

Hydrogen Peroxide



Method number:	1019
Version:	1.0
Target concentration:	1.0 ppm (1.4 mg/m ³)
OSHA PEL:	1.0 ppm (1.4 mg/m ³)
ACGIH TLV:	1.0 ppm (1.4 mg/m ³) vapor or mist
Procedure:	Samples are collected by drawing workplace air through two 25-mm quartz filters, coated with titanium oxysulfate, using personal sampling pumps. Samples are extracted with 10 mL of 1 M H ₂ SO ₄ and analyzed by spectrophotometry.
Recommended sampling time and sampling rate:	
TWA:	240 min at 1 L/min (240 L) 120 min at 2 L/min (240 L) for vapor and mist
short term:	15 min at 2 L/min (30 L)
Reliable quantitation limit:	
TWA:	36.6 ppb (50.8 µg/m ³)
short-term:	292 ppb (407 µg/m ³)
Standard error of estimate at the target concentration:	5.8%
Special requirements:	Samples should be protected from light during shipping and storage. Other chemicals used in the area sampled should be reported to the laboratory and the potential impact on analysis should be considered.
Status of method:	Fully validated method. This method has been subjected to the established evaluation procedures of the Methods Development Team.

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1. General Discussion

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

1.1 Background

1.1.1 History

In 1977 OSHA issued Method VI-6 for the sampling and analysis of hydrogen peroxide.¹ When using Method VI-6 samples are collected with a midjet fritted glass bubbler containing a titanium oxysulfate collection solution and analyzed by spectrophotometry. OSHA next issued ID-126-SG, with samples collected using a midjet fritted glass bubbler containing a titanium oxysulfate collection solution and analyzed by differential pulse polarography.²

In 2000, Christensen et al. demonstrated the use of glass fiber filters impregnated with titanium tetrachloride, with analysis by spectrophotometry, for the sampling of hydrogen peroxide.³ Hecht et al. then modified the sampler using quartz filters soaked with a solution of titanium oxysulfate in sulfuric acid.⁴ Quartz filters coated with titanium oxysulfate are now commercially available and are validated in this method as a replacement to the fritted glass bubbler method.

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)

“Inhalation of high concentrations of the vapor or the mist of hydrogen peroxide has caused extreme irritation and inflammation of the nose and throat. Severe systemic poisoning has also caused headache, dizziness, vomiting, diarrhea, tremors, numbness, convulsions, pulmonary edema, unconsciousness and shock.”⁵

1.1.3 Workplace exposure

Hydrogen peroxide is used in “the bleaching or deodorizing of textiles, wood pulp, hair, fur, and foods; in the treatment of water and sewage; as a disinfectant; as a component of rocket fuels; and in the manufacture of many chemicals and chemical products.”⁶ In 2000 the estimated U.S. production of hydrogen peroxide was 7×10^5 tons.⁷

¹ Hydrogen Peroxide (OSHA Method VI-6), 1977. United States Department of Labor, Occupational Safety and Health Administration Web site. http://www.osha.gov/dts/sltc/methods/inorganic/id006/hydrogen_peroxide.html (accessed May 2015).

² Hydrogen Peroxide (OSHA Method ID-126-SG). United States Department of Labor, Occupational Safety and Health Administration Web site. <http://www.osha.gov/dts/sltc/methods/partial/t-id126sg-pv-01-0201-m/t-id126sg-pv-01-0201-m.html> (accessed May 2015).

³ Christensen, C. S.; Brødsgaard, S.; Mortensen, P.; Egmos, K.; Linde, S. A. Determination of hydrogen peroxide in workplace air: interferences and method validation. *J. Environ. Monit.*, **2000**, *2*, pp 339-343.

⁴ Hecht, G.; Héry, M.; Hubert, G.; Subra, I. Simultaneous Sampling of Peroxyacetic Acid and Hydrogen Peroxide in Workplace Atmospheres. *Ann. occup Hyg.*, **2004**, *8*, pp 715-721.

⁵ American Conference of Governmental Industrial Hygienists, Inc. *Documentation of the Threshold Limit Values and Biological Exposure Indices*, 7th ed.; Cincinnati, OH, 2001; Vol. 2, pp. Hydrogen Peroxide – 1 through Hydrogen Peroxide – 2.

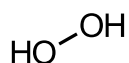
⁶ American Conference of Governmental Industrial Hygienists, Inc. *Documentation of the Threshold Limit Values and Biological Exposure Indices*, 7th ed.; Cincinnati, OH, 2001; Vol. 2, pp. Hydrogen Peroxide – 1 through Hydrogen Peroxide – 2.

⁷ Kirk-Othmer *Encyclopedia of Chemical Technology*, 4th ed.; Kroschwitz, J. I., Ex. Ed.; John Wiley & Sons, Inc.: New York, 1993; Vol. 13, pp 981.

