and statistical examination of these data indicate the appropriate regression model and fitting technique were weighted-least-squares linear regression with a x^{-1} weighting factor. Results from these analyses are listed in Table A-2 and plotted with the selected regression model

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and fitting technique in Figure A-2. Five standards prepared over this range are used for analytical calibration as described in OSHA Method 5004.

Table A-2. Analytical calibration data for acetone.

x 8-hour TWA T _M (µg/sample)	0.0055x (78.39)	0.28x (3920)	0.50x (7055)	0.72x (10191)	0.94x (13327)	1.2x (17246)	1.4x (20382)	1.7x (24302)	2.0x (28221)	2.2x (31357)
area ratio	0.01387	0.6525	1.227	1.757	2.236	2.918	3.473	4.129	4.832	5.339
	0.01454	0.6734	1.200	1.732	2.274	2.967	3.453	4.190	4.810	5.266
	0.01415	0.6795	1.225	1.758	2.278	2.971	3.500	4.234	4.856	5.330

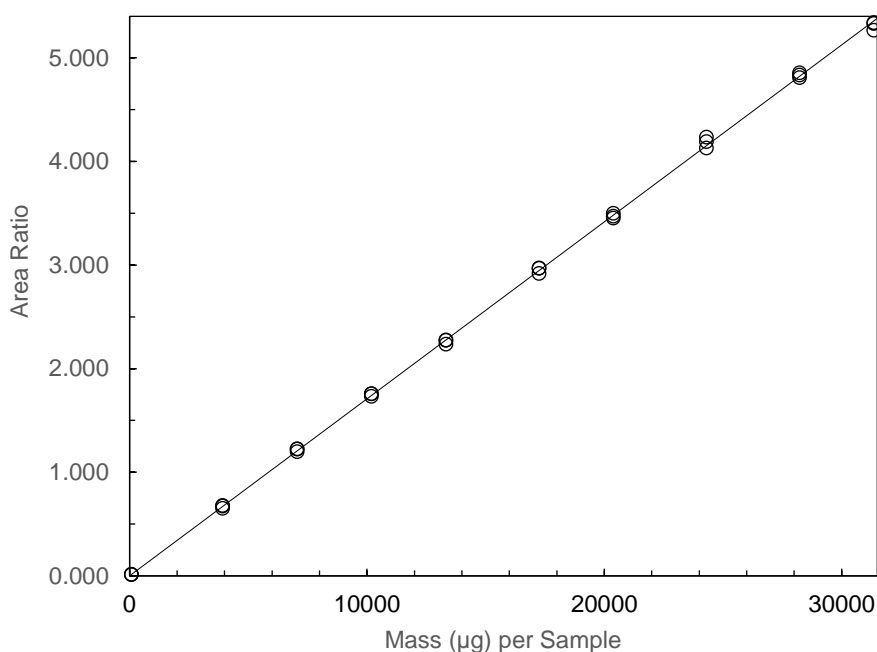


Figure A-2. Plot of data used to determine the analytical calibration procedure for acetone ($y = 1.71 \times 10^{-4}x + 8.80 \times 10^{-4}, w_i = x^{-1}$).

4 Post Sampling Storage

The post sampling storage stability test samples for acetone were prepared by sampling a dynamically generated controlled test atmosphere. Sampling from this system followed the recommended sampling parameters. The nominal concentration of acetone for ambient storage 8-hour TWA testing was the target concentration (calculated to be 987.8 ppm). The relative humidity and temperature of the air sampled were 80% and 22 °C. Eighteen samples were prepared and three of these were analyzed on the day that samples were created. The remaining fifteen samples were stored on a bench-top at ambient temperature (about 22°C). Three samples were selected and analyzed from those remaining at 2 to 4-day intervals. The results of these analyses (uncorrected for analytical recovery) are provided in Table A-3. The linear regression equation determined from these results was $y = 0.0285x + 93.0$.

The change in recovery (Δ_{ss}) of acetone calculated from the regression line generated for the 18-day post sampling storage test was 0.51%.

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Table A-3. Ambient post sampling storage stability data for acetone.

time (days)	sample 1 (%)	sample 2 (%)	sample 3 (%)
0	91.4	92.5	92.4
4	90.8	91.3	92.3
9	97.1	94.9	96.3
11	93.8	96.0	94.8
15	93.7	93.0	93.9
18	91.3	91.3	91.2

5 Method Precision and Bias

The method precision and bias were determined by sampling dynamically generated controlled test atmospheres. Six samples were collected at each of five levels across a concentration range of 0.1 to 2 times the 8-Hour TWA T_C at 50 mL/min for 120 min. Samples collected at each level were analyzed immediately after collection and independently from the other levels, including use of freshly prepared calibration standards. The results of these analyses are provided in Table A-4, along with the concentration, temperature, and relative humidity of each test atmosphere. The percent coefficient of variation of the means of the five levels tested (CV_m) was 0.88%, and the pooled coefficient of variation of each of the five levels tested (CV_{pl}) was 1.21%. The resulting 8-hour TWA method precision (u_{mp}) for acetone was determined to be 1.4%. The mean recovery of the thirty samples was 99.9%, resulting in a method bias (B_{mp}) of 0.10% and a coefficient of variation (CV_{mb}) of 1.4%.

Table A-4. Method precision data for acetone.

concn (ppm)	temp (°C)	RH (%)	sample 1 (%)	sample 2 (%)	sample 3 (%)	sample 4 (%)	sample 5 (%)	sample 6 (%)	mean (%)
100.7	22	80	98.0	97.9	98.0	100.7	101.4	99.0	99.2
500.2	22	80	98.9	102.2	101.3	100.5	102.3	100.4	100.9
983.1	21	82	98.5	101.0	101.2	100.4	101.2	100.9	100.5
1495	22	82	100.9	101.1	98.7	100.0	100.6	99.3	100.1
1989	21	80	97.2	99.0	97.8	98.7	100.0	100.1	98.8

6 Analytical Recovery and Stability of Prepared Samples

Analytical recovery is affected by the extraction solvent, the ISTD, the sampling medium, and the technique used to extract samples. The data presented demonstrate validity for the extraction solvent, ISTD, sampling medium, and extraction technique described in OSHA Method 5004. If other combinations of these are to be used, testing must be completed to satisfy the requirements found in current OSHA sampling and analysis method validation guidelines. Acceptable testing results must be documented.

The analytical recovery (R_A) was determined by liquid-spiking six replicate sorbent tubes across a range of analyte mass values that would be obtained from sampling at 0.1 to 2 times the 8-Hour TWA T_C for 120 min. Samples were analyzed following one hour of storage at ambient temperature. The R_A was 94.78%. The percent coefficient of variation of the thirty spiked samples (CV_{R_A}) was 1.6%. The data are shown in Table A-5.

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Table A-5. Analytical recovery data for acetone.

× 8-hour TWA T_M	µg per sample	sample 1 (%)	sample 2 (%)	sample 3 (%)	sample 4 (%)	sample 5 (%)	sample 6 (%)	mean (%)
0.1×	1568	94.3	93.4	94.7	93.8	93.4	93.2	93.8
0.5×	5487	92.3	94.5	91.0	95.0	95.7	94.1	93.8
1.0×	14111	95.7	94.3	94.8	93.7	93.1	93.7	94.2
1.5×	21168	96.3	97.8	95.8	95.9	98.0	94.7	96.4
2.0×	28221	96.6	95.5	95.4	94.6	96.1	96.1	95.7

The stability of sample extracts was determined by liquid-spiking six replicate sorbent tubes with a mass of analyte that would be obtained from sampling at the 8-Hour TWA T_C for 120 min (calculated to be 14111 µg). Samples were analyzed following one hour of storage at ambient temperature. All six vials were re-analyzed at 24, 48, and 72 hours after the initial analyses, with all vials remaining in the autosampler tray kept at 22 °C. Freshly prepared standards were used for each analysis event, and each sample septum was punctured four times for each injection. The results of these analyses are provided in Table A-6. The linear regression equation determined from these results was $y = -1.42x + 94.5$.

The change in recovery (Δ_{ps}) of acetone calculated from the regression line generated for the 3-day storage test was 4.2%. The Δ_{ps} of acetone calculated from the regression line, with sample vials recapped within two days of the initial analysis as described in Method 5004, was 2.8%.

