SULFUR DIOXIDE IN WORKPLACE ATMOSPHERES (BUBBLER)

Method Number:	ID-104
Matrix:	Air
OSHA PEL	
Sulfur Dioxide (Final Rule Limit):	2 ppm (Time Weighted Limit) 5 ppm (Short-Term Exposure Limit)
Sulfur Dioxide (Transitional Limit):	5 ppm (Time Weighted Limit)
Collection Device:	A calibrated personal sampling pump is used to draw a known volume of air through a midget-fritted glass bubbler containing 10 to 15 mL of 0.3 N hydrogen peroxide.
Recommended Air Volume:	15 to 60 L
Recommended Sampling Rate:	1 L/min
Analytical Procedure:	Samples are directly analyzed with no sample preparation by ion chromatography as total sulfate.
Detection Limit	
Qualitative:	0.0041 ppm (60-L air volume)
Quantitative:	0.010 ppm (60-L air volume)
Precision and Accuracy	
Validation Level:	2.5 to 10.0 ppm (60-L air volume)
CV_T	0.012
Bias	-0.046
Overall Error	±7%
Method Classification:	Validated Method
Chemist:	Ted Wilczek, Edward Zimowski
Date (Date Revised):	1981 (December, 1989)

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1. Introduction

This method describes the collection and analysis of airborne sulfur dioxide (SO_2) using midget-fritted glass bubblers (MFGBs) in the workplace. It is applicable for both short-term (STEL) and time weighted average (TWA) exposure evaluations.

1.1 History

An earlier method used by OSHA involved collecting SO_2 in 0.3 N hydrogen peroxide (H_2O_2) which converted SO_2 to sulfuric acid. The amount of SO_2 in the air is determined in the laboratory by volumetric titration of the sulfuric acid with barium perchlorate and a Thorin indicator (8.1.). The titration is susceptible to interferences from volatile phosphates and metals (8.1.), and the end point is difficult to determine. Also, a report indicated the chloride ion has an adverse effect on the endpoint (8.2.). Method no. ID-104 has replaced the titration with ion chromatography (IC). A method using a solid sorbent sampling media and analysis by IC was recently evaluated (8.3.); however, the sorbent material appears prone to contamination.

1.2 Principle

Sulfur dioxide is collected in a MFGB containing 0.3 N H_2O_2. The H_2O_2 converts the SO_2 to sulfuric acid (H_2SO_4) according to the following equation:

$$SO_2 + H_2O_2 \text{ ---------> } H_2SO_4$$

The H_2SO_4 is analyzed as sulfate using a slightly basic eluent and an ion chromatograph equipped with a conductivity detector.

1.3 Advantages and Disadvantages

1.3.1 This method has adequate sensitivity for measuring workplace atmosphere concentrations of SO_2 and is less affected by interferences found in the barium perchlorate titration method.

1.3.2 The method can be fully automated to improve analytical precision.

1.3.3 Collected samples are analyzed by means of a quick instrumental method, since no sample preparation is required.

1.3.4 Humidity does not affect the collection efficiency.

1.3.5 The sulfuric acid formed is stable and non-volatile.

1.3.6 A disadvantage is the sampling device. The use of bubbler collection techniques may impose inconveniences for industrial hygiene work. There is the possibility of spillage during sampling, handling, and during transportation to the lab.

1.4 Potential sources of occupational exposure to SO_2 (8.4., 8.5.) Sulfur dioxide is used in industry as a(n):

- intermediate in the manufacture of sulfuric acid
- bleaching agent
- disinfectant
- fumigant
- solvent
- refrigerant
- food preservative
- reagent in the manufacture of magnesium, sodium sulfite, and other chemicals

Sulfur dioxide is also an industrial by-product and can be generated from many industrial processes. These include the smelting of sulfide ores, the combustion of coal or fuel oils containing sulfur as an impurity, paper manufacturing, and petroleum refining (8.4.).