1.1.4 Physical properties and other descriptive information⁸

synonyms:	dihydrogen dioxide
IMIS ⁹ :	1470
CAS number:	7722-84-1
boiling point:	152 °C
melting point:	-0.43 °C
specific gravity:	1.463 at 0 °C
molecular weight:	34.01
appearance:	colorless liquid
solubility:	miscible with water
vapor pressure:	5 torr at 30 °C
molecular formula:	H ₂ O ₂

structural formula:



2. Sampling Procedure

All safety practices that apply to the work area being sampled should be followed. The sampling equipment should be attached to the worker in such a manner that it will not interfere with work performance or safety.

2.1 Apparatus

Samples are collected with two 25-mm quartz filters coated with titanium oxysulfate hydrate and preloaded into a 2-piece polystyrene cassettes. For this evaluation, commercially prepared samplers were obtained from SKC, Inc. (catalog no. 225-9030). SKC, Inc. also supplies a 5.5 x 5.5 inch sheet of aluminum foil with each sampler to protect the sample from light.

Samples are collected using a personal sampling pump calibrated to within ±5% of the recommended flow rate with the sampling device in-line.

2.2 Reagents

None required

2.3 Technique

Remove the plastic end plugs from the filter cassette immediately before sampling.

Attach the cassette to the sampling pump so that it is in an approximately vertical position with the inlet facing down during sampling. Position the sampling pump, cassette, and tubing so it does not impede work performance or safety.

Draw the air to be sampled directly into the inlet of the cassette. The air being sampled is not to be passed through any hose or tubing before entering the cassette.

⁸ American Conference of Governmental Industrial Hygienists, Inc. *Documentation of the Threshold Limit Values and Biological Exposure Indices*, 7th ed.; Cincinnati, OH, 2001; Vol. 2, pp. Hydrogen Peroxide – 1 through Hydrogen Peroxide – 2.

⁹ Hydrogen Peroxide (Chemical Sampling Information). United States Department of Labor, Occupational Safety and Health Administration Web site. http://www.osha.gov/dts/chemicalsampling/data/CH_246600.html (accessed May 2015).

Sample for up to 240 min at 1 L/min (240 L) to collect TWA (long term) samples.

Sample for up to 120 min at 2 L/min (240 L) to collect TWA vapor and mist (long term) samples.

Sample for 15 min at 2 L/min (30 L) to collect short term samples.

After sampling for the appropriate time, remove the sample and seal the cassette with plastic end plugs. Wrap each sample with aluminum foil and seal 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 (L/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 a delay is unavoidable, store the samples in a refrigerator as a precaution.

3. Analytical Procedure

3.1 Apparatus

Spectrophotometer. A PerkinElmer Lambda EZ210 UV/Vis Spectrophotometer was used in this validation.

Disposable cuvettes. BRAND GMBH + CO KG UV-Cuvette semi-micro cuvettes were used in this validation (catalog no. 7591 50).

Cuvette caps. Globe Scientific Inc. square plug caps were used in this validation (catalog no. 111167).

Water purifier. A Barnstead NANOpure Diamond system was used to produce 18.0 MΩ-cm DI water in this validation.

Filters and syringes for the filtration of sample solutions prior to analysis. Pall Corporation IC Acrodisc® 25 mm Syringe Filters with 0.45 µm Supor® (PES) Membranes were used in this validation (catalog no. AP-4585).

A means to dispense and dilute solutions. A Hamilton Microlab 600 Series dual syringe diluter/dispenser was used in this validation.

A mechanical shaker. An Eberbach mechanical shaker was used in this evaluation.

Class A 10-mL, 50-mL, and 500-mL volumetric flasks.

Watch glass and 100-mL glass beaker.

Hot plate. A Corning PC-351 hot plate was used in this evaluation.

Sample preparation vials. Kimble 20-mL glass screw-thread scintillation vials were used in this validation (catalog no. 74505-20).

Scintillation vial racks. Polypropylene Scienceware scintillation racks were used in this evaluation.

Analytical balance capable of weighing at least 0.01 mg. A Mettler Toledo XP205 DeltaRange analytical balance was used in this evaluation.

3.2 Reagents

Hydrogen peroxide (H_2O_2), [CAS no. 7722-84-1], for ultratrace analysis. The hydrogen peroxide solution used in this evaluation was $\geq 30\%$ TraceSELECT Ultra, for ultratrace analysis, purchased from Sigma Aldrich (product no. 16911, lot no. 05735JH). See Section 4.11 for more information.

Titanium(IV) oxysulfate (TiOSO_4), [CAS no. 13825-74-6]. The titanium(IV) oxysulfate used in this evaluation was $\geq 29\%$ Ti (as TiO_2) purchased from Sigma Aldrich (product no. 14023, lot no. SZBB2340).

Sulfuric acid (H_2SO_4), [CAS no. 7664-93-9]. The sulfuric acid used in this evaluation was Baker Instra-Analyzed Reagent for trace metal analysis (95.0 – 98.0%) purchased from J.T. Baker.

