

Hydrogen Peroxide



Method no.: VI-6

Matrix: Air

OSHA Standards: 1.4 mg/m³

Analytical Procedure: MFGB - Colorimetric

Detection Limit: 2 µg H₂O₂

Date: February 22, 1977

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1. Principle of the Method

1.1. H₂O₂ vapor is collected in a midget fritted glass bubbler containing 15 mL of TiOSO₄ collecting solution.

1.2. A 5 mL aliquot of the collecting solution is transferred to a 2-cm cuvette and 10 mL of distilled water are added.

1.3. The absorbance of the solution at 410 nm is read and compared to the absorbance of standards.

2. Range and Detection Limit

2.1. When using 2-cm cells and a 15 mL final volume, a 1% absorption or detection limit occurs at about 2 µg H₂O₂. For a 100 liter air sample this translates to a detection limit of about 0.06 mg H₂O₂/m³ or approximately 5 percent of the present TLV of 1.4 mg/m³. The yellow titanium - H₂O₂ complex is visually observed at 10 µg in the collecting solution or 0.1 mg/m³.

2.2. The range for this colorimetric method is useful from 2 µg H₂O₂ up to about 100 µg H₂O₂ which corresponds to 0.06 to 3.0 mg H₂O₂/m³ for a 100 liter air sample.

3. Precision and Accuracy

The average percent error for the method is estimated as 2.9.

4. Advantages and Disadvantages

4.1. The method is simple, specific, and sensitive. The Ti-H₂O₂ color complex is stable for over one week and insensitive to light and temperature. Semi quantitative visual field analysis is made possible by the spontaneous color complex formed by reaction of H₂O₂ with the collecting solution.

5. Apparatus

5.1. Sampling Equipment

5.1.1. A midget fritted glass bubbler.

5.1.2. An air-sampling pump capable of operating at a sampling rate of 0.5 Lpm. The pump must be properly calibrated so that the volume of air sampled can be determined accurately from the flow rate and time.

5.1.3. Thermometer

5.1.4. Manometer

5.1.5. Stopwatch

5.2. Analytical Equipment

5.2.1. Spectrophotometer set at 410 nm.

5.2.2. Matched cuvettes, 2 cm path length

5.2.3. Assorted glassware

6. Reagents

All reagents must be analytical reagent grade or better.

6.1. A stock solution of titanium(IV) is prepared as follows:

Dry the hydrated TiOSO₄·xH₂SO₄·xH₂O (mw > 402) overnight in a desiccator. In a beaker, place 5.5g of the dried TiOSO₄·xH₂SO₄·xH₂O, 20g of (NH₄)₂SO₄ and 100 mL of concentrated H₂SO₄. Heat gradually for several minutes until the chemicals are dissolved. The mixture is cooled to room temperature, poured carefully into 350 mL H₂O, filtered through an HA filter to remove any trace of

turbidity, and then diluted to 500 mL. A 1:50 dilution of this stock solution is titanium reagent or collecting solution.

6.2. A standard H_2O_2 stock solution is prepared by placing 2 mL of 30 percent H_2O_2 in a 500 mL volumetric flask and adding distilled water to the mark. Two mL of this stock are diluted to 200 mL with distilled water. Aliquots of this solution are used as standards. The 10 mL aliquot is about 120 μg .

6.3. The solutions required for H_2O_2 standardization are:

6.3.1. 4N H_2SO_4

6.3.2. 1N KI

6.3.3. 1N $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$

6.3.4. 0.1N $\text{Na}_2\text{S}_2\text{O}_3$

6.3.5. Starch solution prepared by adding 2 g soluble starch to 10 mL boiling water in which 1 g boric acid has been dissolved. This solution is boiled for 1 minute, cooled and stored in a stoppered bottle.

7. OSHA Collection Procedure

7.1. H_2O_2 in air is collected in a midget fritted glass bubbler containing 15 mL of titanium reagent as collecting solution.

7.2. Air is drawn through the bubbler at a rate of 0.5 liter per minute. A 100 liter sample is recommended.

7.3. The solutions are transferred to capped bottles for shipping. Vinyl or waterproof tape is used around the caps to prevent leakage during shipment. The tape is wrapped around the cap in the direction the cap is turned. Each cap is also sealed with an official OSHA seal.

7.4. With each batch of samples, one bottle containing collection solution, labeled as a blank, should be submitted.

7.5. The bottles in which samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

8. Analytical Procedure

8.1. Analysis of Samples and Standards

8.1.1. The volume of each sample received should be determined and recorded. A 5 mL aliquot is transferred to a cuvette and the volume of each adjusted to 15 mL with 10 mL deionized water.

8.1.2. Standard H_2O_2 solutions are made by placing 5 mL of titanium reagent in each of 6 cuvettes. Aliquots of the standard H_2O_2 solution are added to each and the total volume is adjusted to 15 mL with water.

8.1.3. The absorbance of each sample, blank, and standard are determined at 410 nm with a spectrophotometer with 0.00 absorbance corresponding to a reagent blank.

8.2. Standardization of H_2O_2

8.2.1. The following solutions are transferred to a 125 mL erlenmeyer flask.

4 mL stock H_2O_2

21 mL water

10 mL 4N H_2SO_4

6 mL 1N KI

3 drops 1N $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$

8.2.2. The solution is titrated to a very faint yellow with 0.1N $\text{Na}_2\text{S}_2\text{O}_3$ and then 1 mL starch solution is added to produce a blue color. The titration is continued until the solution is colorless.

8.2.3. The total amount of $\text{Na}_2\text{S}_2\text{O}_3$ required to reach the colorless end point is determined.

8.3. Interferences

Positive interference can be expected from any compound collected that liberates H_2O_2 on acid hydrolysis. Negative interferences are a function of the reactivity of H_2O_2 with other compounds present in the air sample.

9. Calculations

9.1. A standard curve is plotted from the absorbance values obtained for the standard H_2O_2 solutions.

Typical values used for a curve are given:

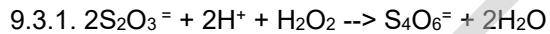
Standard Aliquot (mL)	(410 nm)	µg H ₂ O ₂
10	0.150	120
4	0.087	48
2	0.049	24
1	0.024	12
0.5	0.012	6

9.2. The weight of H₂O₂ in a sample aliquot is determined from the calibration curve using the measured absorbance of the color developed by the sample aliquot.

The total weight of H₂O₂ in the sample is calculated by the equation:

$$\mu\text{g}(\text{H}_2\text{O}_2) = [(\text{aliquot } \mu\text{g} - \text{blank aliquot } \mu\text{g})(\text{sample volume, mL})] / (\text{sample aliquot volume, mL})$$

9.3. The following equation and calculations are used for standardization of 4 mL stock H₂O₂ standard.



9.3.2. The H₂O₂ normality is determined from the S₂O₃²⁻ titrant volume, and the corresponding concentration of H₂O₂ is determined by the relationship:

$$\text{ppm}(\text{H}_2\text{O}_2) = \text{N}(\text{H}_2\text{O}_2) \times 17.0 \times 1000$$

9.3.3. The 4 mL standard solution weight is 1 percent of the 4 mL stock value since a 100:1 dilution was made.

9.4. The concentration of H₂O₂ in air is expressed in mg H₂O₂ per cubic meter of air.

$$\text{mg H}_2\text{O}_2/\text{m}^3 = \mu\text{g H}_2\text{O}_2/\text{L}$$

10. References

- 10.1. Cohen, I., Purcell, T., Anal. Chem., 39, 131 (1967).
- 10.2. AOAC Methods of Analysis, 12th Ed. Washington D.C. 605 (1975).