Method no.:	ID-126-SG
Matrix:	Air
OSHA Standard:	1 ppm TWA
Validation Level:	0.5 ppm to 2 ppm
Collection Procedure:	$TiOSO_4$ in a midget fritted-glass impinger
Recommended Air Volume:	100 liters at 1 L/min
Analytical Procedure:	Different Pulse Polarography
Determination Limit or Reliable Quantitation Limit:	0.10 ppm
Precision:	$CV_1 = 0.0261$
Method Classification:	New/Interin

1. Introduction

1.1 Scope

1.1.1 This method describes the sampling of hydrogen peroxide using $TiOSO_4$ and the analysis of hydrogen peroxide by differential pulse polarography.

1.2 Advantages and Disadvantages

1.2.1 The analytical method is simple and specific.

1.2.2 The $TiOSO_4$ complex is stable for over seven weeks. (See the H_2O_2 backup report).

1.2.3 The collection of hydrogen peroxide can be monitored by observing the clear $TiOSO_4$ solution change to a yellow color when the $TiOSO_4$-H_2O_2 complex forms.

1.2.4 The method has better sensitivity than the calorimetric method (7.1) and has fewer interferences (see H_2O_2 backup report).

1.3 Principle (7.4)

1.3.1 The sample is collected using a midget fritted-glass bubbler containing 15 mL $TiOSO_4$.

1.3.2 The sample is analyzed for H_2O_2 by differential pulse polarography at a dropping mercury electrode. The current (in µA) of known standards are plotted against the concentrations of the standards to quantitate the H_2O_2.

2. Range and Detection Limit

2.1 The detection limit is 0.10 ppm for a 100 L air Sample. The working analytical range is 5 to 100 µg.

3. Precision and Accuracy

3.1 Eighteen samples were spiked at three levels corresponding to levels of 1/2, 1, and 2 times the PEL. The CV_1 (pooled) for the three levels is 0.0261.

4. Interferences

4.1 Very high levels of strong oxidants and reductants will interfere with the analysis. See the H_2O_2 backup report.

5. Sampling

5.1 Apparatus

5.1.1. An air sampling pump capable of operating at sampling rate of 1.0 L/min. The pump must be properly calibrated so that the volume of air sampled can be determined accurately from the flow rate and time.

5.1.2 Midget fritted-glass bubbler.

5.1.3 0.00115 M $TiOSO_4$ collection solution.

5.2 Procedure

5.2.1 Sampling is done in accordance with current instructions contained in OSHA directives to the industrial hygienist.

5.2.2 The sample is collected in a midget fritted-glass bubbler containing 10 to 15 mL of 0.00115 M $TiOSO_4$ solution (6.2.3) using a flow rate of 1.0 liter per minute. A 100 liter air sample is recommended.

5.2.3 Ship to the laboratory as soon as possible. Do not use metal cap liners in the vial caps and tape the lids shut. Send one blank with every 10 samples.

6. Analytical Procedure

6.1 Apparatus

6.1.1 25-mL Class A burette with Teflon stopcock.

6.1.2 Glass volumetric pipettes.

6.1.3 Micropipettes with tips.

6.1.4 125-mL Erlenmeyer flask.

6.1.5 Polargraphic analyzer - model 374 or 384 manufactured by Princeton Applied Research (PAR) or equivalent.

6.1.6 Static mercury drop electrode - PAR 303 or- equivalent.

6.1.7 15-mL glass or polyethylene polargraphic cells.

6.1.8 Nitrogen purification apparatus.

6.2 Reagents - All chemicals should be ACS reagent grade or equivalent, and the dilution water must be deionized.

6.2.1 0.0575 M Titanium oxysulfate: Add 4.6 g $TiOSO_4$, 20 g $(NH_4)_2SO_4$and 100 mL concentrated H_2SO_4 to a 500 mL beaker. See precautions in 6.3.1. Heat gradually for several minutes until the chemicals are dissolved. Cool the mixture to room temperature and pour carefully into about 350 mL deionized water in a 500 mL volumetric flask. Filter the solution through an HA filter to remove any particulates, and dilute to 500 mL. The solution should be stable for 6 months.

6.2.2 0.00575 N Titanium oxysulfate: Take a 1-10 dilution of the 0.0575 M $TiOSO_4$ stock solution by adding 10 mL of the stock solution (6.2.1) to a 100 mL volumetric flask and diluting to volume with deionized water. This solution should be made fresh monthly.