DI water, 18.0 M Ω -cm.

$\text{TiOSO}_4/\text{H}_2\text{SO}_4$ solution. Prepare by adding 3.5 g TiOSO_4 , 2.5 mL H_2SO_4 , and 40 mL DI water to a 100 mL beaker. Cover beaker with watch glass, place on a hot plate and heat at about 90 °C, swirling occasionally, until solution becomes clear. Remove from hot plate and allow solution to cool to room temperature. Transfer to a 50-mL volumetric flask, rinsing beaker with several milliliters of DI water, and dilute to mark. Solution can be stored in an air-tight container for 6 months.

Two molar H_2SO_4 solution. Prepare by adding 55 mL of H_2SO_4 to a 500-mL volumetric flask containing approximately 400 mL of DI water. Allow solution to cool to room temperature and dilute to mark.

3.3 Standard preparation

Immediately before preparing working standards prepare a stock standard by injecting 50 μL of an approximately 30% H_2O_2 solution into a 10-mL volumetric flask and diluting to mark with DI water. Use the density and concentration of the 30% H_2O_2 solution provided by the manufacturer. For example:

$$(50 \mu\text{L} \times 1.11 \text{ mg}/\mu\text{L} \times 0.308) / 10.0 \text{ mL} = 1.709 \text{ mg}/\text{mL} \text{ of } \text{H}_2\text{O}_2$$

[Density (1.11 mg/ μL) and concentration (30.8%) as reported by the manufacturer of the solution used in validation of method.]

Prepare working standards by injecting microliter amounts of the stock standard into a 10-mL volumetric containing 400 μL $\text{TiOSO}_4/\text{H}_2\text{SO}_4$ solution and 5 mL of 2 M H_2SO_4 . Dilute to the mark with water. For example, to prepare a target level standard of 333.3 $\mu\text{g}/\text{sample}$ H_2O_2 , inject 195 μL of the stock standard into a 10-mL volumetric flask containing 400 μL $\text{TiOSO}_4/\text{H}_2\text{SO}_4$ solution and 5 mL of 2 M H_2SO_4 then dilute to the mark with water. Prepare new working standards weekly and store in air-tight containers when not in use.

Transfer working standards to plastic disposable cuvettes and cap. Inspect the solution in each cuvette for air bubbles and gently tap cuvette if necessary to remove air bubbles.

Bracket sample concentrations with standard concentrations. If sample concentration falls outside the range of prepared working standards dilute with 50:50 2 M H_2SO_4 :DI water and reanalyze.

3.4 Sample preparation

Open cassette and carefully transfer the two 25-mm coated quartz filters into one clean 20-mL scintillation vial.

Add 5 mL of 2 M H₂SO₄, 5 mL of DI water, and cap tightly.

Place scintillation vials in a scintillation rack. Secure rack on a mechanical shaker and shake samples for 60 min.

Filter 3 mL of sample, transfer filtrate to a plastic disposable cuvette and cap cuvette. Inspect the sample in cuvette for air bubbles and gently tap cuvette if necessary to remove air bubbles.

Analyze as described in Section 3.5.

3.5 Analysis

3.5.1 Analytical conditions

Spectrophotometer conditions

measurement type:	photometry
data mode:	Abs
number of wavelengths:	1
wavelength:	410.0 nm
slit width:	2 nm
path length:	10.0 mm

3.5.2 A calibration curve can be constructed by plotting response of standards versus micrograms of analyte per sample. Bracket the samples with freshly prepared analytical standards over a range of concentrations.

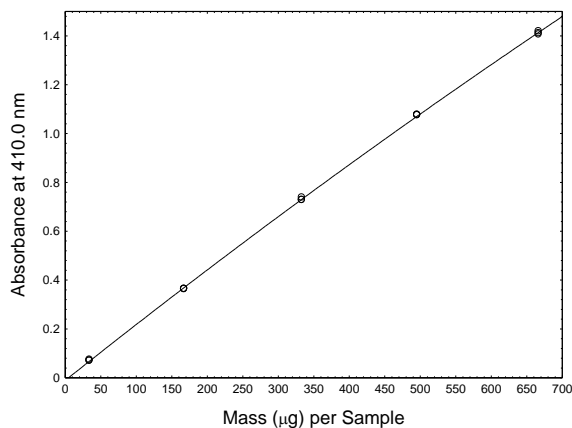


Figure 3.5.2. Calibration curve for H₂O₂ ($y = -2.66 \times 10^{-7}x^2 + 0.0023x - 0.0107$).

3.6 Interferences

Any compound with a response, or reacts with the titanium oxysulfate to produce a response, at 410 nm is a potential interferent. If any potential interferences were reported, they should be considered before samples are extracted.