Table A-6. Stability of prepared sample data for acetone.

day	sample 1 (%)	sample 2 (%)	sample 3 (%)	sample 4 (%)	sample 5 (%)	sample 6 (%)
0	95.4	96.0	94.3	94.9	94.5	94.4
1	92.9	92.8	91.5	92.4	91.6	92.1
2	91.8	92.3	91.5	92.5	92.1	91.4
3	89.2	92.1	90.0	91.1	89.8	89.4

7 Sampler Capacity

The sampling capacity of a single 600 mg sorbent tube was tested by sampling a dynamically generated controlled test atmosphere containing acetone nominally at two times the target concentration (calculated to be 2041 ppm). The relative humidity and temperature of the air sampled were 82.0% and 21.6 °C, and the sampling flow rate was 50 mL/min. A sorbent tube testing system was made by placing two sampling tubes in series. The rear tube was changed at 150, 155, 160, 165, 170, 175, and 180 minutes. Data from three sorbent tube testing systems, shown in Table A-7, were used to determine a recommended sampling volume of 6 liters for acetone, as 80% of the volume needed to produce 5% breakthrough. These results provide a recommended sampling time of 120 min as described in OSHA Method 5004. Results are plotted in Figure A-3.

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Table A-7. Sampler capacity data for acetone.

sample no.	air volume (L)	sampling time (min)	cumulative downstream concn (mg/m ³)	breakthrough (%)
1	7.36	150	13.06	0.269
	7.61	155	44.55	1.19
	7.85	160	150.0	3.37
	8.10	165	298.6	6.43
	8.34	170	523.2	11.1
	8.59	175	749.1	15.7
	8.83	180	1079	22.5
2	7.50	150	10.46	0.216
	7.75	155	55.80	1.37
	8.00	160	209.6	4.54
	8.25	165	428.3	9.05
	8.50	170	646.0	13.6
	8.75	175	875.3	18.3
	9.00	180	1210	25.2
3	7.68	150	66.41	1.37
	7.94	155	115.2	2.38
	8.20	160	319.9	6.60
	8.45	165	548.9	11.3
	8.71	170	779.3	16.1
	8.96	175	1007	20.8
	9.22	180	1344	27.7

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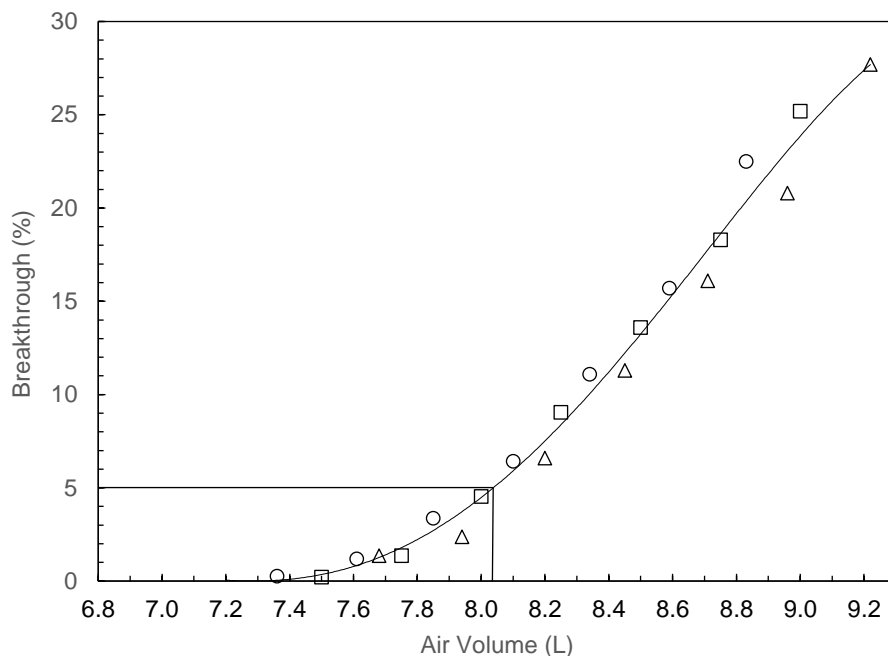


Figure A-3. Plot of data used to determine sampler capacity for acetone. The 5% breakthrough volume shown is based on the curve in the figure, which is fit to the data provided in Table A-6.

8 Effect of Humidity

The effect of humidity was tested by sampling a dynamically generated controlled test atmosphere containing acetone nominally at two times the target concentration (calculated to be 2005 ppm). The relative humidity and temperature of the air sampled were 29% and 21 °C, and the sampling flow rate was 50 mL/min. Samples were collected on six sorbent tubes for 120 min. After immediate analysis, results for acetone as a percentage of expected recovery using dry air were 95.5%, 95.6%, 95.8%, 96.9%, 97.4%, 96.5%. The mean percentage of expected recovery was 96.3%. The effect of humidity (Δ_h), calculated as the absolute difference between the mean low humidity recovery and the mean humid recovery taken from the 1989-ppm method precision test described in Section 5 was 2.5%.

9 Sampling and Analytical Interferents

Confirm the presence of acetone when the OSHA PEL value has been exceeded as described in Section 3.8 of OSHA Method 5004.

10 Analytical Reproducibility

Analytical reproducibility samples were prepared by sampling a dynamically generated controlled test atmosphere containing acetone nominally at the target concentration (calculated to be 986.2 ppm). The relative humidity and temperature of the air sampled were 84% and 21 °C, and the sampling flow rate was 50 mL/min. Samples were collected on six sorbent tubes for 120 min. The resulting samples were submitted to the OSHA Technical Center for analysis using the procedures described in OSHA Method 5004 after storage for 13 days at -2 °C. The analytical results

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corrected for R_A are provided in Table A-7. No sample result for acetone fell outside the permissible bounds set by the expanded uncertainty determined in Section 11.

Table A-7. Reproducibility data for acetone.

sampled ($\mu\text{g}/\text{sample}$)	recovered ($\mu\text{g}/\text{sample}$)	recovery (%)	deviation (%)
13751	13526	98.4	-1.6
13806	13814	100.1	+0.1
14233	14092	99.0	-1.0
13612	13683	100.5	+0.5
13517	13519	100.0	0.0
13769	13731	99.7	-0.3

11 Estimation of Uncertainty

Sampling and storage percent relative standard uncertainty components for acetone are provided in Table A-8. The sampling and storage percent relative uncertainty (u_s) was determined to be 3.6% for 8-hour TWA sampling.

Table A-8. Sampling and storage uncertainty.

uncertainty component	8-hour TWA (%)	notes
flow rate measurement (u_{fr})	0.14	$u_{fr} = CV_{fr}/\sqrt{n}$, calculated from three replicate flow measurements using the flow meter with a representative sampler inline (49.36, 49.33, and 49.14 mL/min)
flow rate calibration (u_{fc})	0.58	$u_{fc} = 1\%/\sqrt{3}$, assumes a maximum flow meter calibration tolerance of $\pm 1\%$ at 50 mL/min
pump flow stability (u_{fs})	3.5	$u_{fs} = 6\%/\sqrt{3}$, assumes flow rate is maintained to within $\pm 6\%$ at 50 mL/min
sampling time (u_{st})	0.34	$u_{st} = [(B_{st} \times t_{st}^{-1})/\sqrt{6}] \times 100\%$, time sampled to nearest minute, where $B_{st} = 1$ min and $t_{st} = 120$ minutes sampled
sampling efficiency (u_{se})	0.00	Sampler capacity not exceeded at recommended sampling time and rate, see Section 7
post sampling storage (u_{ss})	0.29	$u_{ss} = \Delta_{ss}/\sqrt{3}$, where $\Delta_{ss} = 0.51\%$, see Section 4
sampling and storage uncertainty (u_s)	3.6	

Analytical percent relative standard uncertainty components for acetone are provided in Table A-9. The analytical percent relative uncertainty (u_s) was determined to be 7.0% for 8-hour TWA sampling.