6.2.3 0.00575 M Titanium oxysulfate: Take a 1:50 dilution of the stock $TiOSO_4$ solution (6.2.1) by adding 2 mL of the stock to a 100 mL volumetric flask and diluting to volume with deionized water. This solution should be made fresh monthly.

6.2.4 Supporting electrolyte: Add 53 g $(NH_4)_2SO_4$, 38 g EDTA, and 75 mL of 28.8% $(NH_4)OH$ to about 500 mL deionized water in a 1000 mL volumetric flask. Let cool, then dilute to 1000 mL with D.I. water.

6.2.5 4 N Sulfuric acid: Slowly add 112 mL H_2SO_4 to about 500 mL deionized water in a 1 L volumetric flask, stir and let cool. See precautions in 6.3.1. Dilute to 1 L with deionized water.

6.2.6 Starch indicator solution: To 5 g starch add a little cold water and grind in a mortar to a thin paste. Scrape into 1 L of boiling distilled water, stir, and let the covered solution settle overnight. Decant the clear supernate into a brown bottle and preserve with 4 g zinc chloride.

6.2.7 0.1 M Sodium Thiosulfate: Add 24.82 g $Na_2S_2O_3 \cdot H_2O$ to about 500 mL deioized water in a 1000 mL volumetric flask and let dissolve. Dilute to volume deionized water. Add two or three mL chloroform to minimize bacterial decomposition.

6.2.8 1 M Ammonium molybdate: Add 20.6 g $(NH_4)_6Mo_7O_{24}$ to about 50 mL deionized water in a 100 mL volumetric flask and dissolve. Dilute to volume with deionized water. Store in glass.

6.2.9 1 M Potassium iodide: Add 33.2 g of KI crystals to 100 mL deionized water, dissolve, and dilute to 1 L. Store in a brown bottle.

6.3 Precautions

6.3.1 When handling mercury, hydrogen peroxide, or sulfuric acid, gloves and safety glasses must be worn. Extreme care must be observed to avoid splashing or spilling on skin. Add sulfuric acid to water very carefully and never add water to sulfuric acid. Sulfuric acid gives off a great deal of heat when added to water and can splatter or boil violently. To prevent tile heat from shattering the volumetric flask, place the flask in a cool water bath and add the sulfuric acid a little at a time.

6.3.2 Refer to the polarographic instruction manual for instrumental safety precautions (7.2, section I-1, and 7.3 section I-1).

6.4 Sample Preparation

6.4.1 Open the collection vial and measure the sample volume using a graduated cylinder. Take an aliquot of sample and transfer to a 15-mL polarographic cell. The sample aliquot size will depend on the intensity of the color of the collecting solution. If the sample is very yellow, use a 1 mL aliquot of sample and add 4.0 mL of the 0.00115 N $TiOSO_4$ (6.2.4) If the sample is colorless, use a 5 mL aliquot.

6.4.2 Add 5 mL of the supporting electrolyte (6.2.4) to give a total volume of 10 mL and analyze by differential pulse polarography.

6.5 Standard Preparation

6.5.1 A hydrogen peroxide stock solution is prepared by placing 2 mL of 30% H_2O_2 in a 500 mL volumetric flask and diluting to volume with deionized water. This is approximately 1200 µg/mL H_2O_2.

6.5.2 A hydrogen peroxide standard solution is prepared by placing 1 mL of the H_2O_2 stock (6.5) in a 100 mL volumetric flask and diluting to volume with deionized water. This is approximately 12 µg/mL H_2O_2.

6.5.3 Prepare a series of standards in the analytical range of 6 to 48 µg by adding the following serial dilutions. Add to the polarographic cell the appropriate aliquot of the H_2O_2 standard solution (6.5.2) and aliquots of deionized water using the calibrated nicropipettes. Add 1 mL of the 0.00575 M $TiOSO_4$ (6.2.2) and 5 mL of the supporting electrolyte (6.2.4) to make a total volume of 10 mL.