1.5 Physical Properties: Sulfur dioxide (CAS No. 7446-09-5) is a colorless, nonflammable gas with a characteristic, strong and suffocating odor. It is intensely irritating to the eyes and respiratory tract. It is soluble in water, methane, ethanol, chloroform, ethyl ether, acetic acid, and sulfuric acid (8.4., 8.5.).

Physical Constants	
Chemical Formula:	SO_2
Formula Weight:	64.07
Boiling Point:	-10.0 °C
Melting Point:	-72.7 °C
Vapor Density:	2.3 (air =1)

2. Range and Detection Limit (8.6.)

This method was evaluated over the range of 2.5 to 10.0 ppm (atmospheric conditions of 640 mmHg and 24 °C). Total air sample volumes of 60 L were used. The analytical portion of the evaluation was conducted using a model 10 ion chromatograph with a 3 x 500-mm separator and 6 x 250-mm suppressor columns. The following results were obtained using this equipment.

2.1 The sensitivity of the method for the instrumentation used during the validation study was 1.5 µS/cm/µg as sulfate ion. A 100 µL injection of a 10 µg/mL solution of sulfate gave a 27-mm chart deflection on a 500-mV chart recorder. The ion chromatograph was set on a range of 30 µS/cm.

2.2 The qualitative detection limit of the analytical method was 0.013 µg of SO_2 per injection (200-µL sample injection) or 0.65 µg SO_2 in a 10-mL sample volume.

2.3 The quantitative limit was 0.033 µg SO_2 per 200-µL injection or 1.7 µg SO_2 in a 10-mL sample volume. The coefficient of variation of replicate determinations of standards at this level was less than 0.10.

3. Method Performance (8.6.)

This method was evaluated in 1981 using commercial analytical equipment mentioned in Section 2. Advances in ion chromatographic and sampling instruments should enable users to obtain similar or better results than those mentioned below.

3.1 The coefficient of variation (CV_T) for the overall sampling and analytical method in the range of 2.5 to 10 ppm (640 mmHg and 24 °C) was 0.012.

3.2 In validation experiments, this method was capable of measuring within ±25% of the true value (95% confidence level) over the validation range. The bias was -0.046 and overall error was ±7%.

3.3 The collection efficiency was 100% for the 0.3 N H_2O_2 sampling solution.

3.4 A breakthrough test was conducted at a concentration of 9.4 ppm. No breakthrough occurred after 240 min at a sampling rate of 1 L/min.

3.5 In storage stability studies, the average recovery of samples analyzed after 31 days were within 1% of the average recovery of samples analyzed immediately after collection.

4. Interferences

4.1 The presence of other particulate sulfate compounds and sulfuric acid in the air will interfere in the analysis of sulfur dioxide. These two interferences can be removed by the use of a modified prefilter.

4.2 Sulfur trioxide gas (SO_3), if present in a dry atmosphere, can give a positive bias in the SO_2 determination.

4.3 Any substance that has the same retention time as the sulfate ion with the ion chromatographic operating conditions as described in this method is an interference. If the possibility of an interference exists, changing the separation conditions (column length, eluent flow rate and strength, etc.) may circumvent the problem.

4.4 When other substances are known or suspected to be present in the air sampled, the identities of the substances should be transmitted with the sample.

5. Sampling

5.1 Equipment

5.1.1 Hydrogen peroxide (30% H_2O_2), reagent grade or better.

5.1.2 Collection solution, 0.3 N H_2O_2. Carefully dilute 17 mL of 30% H_2O_2 solution to 1 L with deionized water.

5.1.3 Personal sampling pumps capable of sampling within ±5% of the recommended flow rate of 1 L/min are used.

5.1.4 Midget-fritted glass bubblers (MFGBs), 25-mL, part no. 7532 (Ace Glass Co., Vineland, NJ).

5.1.5 Shipping vials: Scintillation vials, 20-mL, part no. 74515 or 58515, (Kimble, Div. of Owens-Illinois Inc., Toledo, OH) with polypropylene or Teflon cap liners. Tin or other metal cap liners should not be used.