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Table A-9. Analytical uncertainty.

uncertainty component	8-hour TWA (%)	notes
calibration standards (u_{cs})	0.87	Calculated from the manufacturer listed tolerance levels of the volumetric flasks specified for use in Section 3.4, from repeatability tests of the syringe, and the manufacturer reported purity of 99.99% for acetone
analytical recovery (u_{ar})	0.29	$u_{ar} = CV_{RA}/\sqrt{n}$, where $CV_{RA} = 1.6\%$ and $n = 30$, see Section 6, assumes results are corrected for analytical recovery
stability of prepared samples (u_{ps})	1.6	$u_{ps} = \Delta_{ps}/\sqrt{3}$, where $\Delta_{ps} = 2.8\%$, see Section 6
method precision (u_{mp})	1.4	$u_{mp} = \sqrt{(CV_m)^2 + (1 - 1/n) \times (CV_{pl})^2}$, where $CV_m = 0.88\%$, $CV_{pl} = 1.2\%$, and $n = 6$, see Section 5
method bias (u_{mb})	3.0	$u_{mb} = \sqrt{(B_{mb}/\sqrt{3})^2 + (CV_{mb}/\sqrt{n})^2 + (u_{rc})^2}$, where $B_{mb} = 0.10\%$, $CV_{mb} = 1.4\%$, and $n = 30$, see Section 5; $u_{rc} = 3\%$, see Reference 3
effect of humidity (u_h)	1.4	$u_h = \Delta_h/\sqrt{3}$, where $\Delta_h = 2.5\%$, see Section 8
instrument response drift (u_{dr})	5.8	$u_{dr} = 10\%/\sqrt{3}$, assumes a maximum instrument response drift of $\pm 10\%$
analytical uncertainty (u_a)	7.1	

The combined percent relative standard uncertainty of the sampling and analysis procedure ($u = \sqrt{(u_s)^2 + (u_a)^2}$) was determined to be 8.0% for 8-hour TWA samples. The expanded uncertainty ($U = 2 \times u$) was determined to be 16% for 8-hour TWA samples.

References

- Cummins, K. Acetone (OSHA Method 69), 1998. United States Department of Labor, Occupational Safety & Health Administration website. www.osha.gov (accessed May 2024).
- Sampling and Analytical Methods, 2024. United States Department of Labor, Occupational Safety & Health Administration website. www.osha.gov (accessed May 2024).
- ISO/DIS 22065:2018, Workplace air - Procedures for measuring gases and vapours using pumped samplers - Requirements and test methods.

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Appendix B, 2-Butanone (Methyl ethyl ketone)

OSHA PEL:	200 ppm (590 mg/m ³) 8-Hour TWA, General Industry, Construction, Shipyard
Recommended sampling time and sampling rate:	180 min at 50 mL/min (9 L)
Limit of quantitation:	0.31 ppm (0.92 mg/m ³ , 8-Hour TWA)
Reporting limit:	1.8 ppm (5.4 mg/m ³ , 8-Hour TWA)
Uncertainty (<i>u</i>):	8.0%
Author:	Michael Simmons

1 Introduction

1.1 Previous Methods used by OSHA for Sampling and Analysis of 2-Butanone (Methyl ethyl ketone)

The specific analyte described in this appendix is 2-butanone (methyl ethyl ketone), CAS No. 78-93-3. The active sampling methodologies described in this appendix for 2-butanone (methyl ethyl ketone), replaces OSHA's use of OSHA Method 1004.¹ That method requires the collection of samples using Anasorb CMS sorbent tubes with a sampling time and rate of 240 minutes at 50 mL/min, extraction using 99/1 (v/v) carbon disulfide/*N,N*-dimethylformamide, and analysis by gas chromatography (GC) using a flame ionization detector (FID).

1.2 Method Validation

The procedures used to develop the method validation data are described in *Sampling and Analytical Methods*.² Air concentrations listed in ppm are referenced to 25 °C and 760 Torr. The target concentration (*T_c*) for method evaluation was the OSHA 8-hour TWA PEL. The target mass (*T_m*) is the equivalent analyte mass per sample collected on a sampler at the *T_c* using the recommended sampling time and sampling rate.

Dynamically generated controlled test atmospheres were created in a walk-in hood. House air was regulated using a flow-temperature-humidity control system. A measured flow of liquid 2-butanone (methyl ethyl ketone) and hexone (methyl isobutyl ketone) was introduced with a syringe pump through a short length of uncoated fused silica capillary into a heated zone near the air flow entrance of the test atmosphere generator, where it was evaporated into a measured flow of dilution air from the flow-temperature-humidity control system. The resulting vapor and dilution air flowed into a mixing chamber, and then into a sampling chamber. Sampling was completed using sampling ports on the sampling chamber. Temperature and humidity measurements were obtained near the exit of the sampling chamber.

2 Limit of Detection, Limit of Quantitation, and Reporting Limit

The limit of detection (LOD) is the analyte mass introduced onto the chromatographic column that produces a response greater than 3.3× the standard error of estimate (*S_{y/x}*) divided by the slope of the linear regression equation. The linear regression equation is derived from analyses of three spiked samples at five evenly spaced levels, totaling fifteen spiked media samples. Sorbent tubes were spiked such that the highest mass loading produced a peak approximately 10 times greater than that of a sample blank at or near the chromatographic retention time of the analyte. The limit of quantitation (LOQ) is expressed as an air concentration that provides sufficient analyte mass per sample to produce a response greater than 10 × *S_{y/x}* divided by the slope of the linear regression equation line described above. The spiked samplers and three sample blanks were analyzed with the recommended analytical parameters. The resulting data

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provided the $S_{y/x}$ and the slope values for LOD and LOQ determinations. The resulting data provided the $S_{y/x}$ and the slope values for LOD and LOQ determinations. Results obtained from these analyses are listed in Table B-1 and plotted in Figure B-1.

Table B-1. LOD and LOQ data for 2-butanone (methyl ethyl ketone).

µg/sample	0.00	4.19	8.37	12.6	16.7	20.9
	0.00	1.04×10^{-3}	1.91×10^{-3}	3.03×10^{-3}	3.86×10^{-3}	4.73×10^{-3}
area ratio	0.00	1.54×10^{-3}	2.30×10^{-3}	2.97×10^{-3}	4.11×10^{-3}	5.27×10^{-3}
	0.00	9.47×10^{-4}	2.29×10^{-3}	3.11×10^{-3}	3.92×10^{-3}	4.90×10^{-3}

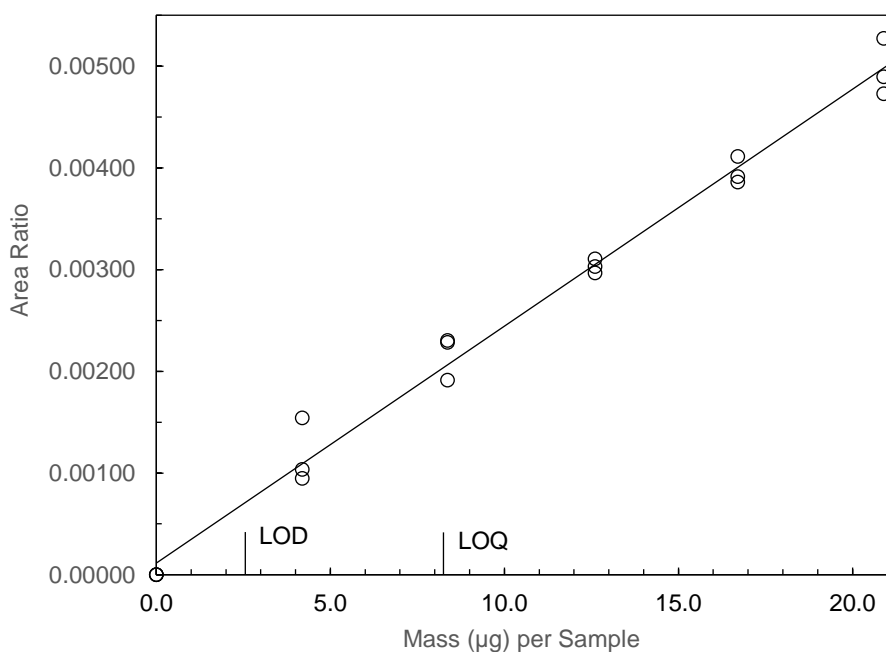


Figure B-1. Plot of data used to determine the LOD and LOQ for 2-butanone (methyl ethyl ketone) ($y = 2.33 \times 10^{-4}x + 1.15 \times 10^{-4}$, $S_{y/x} = 1.93 \times 10^{-4}$, LOD = 2.73 µg/sample, LOQ = 8.28 µg/sample or 0.312 ppm at the 8-hour TWA).

The reporting limit (RL) is expressed as an air concentration at the equivalent mass per sample at the lowest analytical calibration standard providing the recovery is within $\pm 25\%$. Six replicate sorbent tubes were liquid-spiked with 48.31 µg of 2-butanone (methyl ethyl ketone). After one hour of storage at ambient temperature the samples were analyzed using the analytical calibration procedure described in OSHA Method 5004. After analysis, results for 2-butanone (methyl ethyl ketone) as a percentage of expected recovery were 100.6%, 97.2%, 93.7%, 98.2%, 102.7%, and 96.5%. The mean percentage of expected recovery was 98.2%. The reporting limit is 1.82 ppm at the 8-hour TWA.