Stock Solution (ppm)	Aliquot H_2O_2 (mL)	Aliquot D.I. H_2O (mL)	Final Standard (µg)
12	4..0	0.0	48
12	3.0	1.0	36
12	2.0	2.0	24
12	1.0	3.0	12
12	0.5	3.5	6

6.6 Analysis

6.6.1 Turn on the polarograph, Model 384 and 303 and allow to warm up for at least 30 minutes.

6.6.2 Analyze the standards and samples by differential pulse polarography using the following instrumental conditions:

Initial Potential	-0.820 V
Final Potential	-1.020 V
Purge Time	300 sec
Scan Increment	2 mV
Replications	1
Drop Time	0.5 seconds
Peak Location	Yes
Peak Potential	-0.940 V
Date	as needed

This method is stored as Method No. 2 in the PAR, Model 384.

6.6.3 Prepare the samples and working standard solutions as described in sections 6.4 and 6.5.

6.6.4 Purge each standard and sample for 5 minutes pre-purified nitrogen.

6.6.5 Analyze the reagent blank, standards, and the samples. A standard should be re-analyzed after every 4 or 5 samples.

6.6.6 Record the peak current and potential for each standard and sample in the laboratory notebook. The differential pulse polarogram of hydrogen peroxide gives a peak at approximately -0.940 V.

6.6.7 If any of the samples have enough hydrogen peroxide to be over the PEL, the 1200 µg/mL stock (6.5.1) must be standardized against the 0.1 H sodium thiosulfate (6.2.7) before a standard curve is prepared. See 6.6.9 through 6.6.12.

6.6.8 Use any available least square regression program to plot a calibration curve of peak current vs. concentration (ppm, ppb, or total µg) of the standards.

6.6.9 To standardize the H_2O_2 stock solution, transfer the following solutions to a 125-mL Erlenmeyer flask.

1. 10 mL stock 1200 µg/mL H_2O_2 (6.5.1)

2. 10 mL 2N H_2SO_4 (6.2.5)

3. 6 mL 1N KI (6.2.9)

4. 3 drops 1N $(NH_4)_6Mo_7O_{24}$ (6.2.8)

5. 20 mL D.I. water

6.6.10 The solution is titrated to a very faint yellow with 0.1 N $Na_2S_2O_3$ (6.2.7) and then 1 mL starch solution (6.2.6) is added to produce a blue color. The titration is continued until the solution becomes colorless.

6.6.11The total amount of $Na_2S_2O_3$ required to reach the endpoint is determined (about 10 mL) and recorded.

6.6.12 Calculate the concentration of the 1200 µg/mL H_2O_2 stock, the 12 µg/mL standard, and the actual concentrations of the standards to be used in the standard curve.

6.7 Calculations

6.7.1 Subtract the initial volume of sodium thiosulfate from the volume at the endpoint. This is the total volume of $Na_2S_2O_3$ used.

Since:

$2\ S_2O_3^{=} + H_2O_2 + 2\ H^{+} \text{-----> } S_4O_6^{=} + 2\ H_2O$

Then:

$M\ Na_2S_2O_3 \times V\ Na_2S_2O_3 = 2 \times M\ H_2O_2 \times V\ H_2O_2$

or:

$0.1 \times mL\ Na_2S_2O_3$ used = $M\ H_2O_2 \times 2 \times 10$ mL, and:

mmoles H_2O_2 = mmoles $Na_2S_2O_3 \times 1/2$ then:

$$\text{mg } H_2O_2 = \text{mmoles } Na_2S_2O_3\ 1/2 \times 34$$
$$= \text{mmoles } Na_2S_2O_3 \times 17$$

6.7.2 The weight of H_2O_2 in a sample aliquot is determined from the calibration curve. The total weight of H_2O_2 is calculated front the equation:

$$\text{µg } H_2O_2 = \frac{\textit{(aliq. µg - blank aliq.)(sample vol. mL)}}{\text{(sample aliquot vol, mL)}}$$

6.7.3 The concentration of H_2O_2 is calculated in µg/L, converted to mg/m^3, and then to ppm.

µg H_2O_2/liters sampled = mg/m^3 and;

ppm $H_2O_2 = mg/m^3 \times 24.45/34 = mg/m^3 \times 0.719$ ppm

7. References

7.1 Hydrogen Peroxide Colorimetric Method, Method No: VI-6, Last Revised on January 26, 1978.

7.2 Instruction Manuals Polarographic Analyzer, Model 374 and Hanging Mercury Drop Electrode Model 303, Princeton Applied Research, Princeton, NJ.