5.1.6 A stopwatch and bubble tube or meter are used to calibrate pumps.

5.1.7 Various lengths of polyvinyl chloride (PVC) tubing are used to connect bubblers to the pumps.

5.1.8 If particulate sulfate or sulfuric acid is suspected to also be in the atmosphere, a modified prefilter assembly is used. This assembly consists of:

1. Sampling cassettes, polystyrene, 37-mm.
2. Mixed-cellulose ester (MCE) filters, 37 mm.
3. Support rings, cellulose, part no. 225-23 (SKC Inc., Eighty Four, PA). Rings can also be made from 37-mm cellulose backup pads. Place a half-dollar in the center of the pad and then cut the outer ring formed. Place this ring in the cassette to provide support for the MCE filter.

5.2 Sampling Procedure

5.2.1 Calibrate the sampling pump with a MFGB containing about 10 to 15 mL of collection solution in-line.

5.2.2 Place 10 to 15 mL of collection solution in an MFGB. Connect the MFGB to a calibrated sampling pump and then place the sampling device in the breathing zone of the employee.

5.2.3 If particulate sulfate or sulfuric acid are suspected to be present, attach the modified prefilter (Section 5.1.8.) to the MFGB with PVC tubing so that sampled air enters the cassette first. Minimize the amount of tubing from the filter to the MFGB.

5.2.4 Sample at a flow rate of 1 L/min. For STEL determinations, sample for at least 15 min. For measurements of TWA exposures, sample from 60 to 240 min. Take enough samples to cover the shift worked by the employee.

5.2.5 Transfer the collection solution into a 20-mL glass scintillation vial. Rinse the bubbler with 2 to 3 mL of unused collection solution and transfer the rings into the sample vial. Place the Teflon- or polypropylene-lined cap tightly on each vial and seal with vinyl or waterproof tape around the caps to prevent leakage during shipment.

5.2.6 Prepare blank solutions by taking 10 to 15 mL of the unused collection solution and transfer to individual 20-mL glass vials. Seal vials as mentioned in Section 5.2.5.

5.2.7 Request sulfur dioxide analysis on the OSHA 91A form. If sulfuric acid is also suspected in the sampled atmosphere and a prefilter assembly was used, the MCE filter can be submitted for sulfuric acid analysis.

5.2.8 Ship the samples to the laboratory using appropriate packing materials to prevent breakage.

6. Analysis

6.1 Precautions

6.1.1 Refer to instrument and standard operating procedure (SOP) manuals (8.7.) for proper operation.

6.1.2 Observe laboratory safety regulations and practices.

6.1.3 Sulfuric acid (H_2SO_4) can cause severe burns. Wear protective eyewear, gloves, and lab coat when using concentrated H_2SO_4.

6.2 Equipment

6.2.1 Ion chromatograph (model no. 2010i or 4500, Dionex, Sunnyvale, CA) equipped with a conductivity detector.

6.2.2 Automatic sampler (model no. AS-I, Dionex) and 0.5 mL sample vials (part no. 038011, Dionex).

6.2.3 Laboratory automation system: Ion chromatograph interfaced to a data reduction and control system (model no. AutoIon 450, Dionex).

6.2.4 Micromembrane suppressor (model no. AMMS-1, Dionex).

6.2.5 Anion separator column (model no. HPIC-AS4A, Dionex) with pre-column (model no. HPIC-AG4A, Dionex).

6.2.6 Disposable syringes (1 mL) and syringe pre-filters, 0.5 um pore size, (part no. SLSR 025 NS, Millipore Corp., Bedford, MA). (Note: Some syringe pre-filters are not cation- or anion-free. Tests should be done with blank solutions first to determine suitability for the analyte being determined).