3 Analytical Calibration

Thirty analytical standards over a range of 0.0091 to 2.3 times the 8-hour TWA T_M were analyzed with the recommended analytical parameters described in OSHA Method 5004. Graphical and statistical examination of these data indicate the appropriate regression model and fitting technique were weighted-least-squares linear regression with a x^{-1} weighting factor. Results from these analyses are listed in Table B-2 and plotted with the selected regression model

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and fitting technique in Figure B-2. Five standards prepared over this range are used for analytical calibration as described in OSHA Method 5004.

Table B-2. Analytical calibration data for 2-butanone (methyl ethyl ketone).

× 8-hour TWA T_M ($\mu\text{g}/\text{sample}$)	0.0091× (48.31)	0.18× (966.2)	0.46× (2416)	0.73× (3865)	1.0× (5314)	1.3× (6764)	1.5× (8213)	1.8× (9662)	2.1× (11112)	2.3× (12078)
area ratio	0.009179	0.1878	0.4708	0.7546	1.036	1.307	1.580	1.857	2.139	2.319
	0.009832	0.1794	0.4611	0.7531	1.022	1.293	1.564	1.879	2.142	2.349
	0.009719	0.1832	0.4655	0.7677	1.031	1.317	1.600	1.878	2.110	2.353

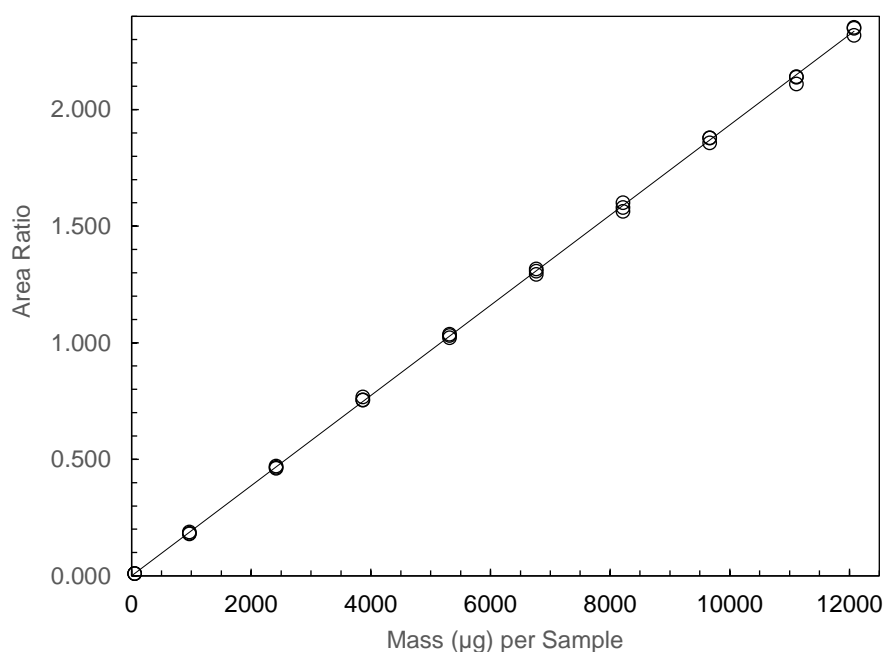


Figure B-2. Plot of data used to determine the analytical calibration procedure for 2-butanone (methyl ethyl ketone) ($y = 1.93 \times 10^{-4}x + 3.20 \times 10^{-4}, w_i = x^{-1}$).

4 Post Sampling Storage

The post sampling storage stability test samples for 2-butanone (methyl ethyl ketone) were prepared by sampling a dynamically generated controlled test atmosphere. Sampling from this system followed the recommended sampling parameters. The nominal concentration of 2-butanone (methyl ethyl ketone) for ambient storage 8-hour TWA testing was the target concentration (calculated to be 200 ppm). The relative humidity and temperature of the air sampled were 76% and 24 °C. Eighteen samples were prepared and three of these were analyzed on the day that samples were created. The remaining fifteen samples were stored on a bench-top at ambient temperature (about 22 °C). Three samples were selected and analyzed from those remaining at 3 to 4-day intervals. The results of these analyses (uncorrected for analytical recovery) are provided in Table B-3. The linear regression equation determined from these results was $y = -0.0219x + 98.5$.

The change in recovery (Δ_{ss}) of 2-butanone (methyl ethyl ketone) calculated from the regression line generated for the 17-day post sampling storage test was 0.37%.

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Table B-3. Ambient post sampling storage stability data for 2-butanone (methyl ethyl ketone).

time (days)	sample 1 (%)	sample 2 (%)	sample 3 (%)
0	96.3	100.9	103.1
3	97.4	97.3	97.7
7	95.6	97.3	98.1
10	97.2	98.7	97.5
14	97.5	98.8	99.9
17	95.6	99.2	101.0

5 Method Precision and Bias

The method precision and bias were determined by sampling dynamically generated controlled test atmospheres. Six samples were collected at each of five levels across a concentration range of 0.1 to 2 times the 8-Hour TWA T_c at 50 mL/min for 180 min. Samples collected at each level were analyzed immediately after collection and independently from the other levels, including use of freshly prepared calibration standards. The results of these analyses are provided in Table B-4, along with the concentration, temperature, and relative humidity of each test atmosphere. The percent coefficient of variation of the means of the five levels tested (CV_m) was 1.4%, and the pooled coefficient of variation of each of the five levels tested (CV_{pl}) was 0.90%. The resulting 8-hour TWA method precision (u_{mp}) for 2-butanone (methyl ethyl ketone) was determined to be 1.6%. The mean recovery of the thirty samples was 98.7%, resulting in a method bias (B_{mp}) of 1.3% and a coefficient of variation (CV_{mb}) of 1.5%.

Table B-4. Method precision data for 2-butanone (methyl ethyl ketone).

concn (ppm)	temp (°C)	RH (%)	sample 1 (%)	sample 2 (%)	sample 3 (%)	sample 4 (%)	sample 5 (%)	sample 6 (%)	mean (%)
19.7	24	76	97.6	99.5	99.1	99.3	101.0	100.8	99.6
101	24	76	100.3	100.0	100.4	100.4	100.8	101.0	100.5
199	24	75	95.9	97.3	96.9	98.2	97.4	98.7	97.4
302	24	77	97.4	97.8	98.4	99.5	99.0	100.0	98.7
403	24	76	96.5	97.8	98.7	97.7	97.1	97.4	97.5

6 Analytical Recovery and Stability of Prepared Samples

Analytical recovery is affected by the extraction solvent, the ISTD, the sampling medium, and the technique used to extract samples. The data presented demonstrate validity for the extraction solvent, ISTD, sampling medium, and extraction technique described in OSHA Method 5004. If other combinations of these are to be used, testing must be completed to satisfy the requirements found in current OSHA sampling and analysis method validation guidelines. Acceptable testing results must be documented.

The analytical recovery (R_A) was determined by liquid-spiking six replicate sorbent tubes across a range of analyte mass values that would be obtained from sampling at 0.1 to 2 times the 8-Hour TWA T_c for 180 min. Samples were analyzed following one hour of storage at ambient temperature. The R_A was 98.96%. The percent coefficient of variation of the thirty spiked samples (CV_{R_A}) was 0.57%. The data are shown in Table B-5.

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Table B-5. Analytical recovery data for 2-butanone (methyl ethyl ketone).

× 8-hour TWA T _M	µg per sample	sample 1 (%)	sample 2 (%)	sample 3 (%)	sample 4 (%)	sample 5 (%)	sample 6 (%)	mean (%)
0.1×	531.4	99.1	99.2	99.4	98.8	98.8	98.8	99.0
0.5×	2657	99.8	98.5	99.2	98.4	98.6	99.2	99.0
1.0×	5314	98.6	97.4	98.7	98.7	98.9	98.2	98.4
1.5×	8213	98.8	99.6	97.7	98.4	99.1	98.8	98.7
2.0×	10629	99.1	97.8	98.3	98.0	98.5	97.1	98.3

The stability of sample extracts was determined by liquid-spiking six replicate sorbent tubes with a mass of analyte that would be obtained from sampling at the 8-Hour TWA T_C for 180 min (calculated to be 5314 µg). Samples were analyzed following one hour of storage at ambient temperature. All six vials were re-analyzed at 24, 48, and 72 hours after the initial analyses, with all vials remaining in the autosampler tray kept at 22 °C. Freshly prepared standards were used for each analysis event, and each sample septum was punctured four times for each injection. The results of these analyses are provided in Table B-6. The linear regression equation determined from these results was $y = -1.89x + 100.2$.

The change in recovery (Δ_{ps}) of 2-butanone (methyl ethyl ketone) calculated from the regression line generated for the 3-day storage test was 5.7%. The Δ_{ps} of 2-butanone (methyl ethyl ketone) calculated from the regression line, with sample vials recapped within two days of the initial analysis as described in Method 5004, was 3.8%.