7.3 Polarographic Instruction Manual, Model 384, Princeton, NJ.

7.4 Boto, K.G., and Williams, L.F.G., Analytical Chimica Acta, Vol. 85, pp 179-183 (1976).

Substance: Hydrogen Peroxide

OSHA-PEL: 1.0 ppm = TWA

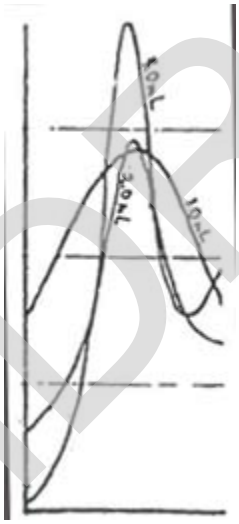
Chemical used for validation: Hydrogen Peroxide. Analytical Reagent. 30 S. Wallinckrodt.

1. Procedure

The general procedure used is described in the OSHA Sampling and Analytical Method (SAM) for hydrogen peroxide. Instrumental analysis was done by Carl Cook (See Reference 8.1). This method replaces the colorimetric method (8.2).

2. Analysis

The analysis of hydrogen peroxide is by differential pulse polarography (DPP). See reference 8.1. 5.0 mL of the supporting electrolyte and 5.0 mL of the sample or standard solution is placed in a 10 mL sample cell. The sample or standard must be in 5.0 mL 0.00115 M $TiOSO_4$. This gives a much sharper and larger peak than 4 or less mL of the 0.00115 M $TiOSO_4$ as can be seen from the diagram below.



3. Generation

Hydrogen peroxide was generated by adding 25 mL of 30 % hydrogen peroxide to a flask and heating the flask while bubbling N_2 through the solution at a rate of 1 LPM. The hydrogen peroxide was collected in 15-mL of $TiOSO_4$ in a midget fretted glass bubbler.

4. Collection Efficiency

Hydrogen peroxide was generated for 40 minutes, and while the 1st impinger collected 500 µg/mL H_2O_2 (about 60 times the PEL), the 2nd impinger showed no hydrogen peroxide collected. This means at levels below 60 times the PEL there is 100 % collection efficiency.

5. Storage Stability

To assess the stability of hydrogen peroxide in $TiOSO_4$, a time study was conducted at the 0.5, 1.0, and 2.0 PEL level.

On 1/9/84, 24 samples were prepared for analysis over a two mouth period to determine the storage stability. Assuming that 100 L of air were taken in 15 mL $TiOSO_4$, there would be 75 µg H_2O_2 found in a sample at 1/2 the PEL. 150 µg at the PEL, and 300 µg at 2 times the PEL. Eight samples were prepared at each level and contained 15 mL of 0.00115 M $TiOSO_4$, plus the spiked H_2O_2 concentration. Table I gives the results of the stability study.

Table I Stability Study Data

Day	µg found	µg expected	f/t
1	75	75	1.000
1	176	150	1.173
1	347	300	1.157
4	76	75	1.113
4	141	150	0.940
4	295	300	0.983
8	74.9	75	0.999
8	149	150	0.993
8	300	300	1.000
15	91.5	75	1.220
15	183	150	1.220
15	367	300	1.223
51	76.3	75	1.017
51	150	150	1.000
51	377	300	1.259

From the results it can be seen that hydrogen peroxide is stable in $TiOSO_4$ for 51 days, or almost 2 months. One problem that was noticed was that although the hydrogen peroxide-$TiOSO_4$ complex is stable for two months, the $TiOSO_4$ stock solution (0.05775 M) and subsequent diluted solutions of the 0.05775 M $TiOSO_4$ stock solution are not stable. A comparison of the 0.05775 M QC stock solution and the 0.05775 M Laboratory stock solution showed significant differences. The QC stock was 12 months old and the lab stock was 3 months old. When analyzed by the calorimetric method, samples spiked with 96 µg in the QC Stock showed 80 µg, whereas samples spiked with 96 µg and collected in the lab stock showed 96 µg. The standards were made using the lab stock $TiOSO_4$. When the samples were analyzed by DPP, all the samples showed 96 µg. This is due either to the fact that the QC stock solution is 9 months older than the lab stock solution or differences in solution preparation. This points out another problem with the colorimetric analysis. The results indicate that age and/or makeup of the $TiOSO_4$ solutions are not as important when the DPP method is used.

6. Interferences

Table II shows the effects of different interferents on the analysis of hydrogen peroxide. 96 µg of hydrogen peroxide was placed in a 10-mL sample cell along with different levels of interferent. From Table II it can be seen that the only serious interferent with the DPP method is $KMnO_4$ which will also prevent the analysis of hydrogen peroxide using a calorimetric method. Additionally KI does not effect the analysis of hydrogen peroxide by DPP but does prevent the analysis or hydrogen peroxide using the colorimetric method.