3.7 Calculations

The amount of H₂O₂ per sample is obtained from the appropriate calibration curve in terms of micrograms per sample, uncorrected for extraction efficiency. This amount is then corrected by subtracting the total amount (if any) found on the blank. The air concentration is calculated using the following formulas.

$$C_M = \frac{M}{VE_E}$$

where C_M is concentration by weight (mg/m³)
 M is micrograms per sample
 V is liters of air sampled
 E_E is extraction efficiency in decimal form

$$C_V = \frac{V_M C_M}{M_r}$$

where C_V is concentration by volume (ppm)
 V_M is 24.46 (molar volume at NTP)
 C_M is concentration by weight (mg/m³)
 M_r is molecular weight of H₂O₂ (34.01 g/mol)

4. Method Validation

Where applicable, this method follows validation protocols drawing from the OSHA SLTC "Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis"¹⁰. These Guidelines detail required validation tests, show examples of statistical calculations, list validation acceptance criteria, and define analytical parameters. Air concentrations listed in ppm are referenced to 25 °C and 760 mmHg (101.3 kPa).

4.1 Detection limit of the analytical procedure (DLAP)

The DLAP is measured as concentration of the analyte detected by the spectrophotometer. Ten analytical standards were prepared with approximately equal descending increments of analyte with the highest standard containing 1.98 µg/mL. This is the concentration that would produce a response approximately 10 times the reagent blank. These standards and the reagent blank were analyzed with the recommended analytical parameters. The data obtained were used to determine the required parameters (standard error of estimate and slope) for the calculation of the DLAP. Values of 0.0196 and 0.0016 were obtained for the slope and standard error of estimate respectively. The DLAP was calculated to be 0.24 µg/mL.

¹⁰ 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 2013).

Table 4.1
Detection Limit of the Analytical Procedure

concentration ($\mu\text{g/mL}$)	absorbance
0	0.004
0.137	0.006
0.342	0.012
0.547	0.013
0.752	0.015
0.957	0.022
1.16	0.024
1.37	0.030
1.57	0.034
1.78	0.040
1.98	0.042

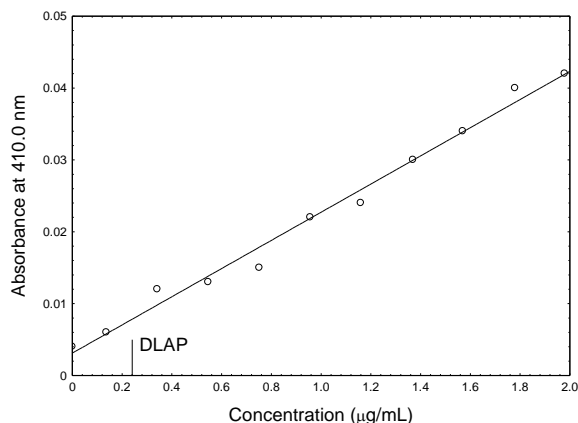


Figure 4.1. Plot of data to determine the DLAP ($y = 0.0196x + 0.0031$).

4.2 Detection limit of the overall procedure (DLOP) and reliable quantitation limit (RQL)

The DLOP is measured as mass per sample and expressed as equivalent air concentrations based on the recommended sampling parameters. Ten samplers were spiked with approximately equal descending increments of analyte, such that the highest sampler loading was $19.8 \mu\text{g/sample}$. This is the amount spiked on a sampler that would produce a response approximately 10 times the response of a sample blank. These spiked samplers and the sample blank were analyzed with the recommended analytical parameters, and the data obtained used to calculate the required parameters (standard error of estimate and the slope) for the calculation of the DLOP. Values of 0.0020 and 0.0024 were obtained for the slope and standard error of estimate respectively. The DLOP was calculated to be $3.6 \mu\text{g/sample}$ (10.8 ppb or $15.0 \mu\text{g/m}^3$ at 240 L).

Table 4.2
Detection Limit of the Overall Procedure

mass per sample (μg)	absorbance
0	0.008
1.37	0.008
3.42	0.012
5.47	0.024
7.52	0.021
9.57	0.028
11.6	0.030
13.7	0.033
15.7	0.038
17.8	0.044
19.8	0.046

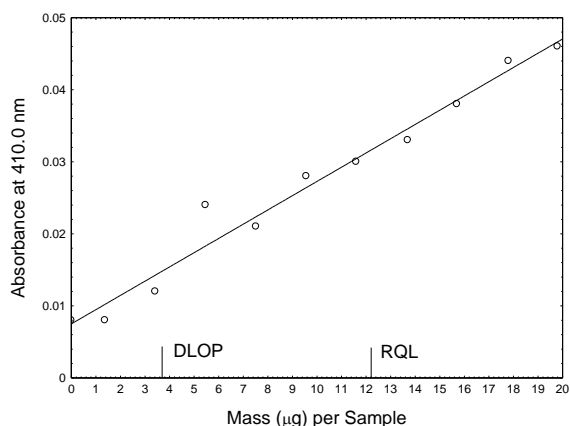


Figure 4.2. Plot of data to determine the DLOP/RQL ($y = 0.0020x + 0.0075$).