Table B-6. Stability of prepared sample data for 2-butanone (methyl ethyl ketone).

day	sample 1 (%)	sample 2 (%)	sample 3 (%)	sample 4 (%)	sample 5 (%)	sample 6 (%)
0	99.9	97.6	100.4	100.1	99.9	98.5
1	99.6	99.0	101.5	99.3	100.7	99.4
2	94.9	94.7	95.3	95.3	96.3	95.8
3	95.2	94.4	95.5	94.1	94.3	94.4

7 Sampler Capacity

The sampling capacity of a single 600 mg sorbent tube was tested by sampling a dynamically generated controlled test atmosphere containing 2-butanone (methyl ethyl ketone) nominally at two times the target concentration (calculated to be 401 ppm). The relative humidity and temperature of the air sampled were 72% and 24 °C, and the sampling flow rate was 50 mL/min. A sorbent tube testing system was made by placing two sampling tubes in series. The rear tube was changed at 205, 220, 225, 230, 235, 240, and 245 minutes. Data from three sorbent tube testing systems, shown in Table B-7, were used to determine a recommended sampling volume of 9 liters for 2-butanone (methyl ethyl ketone), as 80% of the volume needed to produce 5% breakthrough. These results provide a recommended sampling time of 180 min as described in OSHA Method 5004. Results are plotted in Figure B-3.

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Table B-7. Sampler capacity data for 2-butanone (methyl ethyl ketone).

sample no.	air volume (L)	sampling time (min)	cumulative downstream concn (mg/m ³)	breakthrough (%)
1	9.91	205	0.00	0.00
	10.6	220	0.00	0.00
	10.9	225	0.00	0.00
	11.1	230	0.00	0.00
	11.4	235	1.45	0.123
	11.6	240	16.3	1.38
	11.8	245	97.2	8.23
2	10.2	205	0.00	0.00
	11.0	220	1.43	0.121
	11.2	225	6.92	0.586
	11.5	230	27.7	2.35
	11.7	235	76.5	6.48
	12.0	240	150	12.7
	12.2	245	270	22.8
3	10.2	205	0.00	0.00
	11.0	220	11.4	0.966
	11.2	225	36.1	3.05
	11.5	230	77.4	6.55
	11.7	235	138	11.7
	12.0	240	216	18.3
	12.2	245	336	28.4

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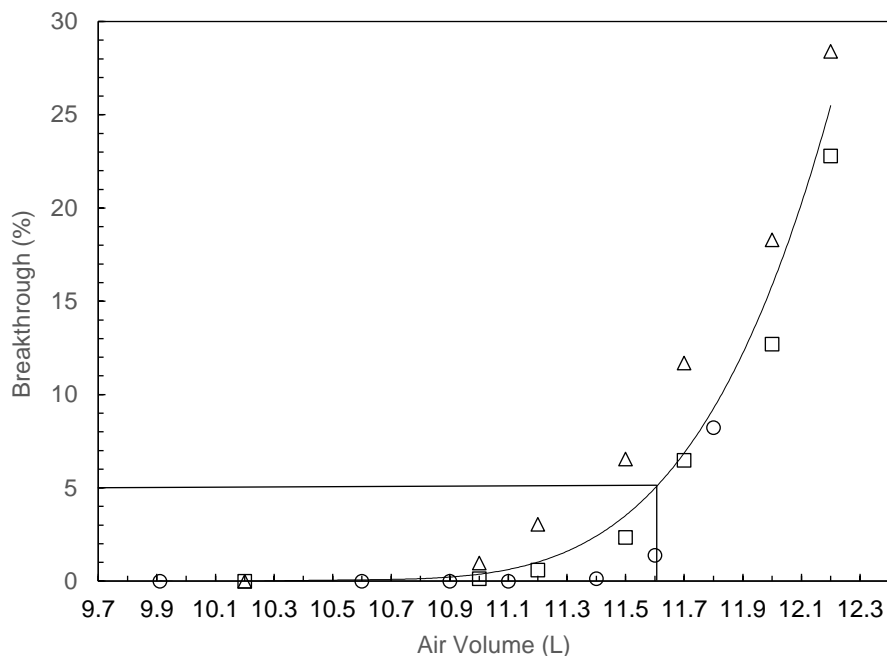


Figure B-3. Plot of data used to determine sampler capacity for 2-butanone (methyl ethyl ketone). The 5% breakthrough volume shown is based on the curve in the figure, which is fit to the data provided in Table A-6.

8 Effect of Humidity

The effect of humidity was tested by sampling a dynamically generated controlled test atmosphere containing 2-butanone (methyl ethyl ketone) nominally at two times the target concentration (calculated to be 397 ppm). The relative humidity and temperature of the air sampled were 20% and 24 °C, and the sampling flow rate was 50 mL/min. Samples were collected on six sorbent tubes for 180 min. After immediate analysis, results for 2-butanone (methyl ethyl ketone) as a percentage of expected recovery using dry air were 96.2%, 92.2%, 93.9%, 94.8%, 97.3%, 97.7%. The mean percentage of expected recovery was 95.4%. The effect of humidity (Δ_h), calculated as the absolute difference between the mean low humidity recovery and the mean humid recovery taken from the 403-ppm method precision test described in Section 5 was 2.1%.

9 Sampling and Analytical Interferents

The presence of methyl alcohol in the sample extract will cause a positive analytical interference for 2-butanone (methyl ethyl ketone). Confirm the concentration of 2-butanone (methyl ethyl ketone) when the OSHA PEL value has been exceeded and the presence of methyl alcohol is suspected, as described in Section 3.8 of OSHA Method 5004.

10 Analytical Reproducibility

Analytical reproducibility samples were prepared by sampling a dynamically generated controlled test atmosphere containing 2-butanone (methyl ethyl ketone) nominally at the target concentration (calculated to be 199.8 ppm). The relative humidity and temperature of the air sampled were 73% and 24 °C, and the sampling flow rate was 50 mL/min. Samples were collected on six sorbent tubes for 180 min. The resulting samples were submitted to the OSHA Technical Center for analysis using the procedures described in OSHA Method 5004 after storage for 13 days at -2 °C. The

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analytical results corrected for R_A are provided in Table A-B. No sample result for 2-butanone (methyl ethyl ketone) fell outside the permissible bounds set by the expanded uncertainty determined in Section 11.

Table B-7. Reproducibility data for 2-butanone (methyl ethyl ketone).

sampled ($\mu\text{g}/\text{sample}$)	recovered ($\mu\text{g}/\text{sample}$)	recovery (%)	deviation (%)
5392	5213	96.7	-3.3
5262	5234	99.5	-0.5
5374	5331	99.2	-0.8
5331	5501	103.2	+3.2
5286	5388	101.9	+1.9
5237	5354	102.2	+2.2

11 Estimation of Uncertainty

Sampling and storage percent relative standard uncertainty components for 2-butanone (methyl ethyl ketone) are provided in Table B-8. The sampling and storage percent relative uncertainty (u_s) was determined to be 3.6% for 8-hour TWA sampling.

Table B-8. Sampling and storage uncertainty.

uncertainty component	8-hour TWA (%)	notes
flow rate measurement (u_{fr})	0.14	$u_{fr} = CV_{fr}/\sqrt{n}$, calculated from three replicate flow measurements using the flow meter with a representative sampler inline (49.36, 49.33, and 49.14 mL/min)
flow rate calibration (u_{fc})	0.58	$u_{fc} = 1\%/\sqrt{3}$, assumes a maximum flow meter calibration tolerance of $\pm 1\%$ at 50 mL/min
pump flow stability (u_{fs})	3.5	$u_{fs} = 6\%/\sqrt{3}$, assumes flow rate is maintained to within $\pm 6\%$ at 50 mL/min
sampling time (u_{st})	0.23	$u_{st} = [(B_{st} \times t_{st}^{-1})/\sqrt{6}] \times 100\%$, time sampled to nearest minute, where $B_{st} = 1$ min and $t_{st} = 180$ minutes sampled
sampling efficiency (u_{se})	0.00	Sampler capacity not exceeded at recommended sampling time and rate, see Section 7
post sampling storage (u_{ss})	0.21	$u_{ss} = \Delta_{ss}/\sqrt{3}$, where $\Delta_{ss} = 0.37\%$, see Section 4
sampling and storage uncertainty (u_s)	3.6	

Analytical percent relative standard uncertainty components for 2-butanone (methyl ethyl ketone) are provided in Table B-9. The analytical percent relative uncertainty (u_s) was determined to be 7.2% for 8-hour TWA sampling.