Table II Effect of Interferent on the Analysis of Hydrogen Peroxide

µg H_2O_2 Added	Interferent Added	H_2O_2/Interferent ratio	µA	Peak location (V)
96	0.4 ppm $SnCl_2$	1:0.02	2.66	-0.948
96	20 ppm $KClO_4$	1:1	2.41	-0.950
96	0.2 ppm $KMnO_4$*	1:0.01		
96	0.8 ppm NH_2OH HCl	1:0.04	1.84	-0.948
96	2860 ppm $Na_2S_2OH{\cdot}HCl$	1:150	2.17	-0.950
96	10 ppm Cr_2O_3	1:.05	2.43	-0.948
96	33200 ppm KI*	1:1800	2.09	-0.950
96	20 ppm $K_2S_2O_8$	1:1	2.26	-0.950

*These were highly colored and would not allow analysis by the colorimetric method.

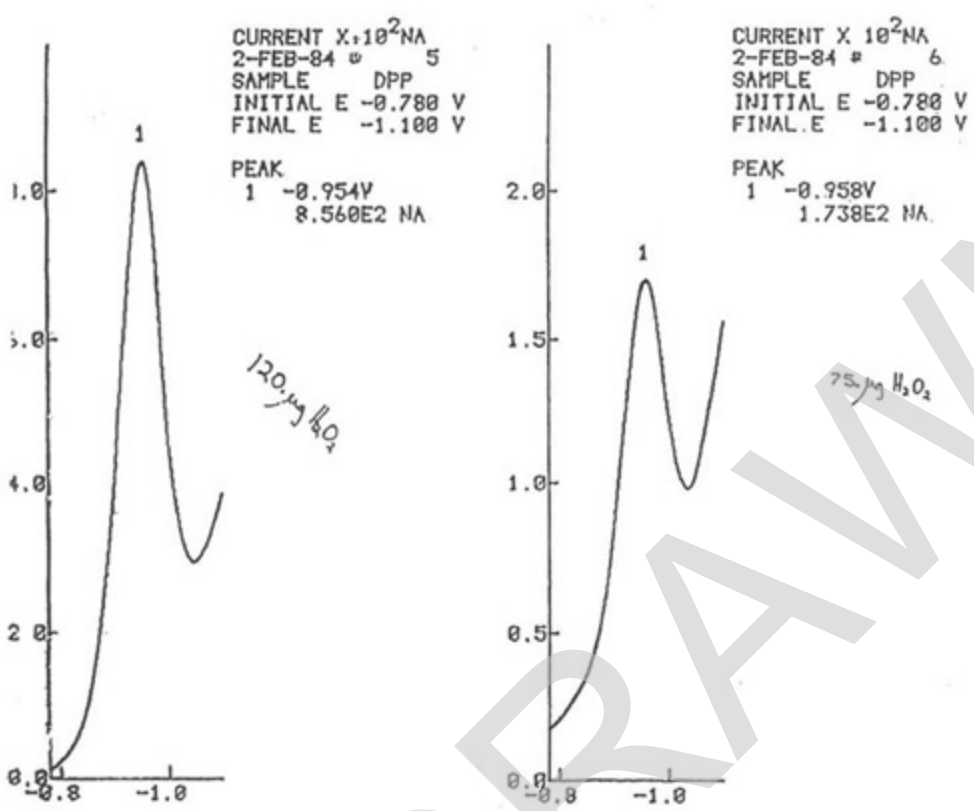
7. Precision and Accuracy

The last day of a study was on day 51, the results from day 51 are tabulated below.

# of Samples Analyzed	Concentration Expected	Concentration	CV_1
6	75.0	76.0	0.0312
6	150.0	150.0	0.0166
6	300.0	378.0	0.0281

The CV_1 [pooled] for the three sets of samples was 0.0261. Six samples for each of the three different concentration ranges were used.

Below are typical polarograms of 120 µg and 75 µg H_2O_2 respectively in a 10-mL sample cell.



8. References

8.1. Hydrogen Peroxide in Workplace Atmospheres, Method No: ID-126-SG.

8.2. Hydrogen Peroxide Colorimetric Method, Method No: VI-6, Last Revised on January 26, 1978.