The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line parameters that were obtained for the calculation of DLOP providing 75% to 125% of the analyte is recovered. The RQL is $12.2 \mu\text{g/sample}$ (36.6 ppb or $50.8 \mu\text{g/m}^3$). Recovery at this concentration is 97.0%.

When short term samples are collected, the air concentration equivalent to the reliable quantitation limit becomes larger. For example, the reliable quantitation limit is 292 ppb (407 $\mu\text{g}/\text{m}^3$) for H_2O_2 when 30 L is sampled.

4.3 Precision of the analytical method

The precision of the analytical method was measured as the mass equivalent to the standard error of estimate determined from the quadratic regression of data points from standards over a range that covers 0.1 to 2 times the target concentration. A calibration curve was constructed from three determinations of the five standards and is shown in Section 3.5.2. The standard error of estimate was 7.1 $\mu\text{g}/\text{sample}$.

Table 4.3
Instrument Calibration

xtarget concn ($\mu\text{g}/\text{sample}$)	0.1x	0.5x	1.0x	1.5x	2.0x
absorbance	0.074	0.364	0.738	1.077	1.411
	0.070	0.364	0.728	1.076	1.419
	0.070	0.363	0.728	1.075	1.406

4.4 Storage stability test

Storage samples for H_2O_2 were prepared by sampling a dynamically generated controlled test atmosphere using the recommended sampling parameters. The concentration of H_2O_2 in the test atmosphere was the target concentration (0.973 ppm or 1.35 mg/m^3), and the relative humidity was 80% at 22 °C. Eighteen storage samples were prepared. Three samples were analyzed on the day of generation. Fifteen samples were protected from light exposure and stored at ambient temperature (about 21 °C). At 3-5 day intervals three samples were selected and analyzed. Sample results are not corrected for extraction efficiency.

Table 4.4.1
High Humidity Ambient Storage Test for H_2O_2 with Samples Protected from Light

time (days)	storage recovery (%)		
0	99.1	101.7	103.6
3	99.6	101.0	92.4
8	98.3	98.6	97.9
11	99.8	98.5	101.1
15	102.0	100.1	94.7
18	101.1	95.5	103.4

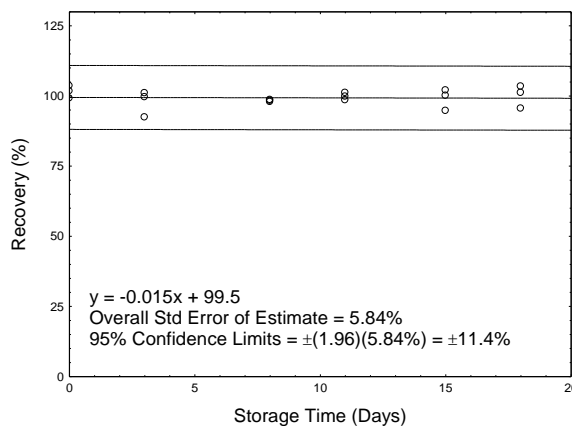


Figure 4.4.1. Ambient storage for H_2O_2 .

Low humidity and light exposed storage tests are not normally performed; however, Christensen et al. noted a 30% decrease in recoveries of H_2O_2 after 2 weeks of storage¹¹. No loss in recoveries was noted during the initial eighteen days storage test so additional storage tests were performed and described below.

¹¹ Christensen, C. S.; Brødsgaard, S.; Mortensen, P.; Egmose, K.; Linde, S. A. Determination of hydrogen peroxide in workplace air: interferences and method validation. *J. Environ. Monit.*, **2000**, 2, pp 339-343.

A low humidity storage test for H₂O₂ was performed by sampling a dynamically generated controlled test atmosphere using the recommended sampling parameters. The concentration of H₂O₂ in the test atmosphere was the target concentration (1.06 ppm or 1.48 mg/m³), and the relative humidity was 8.3% at 21 °C. Nine storage samples were prepared. Three samples were analyzed on the day of generation. Six samples were protected from light exposure and stored at ambient temperature (about 21 °C). At 7 day intervals three samples were selected and analyzed. Sample results are not corrected for extraction efficiency.

Table 4.4.2
Low Humidity Ambient Storage Test
for H₂O₂ with Samples Protected
from Light

time (days)	storage recovery (%)		
0	102.2	103.9	102.6
7	99.7	100.0	100.8
14	102.1	102.8	100.7

A low humidity test, with samplers exposed to light during storage, was performed by sampling a dynamically generated controlled test atmosphere using the recommended sampling parameters. The concentration of H₂O₂ in the test atmosphere was the target concentration (1.07 ppm or 1.49 mg/m³), and the relative humidity was 9.0% at 21 °C. Nine storage samples were prepared. Three samples were analyzed on the day of generation. Six samples were stored on a lab bench at ambient temperature (about 21 °C) with no protection from light exposure. At 7 day intervals three samples were selected and analyzed. Sample results are not corrected for extraction efficiency.