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Table B-9. Analytical uncertainty.

uncertainty component	8-hour TWA (%)	notes
calibration standards (u_{cs})	0.57	Calculated from the manufacturer listed tolerance levels of the volumetric flasks and pipettes specified for use in Section 3.4, from repeatability tests of the syringe, and the manufacturer reported purity of 99.9% for 2-butanone
analytical recovery (u_{ar})	0.10	$u_{ar} = CV_{RA}/\sqrt{n}$, where $CV_{RA} = 0.57\%$ and, $n = 30$, see Section 6, assumes results are corrected for analytical recovery
stability of prepared samples (u_{ps})	2.2	$u_{ps} = \Delta_{ps}/\sqrt{3}$, where $\Delta_{ps} = 3.8\%$, see Section 6
method precision (u_{mp})	1.6	$u_{mp} = \sqrt{(CV_m)^2 + (1 - 1/n) \times (CV_{pl})^2}$, where $CV_m = 1.4\%$, $CV_{pl} = 0.90\%$, and $n = 6$, see Section 5
method bias (u_{mb})	3.1	$u_{mb} = \sqrt{(B_{mb}/\sqrt{3})^2 + (CV_{mb}/\sqrt{n})^2 + (u_{rc})^2}$, where $B_{mb} = 1.3\%$, $CV_{mb} = 1.5\%$, and $n = 30$, see Section 5; $u_{rc} = 3\%$, see Reference 3
effect of humidity (u_h)	1.2	$u_h = \Delta_h/\sqrt{3}$, where $\Delta_h = 2.1\%$, see Section 8
instrument response drift (u_{dr})	5.8	$u_{dr} = 10\%/\sqrt{3}$, assumes a maximum instrument response drift of $\pm 10\%$
analytical uncertainty (u_a)	7.2	

The combined percent relative standard uncertainty of the sampling and analysis procedure ($u = \sqrt{(u_s)^2 + (u_a)^2}$) was determined to be 8.0% for 8-hour TWA samples. The expanded uncertainty ($U = 2 \times u$) was determined to be 16% for 8-hour TWA samples.

References

- Hendricks, W. 2-Butanone & Hexone (OSHA Method 1004), 2000. United States Department of Labor, Occupational Safety & Health Administration website. www.osha.gov (accessed May 2024).
- Sampling and Analytical Methods, 2024. United States Department of Labor, Occupational Safety & Health Administration website. www.osha.gov (accessed May 2024).
- ISO/DIS 22065:2018, Workplace air - Procedures for measuring gases and vapours using pumped samplers - Requirements and test methods.

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Appendix C, Hexone (Methyl isobutyl ketone)

OSHA PEL:	100 ppm (410 mg/m ³) 8-Hour TWA, General Industry, Construction, Shipyard
Recommended sampling time and sampling rate:	180 min at 50 mL/min (9 L)
Limit of quantitation:	0.180 ppm (0.74 mg/m ³ , 8-Hour TWA)
Reporting limit:	0.87 ppm (3.6 mg/m ³ , 8-Hour TWA)
Uncertainty (<i>u</i>):	8.0%
Author:	Michael Simmons

1 Introduction

1.1 Previous Methods used by OSHA for Sampling and Analysis of Hexone (Methyl isobutyl ketone)

The specific analyte described in this appendix is hexone (methyl isobutyl ketone), CAS No. 108-10-1. The active sampling methodologies described in this appendix for hexone (methyl isobutyl ketone), replace OSHA's use of OSHA Method 1004.¹ That method requires the collection of samples using Anasorb CMS sorbent tubes with a sampling time and rate of 240 minutes at 50 mL/min, extraction using 99/1 (v/v) carbon disulfide/*N,N*-dimethylformamide, and analysis by gas chromatography (GC) using a flame ionization detector (FID).

1.2 Method Validation

The procedures used to develop the method validation data are described in *Sampling and Analytical Methods*.² Air concentrations listed in ppm are referenced to 25 °C and 760 Torr. The target concentration (*T_c*) for method evaluation was the OSHA 8-hour TWA PEL. The target mass (*T_m*) is the equivalent analyte mass per sample collected on a sampler at the *T_c* using the recommended sampling time and sampling rate.

Dynamically generated controlled test atmospheres were created in a walk-in hood. House air was regulated using a flow-temperature-humidity control system. A measured flow of liquid 2-butanone (methyl ethyl ketone) and hexone (methyl isobutyl ketone) was introduced with a syringe pump through a short length of uncoated fused silica capillary into a heated zone near the air flow entrance of the test atmosphere generator, where it was evaporated into a measured flow of dilution air from the flow-temperature-humidity control system. The resulting vapor and dilution air flowed into a mixing chamber, and then into a sampling chamber. Sampling was completed using sampling ports on the sampling chamber. Temperature and humidity measurements were obtained near the exit of the sampling chamber.

2 Limit of Detection, Limit of Quantitation, and Reporting Limit

The limit of detection (LOD) is the analyte mass introduced onto the chromatographic column that produces a response greater than 3.3x the standard error of estimate ($S_{y/x}$) divided by the slope of the linear regression equation. The linear regression equation is derived from analyses of three spiked samples at five evenly spaced levels, totaling fifteen spiked media samples. Sorbent tubes were spiked such that the highest mass loading produced a peak approximately 10 times greater than that of a sample blank at or near the chromatographic retention time of the analyte. The limit of quantitation (LOQ) is expressed as an air concentration that provides sufficient analyte mass per sample to produce a response greater than $10 \times S_{y/x}$ divided by the slope of the linear regression equation line described above. The spiked samplers and three sample blanks were analyzed with the recommended analytical parameters. The resulting data

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provided the $S_{y/x}$ and the slope values for LOD and LOQ determinations. Results obtained from these analyses are listed in Table C-1 and plotted in Figure C-1.

Table C-1. LOD and LOQ data for hexone (methyl isobutyl ketone).

µg/sample	0.00	2.08	4.15	6.23	8.31	10.4
	0.00	5.45×10^{-4}	1.54×10^{-3}	1.87×10^{-3}	2.45×10^{-3}	3.45×10^{-3}
area ratio	0.00	9.02×10^{-4}	1.09×10^{-3}	2.16×10^{-3}	2.45×10^{-3}	2.85×10^{-3}
	0.00	7.87×10^{-4}	1.37×10^{-3}	2.06×10^{-3}	2.32×10^{-3}	2.86×10^{-3}

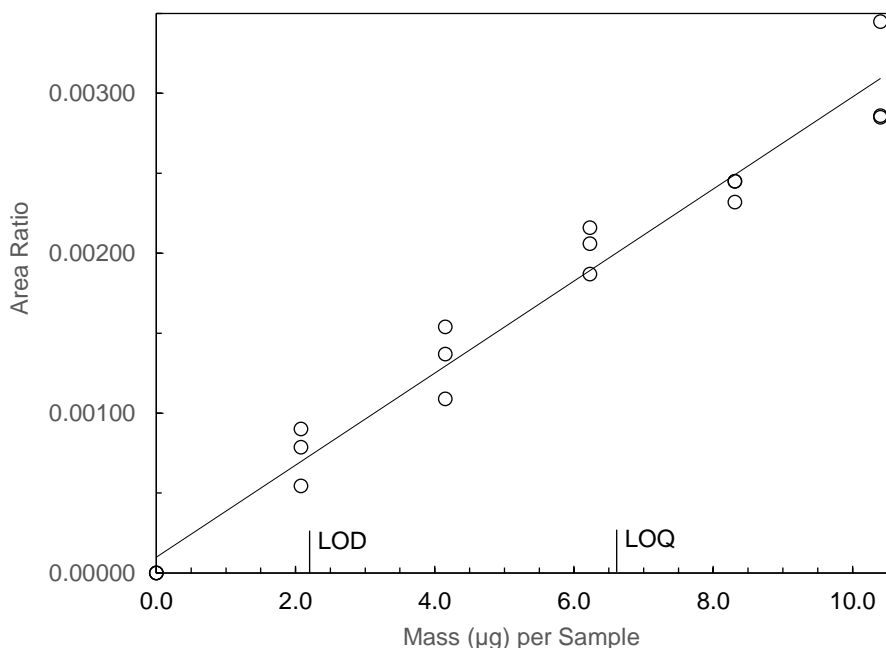


Figure C-1. Plot of data used to determine the LOD and LOQ for hexone (methyl isobutyl ketone) ($y = 2.88 \times 10^{-4}x + 9.92 \times 10^{-5}$, $S_{y/x} = 1.91 \times 10^{-4}$, LOD = 2.19 µg/sample, LOQ = 6.63 µg/sample or 0.180 ppm at the 8-hour TWA).