6.2.7 Miscellaneous volumetric glassware: Micropipettes, volumetric flasks, graduated cylinders, and beakers.

6.2.8 Analytical balance (0.01 mg).

6.3 Reagents - All chemicals should be at least reagent grade.

6.3.1 Deionized water (DI H_2O) with a specific conductance of less than 10 µS.

6.3.2 Eluent [0.0015 M sodium carbonate (Na_2CO_3)/0.0015 M sodium bicarbonate ($NaHCO_3$)]: Dissolve 0.636 g Na_2CO_3 and 0.504 g $NaHCO_3$ in 4.0 liters of DI H_2O.

6.3.3 Sulfuric acid (H_2SO_4), concentrated (98%).

6.3.4 Regeneration solution (0.02 N H_2SO_4): Pipet 1.14 mL concentrated H_2SO_4 into a 2-L volumetric flask which contains about 500 mL DI H_2O. Dilute to volume with DI H_2O.

6.3.5 Sodium sulfate (Na_2SO_4).

6.3.6 Sulfate stock standard (1,000 µg/mL sulfate): Dissolve and dilute 1.4792 g Na_2SO_4 to 1-L with DI H_2O.

6.4 Standard Preparation

Working standards (100, 10, 1.0, and 0.1 µg/mL as sulfate). Make appropriate serial dilutions of the sulfate stock standard with eluent. Prepare these solutions monthly.

6.5 Sample Preparation

6.5.1 Measure and record the total solution volume of each sample with a graduated cylinder.

6.5.2 If the sample solutions contain suspended particulate, remove the particles using a pre-filter and syringe (Note: Some pre-filters are not cation or anion free. Tests should be done with blank solutions first to determine suitability of the filter for the analyte being determined).

6.5.3 Fill the 0.5-mL automatic sampler vials with sample solutions and push a filtercap into each vial. Label the vials.

6.5.4 Load the automatic sampler with labeled samples, standards and blanks.

6.6 Analysis

Set up the ion chromatograph and analyze the samples and standards in accordance with the SOP (8.7.). Typical operating conditions for a Dionex 2010i with a data reduction system are listed below.

Ion Chromatograph

Eluent:	0.0015 M Na_2CO_3/0.0015 M $NaHCO_3$
Column temperature:	ambient
Conductivity detector sensitivity:	1 to 3 µS

Micromember Suppressor

Regenerant flow:	3 to 5 mL/min
Gas pressure:	5 to 10 psi

Pump

Pump pressure:	approximately 1,000 psi
Flow rate:	2 mL/min

Chromatogram

Run time:	6 min
Sample injection loop:	50 µL
Average retention time (sulfate):	approximately 5.4 min

7. Calculations

7.1 Hard copies of chromatograms containing peak area and height data should be obtained from a printer. A typical chromatogram is shown in Figure 1.

7.2 Using a least squares regression program, prepare a concentration-response curve by plotting the concentration of the prepared µg/mL values of the standards (or µg/sample if the same injection and solution volumes are used for samples and standards) versus peak areas or peak heights. Calculate sample concentrations from the curve and blank correct all samples as shown:

$$C\ \mu g\ SO_4^{2-} = (S\ \mu g/mL)(SSV) - (BL\ \mu g/mL)(BLSV)$$

Where:

$C\ \mu g\ SO_4^{2-}$ = Corrected amount (µg) in the sample solution
S µg/mL = µg/mL sample (from curve)
SSV = Sample solution volume (from Section 6.5.1.)
BL µg/mL = µg/mL blank (from curve)
BLSV = Blank solution volume (from Section 6.5.1.)