Table 4.4.3
Low Humidity Ambient Storage Test
for H₂O₂ with Samples Exposed to
Light (Bench Top Storage)

time (days)	storage recovery (%)		
0	104.5	105.1	104.6
7	96.3	95.6	95.2
14	94.9	95.4	94.1

A low humidity test, with samplers exposed to light during storage, was performed by sampling a dynamically generated controlled test atmosphere using the recommended sampling parameters. The concentration of H₂O₂ in the test atmosphere was the target concentration (1.05 ppm or 1.46 mg/m³), and the relative humidity was 9.6% at 21 °C. Nine storage samples were prepared. Three samples were analyzed on the day of generation. Six samples were stored in a drawer at ambient temperature (about 21 °C) but were not covered. At 7 day intervals three samples were selected and analyzed. Sample results are not corrected for extraction efficiency.

Table 4.4.4
Low Humidity Ambient Storage Test
for H₂O₂ with Samples Exposed to
Light (Drawer Storage)

time (days)	storage recovery (%)		
0	103.0	104.8	103.8
7	98.4	99.1	98.4
14	94.8	94.7	93.9

As shown above there is a reduction in recoveries when samples are exposed to light during storage, but when carefully protected the samples are stable. Based on these results it is recommended that samples be wrapped in aluminum foil after sampling. Sampling at low humidity did not affect storage stability.

4.5 Precision (overall procedure)

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). Ninety-five percent confidence intervals are drawn about the regression lines in the storage stability figure shown in Section 4.4.

The precision of the overall procedure at the 95% confidence level for the 18-day storage test (at the target concentration) is ±11.4%. It was obtained from the overall standard error of estimate (5.84%) of the data shown in Figure 4.4.1. It contains an additional 5% for sampling pump error.

The recovery of H₂O₂ from samples used in an 18-day storage test remained above 99.2% when stored at 21 °C and protected from light exposure.

4.6 Reproducibility

Six samples were prepared by sampling a dynamically generated controlled test atmosphere similar to that used in the collection of the storage samples. The concentration of H₂O₂ in the test atmosphere was the target concentration (0.996 ppm or 1.38 mg/m³), and the relative humidity was 79% at 22 °C. The samples were submitted to the OSHA Salt Lake Technical Center for analysis. The samples were analyzed after being stored for 30 days at 21 °C. No sample result for H₂O₂ had a deviation greater than the precision of the overall procedure determined in Section 4.5.

Table 4.6
Reproducibility Data for H₂O₂

theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
339	311	91.7	-8.3
325	302	92.9	-7.1
322	296	91.9	-8.1
326	304	93.3	-6.7
335	316	94.3	-5.7
326	307	94.2	-5.8

4.7 Sampler capacity

Sampler capacity was tested by sampling a dynamically generated controlled test atmosphere containing H₂O₂ at two times the target concentration (2.03 ppm or 2.83 mg/m³) and 80% relative humidity at 22 °C. The samples were collected at 1 L/min. A second sampler was placed in a sampling train behind the first sampler. The percentage of the amount found on the second sampler in relation to the concentration of the test atmosphere was defined as breakthrough. There was no significant (<5%) breakthrough observed after 538 min of testing. This is equivalent to an air volume of 538 L. The recommended air volume for sampling at 1 L/min is 240 L.

Sampler capacity was also tested by sampling a dynamically generated controlled test atmosphere containing H₂O₂ at two times the target concentration (2.11 ppm or 2.94 mg/m³) and 81% relative humidity at 21 °C. The samples were collected at 2 L/min. A second sampler was placed in a sampling train behind the first sampler. There was no significant (<5%) breakthrough observed after 330 min of testing. This is equivalent to an air volume of 660 L. The recommended air volume for sampling at 2 L/min is 240 L.

4.8 Extraction efficiency and stability of extracted samples

The extraction efficiency is affected by the extraction solution, the sampling medium, and the technique used to extract the samples. Other reagents and techniques than described in this method can be used provided they are tested as specified in the validation guidelines.¹²

Extraction efficiency

The extraction efficiency was determined by liquid-spiking four samplers at each concentration level with H₂O₂. These samples were stored overnight at ambient temperature and then analyzed. The overall mean extraction efficiency, over the working range of 0.1 to 2 times the target concentration, was 99.3%. The extraction efficiency at the RQL was 99.8%. The presence of water had no significant effect on extraction efficiency. The extraction efficiencies

¹² 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 2013).

for the RQL and the wet samplers are not included in the overall mean. Wet media were prepared by sampling humid air (80% relative humidity at 21 °C) for 240 min at 1 L/min. The data obtained are shown in Table 4.8.1.