The reporting limit (RL) is expressed as an air concentration at the equivalent mass per sample at the lowest analytical calibration standard providing the recovery is within $\pm 25\%$. Six replicate sorbent tubes were liquid-spiked with 31.95 µg of hexone (methyl isobutyl ketone). After one hour of storage at ambient temperature the samples were analyzed using the analytical calibration procedure described in OSHA Method 5004. After analysis, results for hexone (methyl isobutyl ketone) as a percentage of expected recovery were 98.6%, 95.0%, 89.5%, 94.1%, 97.0%, and 94.0%. The mean percentage of expected recovery was 94.7%. The reporting limit is 0.867 ppm at the 8-hour TWA.

3 Analytical Calibration

Thirty analytical standards over a range of 0.0087 to 2.2 times the 8-hour TWA T_M were analyzed with the recommended analytical parameters described in OSHA Method 5004. Graphical and statistical examination of these data indicate the appropriate regression model and fitting technique were weighted-least-squares linear regression with a x^{-1} weighting factor. Results from these analyses are listed in Table C-2 and plotted with the selected regression model and fitting technique in Figure C-2. Five standards prepared over this range are used for analytical calibration as described in OSHA Method 5004.

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Table C-2. Analytical calibration data for hexone (methyl isobutyl ketone).

× 8-hour TWA T _M (µg/sample)	0.0087× (31.95)	0.17× (639.0)	0.43× (1598)	0.0.69× (2556)	0.95× (3515)	1.2× (4473)	1.5× (5432)	1.7× (6390)	2.0× (7349)	2.2× (7988)
area ratio	0.007705	0.1501	0.3759	0.6033	0.8284	1.403	1.265	1.483	1.710	1.850
	0.007829	0.1430	0.3687	0.6019	0.8182	1.037	1.249	1.501	1.712	1.876
	0.007759	0.1465	0.3720	0.6141	0.8242	1.051	1.276	1.501	1.692	1.879

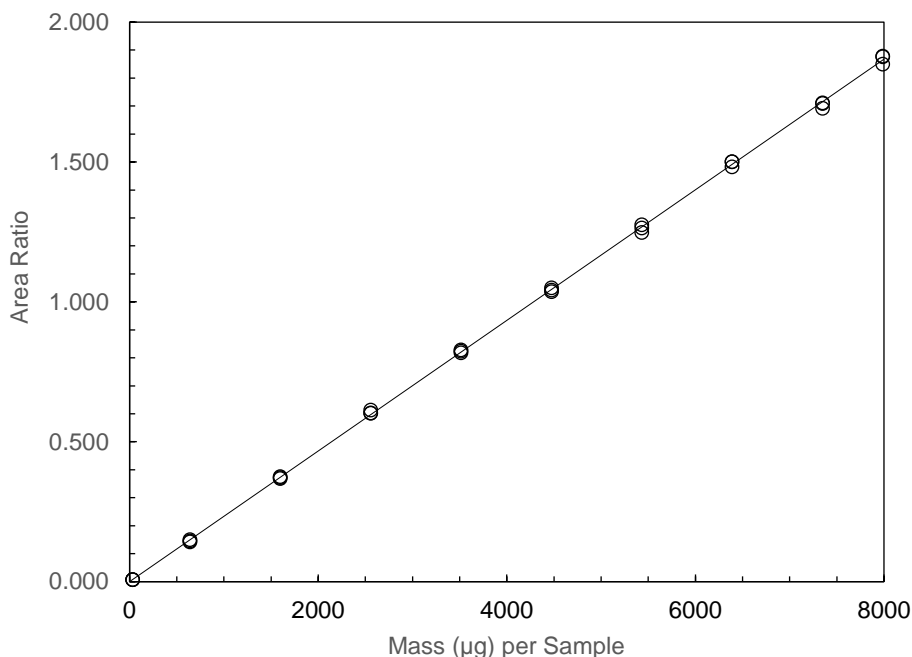


Figure C-2. Plot of data used to determine the analytical calibration procedure for hexone (methyl isobutyl ketone) ($y = 2.33 \times 10^{-4}x + 2.46 \times 10^{-4}, w_i = x^{-1}$).

4 Post Sampling Storage

The post sampling storage stability test samples for hexone (methyl isobutyl ketone) were prepared by sampling a dynamically generated controlled test atmosphere. Sampling from this system followed the recommended sampling parameters. The nominal concentration of hexone (methyl isobutyl ketone) for ambient storage 8-hour TWA testing was the target concentration (calculated to be 103 ppm). The relative humidity and temperature of the air sampled were 76% and 24 °C. Eighteen samples were prepared and three of these were analyzed on the day that samples were created. The remaining fifteen samples were stored on a bench-top at ambient temperature (about 22 °C). Three samples were selected and analyzed from those remaining at 3 to 4-day intervals. The results of these analyses (uncorrected for analytical recovery) are provided in Table C-3. The linear regression equation determined from these results was $y = 0.0225x + 102.2$.

The change in recovery (Δ_{ss}) of hexone (methyl isobutyl ketone) calculated from the regression line generated for the 17-day post sampling storage test was 0.38%.

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Table C-3. Ambient post sampling storage stability data for hexone (methyl isobutyl ketone).

time (days)	sample 1 (%)	sample 2 (%)	sample 3 (%)
0	100.3	105.7	105.7
3	101.5	101.5	101.4
7	100.2	101.4	102.2
10	100.7	102.0	100.8
14	101.9	103.4	105.0
17	100.0	103.9	105.7

5 Method Precision and Bias

The method precision and bias were determined by sampling dynamically generated controlled test atmospheres. Six samples were collected at each of five levels across a concentration range of 0.1 to 2 times the 8-Hour TWA T_c at 50 mL/min for 180 min. Samples collected at each level were analyzed immediately after collection and independently from the other levels, including use of freshly prepared calibration standards. The results of these analyses are provided in Table C-4, along with the concentration, temperature, and relative humidity of each test atmosphere. The percent coefficient of variation of the means of the five levels tested (CV_m) was 1.5%, and the pooled coefficient of variation of each of the five levels tested (CV_{pl}) was 0.93%. The resulting 8-hour TWA method precision (u_{mp}) for hexone (methyl isobutyl ketone) was determined to be 1.7%. The mean recovery of the thirty samples was 98.0%, resulting in a method bias (B_{mp}) of 2.0% and a coefficient of variation (CV_{mb}) of 1.6%.

Table C-4. Method precision data for hexone (methyl isobutyl ketone).

concn (ppm)	temp (°C)	RH (%)	sample 1 (%)	sample 2 (%)	sample 3 (%)	sample 4 (%)	sample 5 (%)	sample 6 (%)	mean (%)
10.2	24	76	97.5	99.2	99.3	99.3	100.8	100.6	99.5
52.0	24	76	99.2	99.1	99.2	99.4	99.4	100.6	99.5
103	24	75	95.1	96.6	96.0	97.0	96.8	98.1	96.6
156	24	77	96.6	96.9	97.4	98.5	98.1	99.1	97.8
208	24	76	95.4	96.6	97.6	96.4	96.2	96.7	96.5

6 Analytical Recovery and Stability of Prepared Samples

Analytical recovery is affected by the extraction solvent, the ISTD, the sampling medium, and the technique used to extract samples. The data presented demonstrate validity for the extraction solvent, ISTD, sampling medium, and extraction technique described in OSHA Method 5004. If other combinations of these are to be used, testing must be completed to satisfy the requirements found in current OSHA sampling and analysis method validation guidelines. Acceptable testing results must be documented.

The analytical recovery (R_A) was determined by liquid-spiking six replicate sorbent tubes across a range of analyte mass values that would be obtained from sampling at 0.1 to 2 times the 8-Hour TWA T_c for 180 min. Samples were analyzed following one hour of storage at ambient temperature. The R_A was 103.5%. The percent coefficient of variation of the thirty spiked samples (CV_{R_A}) was 0.55%. The data are shown in Table C-5.