7.3 The concentration of SO_2 in each air sample is expressed in ppm and is calculated as:

$$ppm\ SO_2 = \frac{MV \times C\ \mu g\ SO_4^{2-} \times Conversion}{Formula\ Weight \times Air\ Volume}$$

Where:

MV (Molar Volume) = 24.45 (@ 25 °C and 760 mmHg)
$C\ \mu g\ SO_4^{2-}$ = blank corrected sample result
Gravimetric conversion (SO_4^{2-} to SO_2) = 0.667
Formula Weight (SO_2) = 64.07
Air Volume = Air sample taken (in L)

This equation reduces to:

$$ppm\ SO_2 = \frac{0.2545 \times C\ \mu g\ SO_4^{2-}}{Air\ Volume}$$

7.4 Reporting Results

Results are reported to the industrial hygienist as ppm sulfur dioxide.

8. References

8.1. **National Institute for Occupational Safety and Health:** NIOSH Manual of Analytical Methods. 2nd. ed., Vol. 4 (Method No. S308) (DHEW/NIOSH Pub. No. 78-175). Cincinnati, OH: National Institute for Occupational Safety and Health, 1978.

8.2. **Steiber, R. and R. Merrill:** Application of Ion Chromatography to the Analysis of Source Assessment Samples. In Ion Chromatographic Analysis of Environmental Pollutants (Volume 2), edited by J.D. Mulik & E. Sawicki. Ann Arbor, MI: Ann Arbor Science Publishers Inc., 1979. pp. 99-113.

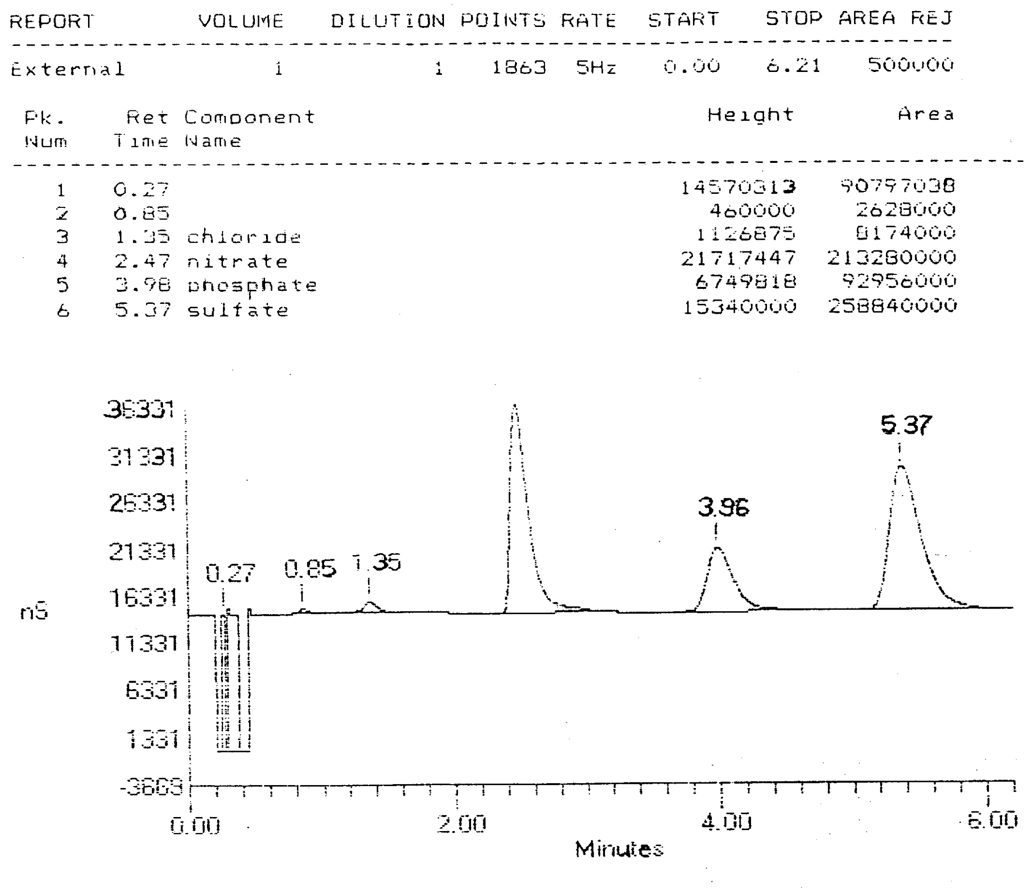
8.3. **Occupational Safety and Health Administration Analytical Laboratory:** OSHA Analytical Methods Manual (USDOL/OSHA-SLCAL Method No. ID-107). Cincinnati, OH: American Conference of Governmental Industrial Hygienists (Pub. No. ISBN: 0-936712-66-X), 1985.