Table 4.8.1
Extraction Efficiency of H₂O₂

x target concn	level	µg per sample	sample number				mean
			1	2	3	4	
0.1		34.2	101.3	103.9	101.4	100.0	101.6
0.25		85.5	99.5	98.4	102.1	100.5	100.1
0.5		170.9	97.9	97.9	98.4	98.9	98.3
1.0		341.9	98.0	98.3	98.0	98.8	98.3
1.5		512.8	99.3	98.8	98.4	99.4	99.0
2.0		683.8	97.5	98.6	97.3	99.2	98.2
RQL		12.3	101.8	101.8	99.1	96.4	99.8
1.0 (wet)		341.9	98.5	97.9	98.3	98.3	98.3

Stability of extracted samples

The stability of extracted samples was investigated by reanalyzing dry target concentration samples at 1 and again at 7 days after the initial analysis. These samples were stored in capped cuvettes at ambient temperature and fresh analytical standards were prepared and used each day. Results are presented as percent of the original analysis.

Table 4.8.2
Stability of Digested Samples at Target Concentration

storage (days)	recovery (%)				mean
	1	2	3	4	
1	101.3	101.0	101.2	101.2	101.2
7	103.9	106.6	103.6	104.7	104.7

4.9 Sampling interferences

Retention

Retention was tested by sampling a dynamically generated controlled test atmosphere containing two times the target concentration (2.00 ppm or 2.78 mg/m³) of H₂O₂ at 80% relative humidity and 22 °C. The test atmosphere was sampled with six samplers at 1 L/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 samples and contaminant-free air at 80% relative humidity and 22 °C at 1 L/min for 180 min. All six samplers were analyzed and the data obtained are shown in Table 4.9.

Table 4.9.1
Retention of H₂O₂

set	recovery (%)			mean
	1	2	3	
first	108.0	102.7	102.9	104.5
second	102.0	101.9	103.0	102.3
second/first				97.9

Low humidity

The effect of low humidity was tested by sampling a dynamically generated controlled test atmosphere containing two times the target concentration (2.10 ppm or 2.92 mg/m³) of H₂O₂ at 18% relative humidity and 22 °C. The test atmosphere was sampled with three samplers at 1 L/min for 240 min. All of the samples were immediately analyzed. Sample results were 99.0%, 99.2%, and 100.1% of theoretical.

Low concentration

The effect of low concentration was tested by sampling a dynamically generated controlled test atmosphere containing 0.1 times the target concentration (0.0993 ppm or 0.138 mg/m³) of H₂O₂ at 79% relative humidity and 22 °C. The test atmosphere was sampled with three samplers at 1 L/min for 240 min. All of the samples were immediately analyzed. Sample results were 99.3%, 101.0%, and 102.7% of theoretical.

Chemical interference

The effect of a potential chemical sampling interference was tested by sampling dynamically generated controlled test atmospheres containing H₂O₂ and peracetic acid (PAA). The PAA solution

Table 4.9.2
Interference of PAA on H₂O₂

PAA / H ₂ O ₂ test atmosphere concn	recovery of H ₂ O ₂ (%)			mean
	1	2	3	
1.03 ppm PAA, 0.29 ppm H ₂ O ₂	105.0	101.9	101.7	102.9
1.95 ppm PAA, 0.54 ppm H ₂ O ₂	110.7	110.6	109.7	110.3
3.93 ppm PAA, 1.10 ppm H ₂ O ₂	128.9	127.7	125.7	127.4

used to generate the test atmospheres was a 39.2% PAA solution (with 4.9% H₂O₂, 42.3% acetic acid, and water) purchased from Sigma Aldrich (product no. 77240). The H₂O₂ of this solution was titrated and the concentration verified. The PAA solution was injected directly into the test atmosphere without dilution to avoid changing the equilibrium concentration of the solution. Three test atmospheres were generated, each with a temperature of 21 °C at 9% relative humidity, and sampled with three samples at 1 L/min for 240 min. All samples were immediately analyzed and the data obtained are shown in Table 4.9.2. Results show that above an air concentration of 2 ppm PAA the interference becomes significant. At levels less than 1 ppm PAA, and at the ACGIH TLV-STEL of 0.4 ppm¹³, the interference is not significant.

Potassium permanganate and potassium iodide can interfere with the analysis of H₂O₂.¹⁴ See Christensen et al. for other potential interferences tested when sampling H₂O₂ with glass filters impregnated with titanium tetrachloride / sulfuric acid.¹⁵

4.10 Short-term sampling

Short-term sampling was tested by sampling a dynamically generated controlled test atmosphere containing H₂O₂ at the target concentration (1.00 ppm or 1.40 mg/m³) and 80% relative humidity at 21 °C. The test atmosphere was sampled with three samplers at 2 L/min for 15 min. All of the samples were immediately analyzed. Sample results were 104%, 103%, and 108% of theoretical.