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Table C-5. Analytical recovery data for hexone (methyl isobutyl ketone).

x 8-hour TWA T_M	μg per sample	sample 1 (%)	sample 2 (%)	sample 3 (%)	sample 4 (%)	sample 5 (%)	sample 6 (%)	mean (%)
0.1x	351.5	103.7	103.6	103.9	103.0	103.7	103.1	103.5
0.5x	1757	104.8	102.9	104.0	103.5	103.3	104.0	103.8
1.0x	3515	103.0	102.2	103.6	103.5	103.2	102.8	103.0
1.5x	5432	103.9	104.5	102.8	103.3	104.2	103.9	103.8
2.0x	7029	103.8	102.8	103.6	102.7	103.2	103.0	103.2

The stability of sample extracts was determined by liquid-spiking six replicate sorbent tubes with a mass of analyte that would be obtained from sampling at the 8-Hour TWA T_C for 180 min (calculated to be 3515 μg). Samples were analyzed following one hour of storage at ambient temperature. All six vials were re-analyzed at 24, 48, and 72 hours after the initial analyses, with all vials remaining in the autosampler tray kept at 22 °C. Freshly prepared standards were used for each analysis event, and each sample septum was punctured four times for each injection. The results of these analyses are provided in Table C-6. The linear regression equation determined from these results was $y = -1.64x + 104.9$.

The change in recovery (Δ_{ps}) of hexone (methyl isobutyl ketone) calculated from the regression line generated for the 3-day storage test was 4.9%. The Δ_{ps} of hexone (methyl isobutyl ketone) calculated from the regression line, with sample vials recapped within two days of the initial analysis as described in Method 5004, was 3.3%.

Table C-6. Stability of prepared sample data for hexone (methyl isobutyl ketone).

day	sample 1 (%)	sample 2 (%)	sample 3 (%)	sample 4 (%)	sample 5 (%)	sample 6 (%)
0	104.4	102.0	105.3	103.9	104.9	103.2
1	104.9	104.0	107.0	103.5	106.2	104.7
2	100.3	99.7	101.2	99.6	102.2	100.9
3	100.5	99.2	101.3	98.5	100.5	99.7

7 Sampler Capacity

The sampling capacity of a single 600 mg sorbent tube was tested by sampling a dynamically generated controlled test atmosphere containing hexone (methyl isobutyl ketone) nominally at two times the 8-hour TWA T_C (calculated to be 206 ppm). The relative humidity and temperature of the air sampled were 72% and 23 °C, and the sampling flow rate was 50 mL/min. A sorbent tube testing system was made by placing two sampling tubes in series. The rear tube was changed at 225, 240, 245, 255, 260, and 265 minutes. No breakthrough in any of three replicate samples was observed after sampling for 265 minutes (corresponding to 13.2 liters). Data from three sorbent tube testing systems were used to determine a recommended sampling volume of 9 liters for hexone (methyl isobutyl ketone). These results provide a recommended sampling time of 180 min as described in OSHA Method 5004.

8 Effect of Humidity

The effect of humidity was tested by sampling a dynamically generated controlled test atmosphere containing hexone (methyl isobutyl ketone) nominally at two times the target concentration (calculated to be 205 ppm). The relative humidity and temperature of the air sampled were 20% and 24 °C, and the sampling flow rate was 50 mL/min. Samples were collected on six sorbent tubes for 180 min. After immediate analysis, results for hexone (methyl isobutyl ketone) as a percentage of expected recovery using dry air were 94.7%, 91.2%, 92.9%, 93.0%, 96.8%, 97.1%. The mean percentage of expected recovery was 94.3%. The effect of humidity (Δ_h), calculated as the absolute difference between

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the mean low humidity recovery and the mean humid recovery taken from the 208-ppm method precision test described in Section 5 was 2.2%.

9 Sampling and Analytical Interferents

Confirm the presence of hexone (methyl isobutyl ketone) when the OSHA PEL value has been exceeded as described in Section 3.8 of OSHA Method 5004.

10 Analytical Reproducibility

Analytical reproducibility samples were prepared by sampling a dynamically generated controlled test atmosphere containing hexone (methyl isobutyl ketone) nominally at the target concentration (calculated to be 103.3 ppm). The relative humidity and temperature of the air sampled were 73% and 24 °C, and the sampling flow rate was 50 mL/min. Samples were collected on six sorbent tubes for 180 min. The resulting samples were submitted to the OSHA Technical Center for analysis using the procedures described in OSHA Method 1025 after storage for 13 days at -2 °C. The analytical results corrected for R_A are provided in Table C-7. No sample result for hexone (methyl isobutyl ketone) fell outside the permissible bounds set by the expanded uncertainty determined in Section 11.

Table C-7. Reproducibility data for hexone (methyl isobutyl ketone).

sampled ($\mu\text{g}/\text{sample}$)	recovered ($\mu\text{g}/\text{sample}$)	recovery (%)	deviation (%)
3874	3675	94.9	-5.1
3780	3673	97.2	-2.8
3861	3756	97.3	-2.7
3829	3874	101.2	+1.2
3797	3786	99.7	-0.3
3762	3770	100.2	+0.2

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11 Estimation of Uncertainty

Sampling and storage percent relative standard uncertainty components for hexone (methyl isobutyl ketone) are provided in Table C-8. The sampling and storage percent relative uncertainty (u_s) was determined to be 3.6% for 8-hour TWA sampling.

Table C-8. Sampling and storage uncertainty.

uncertainty component	8-hour TWA (%)	notes
flow rate measurement (u_{fr})	0.14	$u_{fr} = CV_{fr}/\sqrt{n}$, calculated from three replicate flow measurements using the flow meter with a representative sampler inline (49.36, 49.33, and 49.14 mL/min)
flow rate calibration (u_{fc})	0.58	$u_{fc} = 1\%/\sqrt{3}$, assumes a maximum flow meter calibration tolerance of $\pm 1\%$ at 50 mL/min
pump flow stability (u_{fs})	3.5	$u_{fs} = 6\%/\sqrt{3}$, assumes flow rate is maintained to within $\pm 6\%$ at 50 mL/min
sampling time (u_{st})	0.23	$u_{st} = [(B_{st} \times t_{st}^{-1})/\sqrt{6}] \times 100\%$, time sampled to nearest minute, where $B_{st} = 1$ min and $t_{st} = 180$ minutes sampled
sampling efficiency (u_{se})	0.00	Sampler capacity not exceeded at recommended sampling time and rate, see Section 7
post sampling storage (u_{ss})	0.22	$u_{ss} = \Delta_{ss}/\sqrt{3}$, where $\Delta_{ss} = 0.38\%$, see Section 4
sampling and storage uncertainty (u_s)	3.6	

Analytical percent relative standard uncertainty components for hexone (methyl isobutyl ketone) are provided in Table C-9. The analytical percent relative uncertainty (u_a) was determined to be 7.2% for 8-hour TWA sampling.

Table C-9. Analytical uncertainty.

uncertainty component	8-hour TWA (%)	notes
calibration standards (u_{cs})	0.56	Calculated from the manufacturer listed tolerance levels of the volumetric flasks and pipettes specified for use in Section 3.4, from repeatability tests of the syringe, and the manufacturer reported purity of 99.72% for hexone
analytical recovery (u_{ar})	0.10	$u_{ar} = CV_{RA}/\sqrt{n}$, where $CV_{RA} = 0.55\%$ and $n = 30$, see Section 6, assumes results are corrected for analytical recovery
stability of prepared samples (u_{ps})	1.9	$u_{ps} = \Delta_{ps}/\sqrt{3}$, where $\Delta_{ps} = 3.3\%$, see Section 6

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uncertainty component	8-hour TWA (%)	notes
method precision (u_{mp})	1.7	$u_{mp} = \sqrt{(CV_m)^2 + (1 - 1/n) \times (CV_{pl})^2}$, where $CV_m = 1.5\%$, $CV_{pl} = 0.93\%$, and $n = 6$, see Section 5
method bias (u_{mb})	3.2	$u_{mb} = \sqrt{(B_{mb}/\sqrt{3})^2 + (CV_{mb}/\sqrt{n})^2 + (u_{rc})^2}$, where $B_{mb} = 2.0\%$, $CV_{mb} = 1.6\%$, and $n = 30$, see Section 5; $u_{rc} = 3\%$, see Reference 3
effect of humidity (u_h)	1.3	$u_h = \Delta_h/\sqrt{3}$, where $\Delta_h = 2.2\%$, see Section 8
instrument response drift (u_{dr})	5.8	$u_{dr} = 10\%/\sqrt{3}$, assumes a maximum instrument response drift of $\pm 10\%$
analytical uncertainty (u_a)	7.2	

The combined percent relative standard uncertainty of the sampling and analysis procedure ($u = \sqrt{(u_s)^2 + (u_a)^2}$) was determined to be 8.0% for 8-hour TWA samples. The expanded uncertainty ($U = 2 \times u$) was determined to be 16% for 8-hour TWA samples.

12 References

- Hendricks, W. 2-Butanone & Hexone (OSHA Method 1004), 2000. United States Department of Labor, Occupational Safety & Health Administration website. www.osha.gov (accessed May 2024).
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