¹³ American Conference of Governmental Industrial Hygienists, Inc. *Documentation of the Threshold Limit Values and Biological Exposure Indices*; Cincinnati, OH, 2015; pp. Peracetic Acid – 1 through Peracetic Acid – 5.

¹⁴ Hydrogen Peroxide (OSHA Method ID-126-SG). United States Department of Labor, Occupational Safety and Health Administration Web site. <http://www.osha.gov/dts/sltc/methods/partial/t-id126sg-pv-01-0201-m/t-id126sg-pv-01-0201-m.html> (accessed May 2015).

¹⁵ Christensen, C. S.; Brødsgaard, S.; Mortensen, P.; Egmose, K.; Linde, S. A. Determination of hydrogen peroxide in workplace air: interferences and method validation. *J. Environ. Monit.*, **2000**, 2, pp 339-343.

4.11 Hydrogen peroxide standard

The H₂O₂ solution used in this evaluation was:

≥30% TraceSELECT Ultra, for ultratrace analysis, purchased from Sigma Aldrich (product no. 16911, lot no. 05735JH).

The solution was received at SLTC on 4/4/2014. The manufacturer certificate of analysis reported a quality release data of 8/12/2013, a recommended retest date of 1/2017, and a certified concentration of 30.8%. The manufacturer recommended storage of the solution at 2-8 °C in the dark. During use of this solution it was periodically titrated using a standardized potassium permanganate solution (1 N) and the results are shown in Table 4.11.

Table 4.11
Titration Results of H₂O₂ solution Used in this Evaluation

test data	titration result (%)	vs manufacturer (%)
4/23/2014	31.5	102.3
5/1/2014	31.2	101.3
9/3/2014	31.5	102.3
11/19/2014	31.3	101.6
3/11/2015	31.6	102.6

Based on these results the concentration listed on the certificate of analysis can be used, and periodic standardization of the solution is not necessary if stored as specified by the manufacturer.

4.12 Cassette wall test

To test the need for an interior wall wipe six cassettes were spiked with 333.3 µg H₂O₂ (25 µL of a 13.33 mg/mL H₂O₂ solution). For three samples the spike was deposited directly on the titanium oxysulfate coated quartz filter and for the other three the spike was placed on the top (inlet side) of the interior wall. The cassettes were reassembled and stored inlet side down overnight. All six samples were analyzed, without wiping the cassette wall, and the data obtained are shown in Table 4.12. Results demonstrate that the H₂O₂ had evaporated off the cassette wall and reacted with the titanium oxysulfate coated quartz filter. Wiping of the interior walls is not necessary.

Table 4.12
Recovery of H₂O₂ from Spiked Cassette Walls

set	recovery (%)			mean
	1	2	3	
wall spike	94.8	94.2	94.7	94.6
filter spike	96.9	96.7	97.0	96.9
wall/filter				97.7

4.13 Generation of test atmospheres

A test atmosphere generator, as diagramed in Figure 4.13, was set up in a walk-in hood. House air was regulated using a Miller Nelson Model 401 Flow-Temperature-Humidity Control System. A measured flow of a certified standard of H_2O_2 was nebulized into a measured flow of dilution air coming from the Miller Nelson control system. The H_2O_2 and dilution air flowed into a mixing chamber (76-cm \times 15-cm) and then into a sampling chamber (56-cm \times 9.5-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. The H_2O_2 used was $\geq 30\%$ TraceSELECT Ultra, for ultratrace analysis, purchased from Sigma Aldrich. The test atmosphere generation system was verified using OSHA Method VI-6.¹⁶

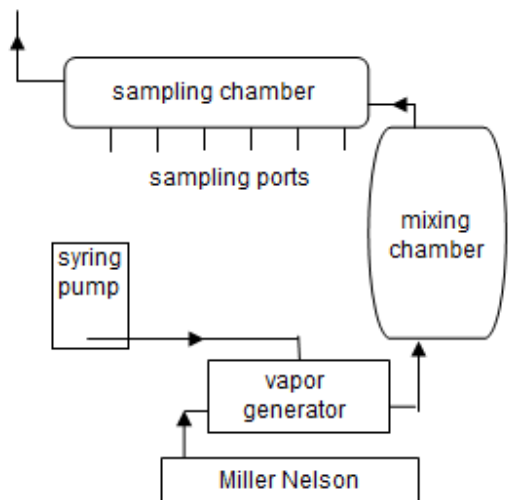


Figure 4.13. Diagram of apparatus used to generate H_2O_2 test atmospheres.

¹⁶ Hydrogen Peroxide (OSHA Method VI-6), 1977. United States Department of Labor, Occupational Safety and Health Administration Web site. http://www.osha.gov/dts/sltc/methods/inorganic/id006/hydrogen_peroxide.html (accessed May 2015).