8.4. **National Institute for Occupational Safety and Health:** Criteria for a Recommended Standard - Occupational Exposure to Sulfur Dioxide (DHEW/NIOSH Pub. No. 74-111). Cincinnati, OH: National Institute for Occupational Safety and Health, 1974.

8.5. **Fassett, D.W. and D.D. Irish, ed.:** Patty's Industrial Hygiene and Toxicology. 2nd rev. ed., Vol. 2. New York: John Wiley and Sons, 1963.

8.6. **Occupational Safety and Health Administration Technical Center:** Sulfur Dioxide Backup Data Report (ID-104). Salt Lake City, UT. Revised, 1989.

8.7. **Occupational Safety and Health Administration Technical Center:** Ion Chromatography Standard Operating Procedure. Salt Lake City, UT. In progress (unpublished).



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REPORT         VOLUME    DILUTION POINTS RATE   START    STOP AREA REJ
---------------------------------------------------------------------
External            1          1    1863   5Hz    0.00    6.21   500000

 Pk.    Ret Component                                Height        Area
 Num    Time Name
------------------------------------------------------------------------
   1    0.27                                       14570313    90797038
   2    0.85                                         460000     2628000
   3    1.35 chloride                               1126875     8174000
   4    2.47 nitrate                               21717447   213280000
   5    3.98 phosphate                              6749818    92956000
   6    5.37 sulfate                               15340000   258840000
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Figure 1. Chloride 3 µg, nitrate 20 µg, phosphate 20 µg, sulfate 20 µg.

SULFUR DIOXIDE (IMPINGER)
BACKUP DATA REPORT

1. Procedure: The general procedure for collection and analysis of sulfur dioxide air samples is described in OSHA Method No. ID 104 (11.1). Sulfur dioxide is collected in a midget bubbler containing 0.3 N hydrogen peroxide in deionized water. The hydrogen peroxide solution converts the sulfur dioxide to sulfuric acid. The amount of sulfur dioxide as sulfate in the hydrogen peroxide solution is determined by ion chromatography.

   This method has been validated for a 60-liter 60 minute time-weighted-average TWA for the OSHA-Permissible Exposure Level (PEL). The validation of the method for sulfur dioxide consisted of the following experimental protocol:

   1.1. Analysis of a total of 18 samples (6 samples at each of three test levels) prepared by spiking with appropriate amounts of sodium sulfate in 0.3 N hydrogen peroxide. These samples represented concentrations of 0.5, 1, and 2 times the OSHA PEL, based upon a 60-minute sample collection at a flow rate of 1.0 liter per minute.

   1.2. Analysis of a total of 18 samples (6 samples at each of the three test levels) collected from dynamically generated test atmospheres at 0.5, 1, and 2 times the OSHA PEL standard, based upon a 60-liter sample at a flow rate of 1.0 liter per minute.

1.3 Determination of the collection efficiency and breakthrough of the hydrogen peroxide collecting solution using midget bubblers at 2 times the OSHA PEL standard.

1.4. Testing of the storage stability of six collected samples at the OSHA PEL standard.

1.5. Determination of the detection limit of the method.

1.6. Study of method comparison.

1.7. Assessment of the precision and accuracy of the method.

2. **Analysis:** A description of the method of analysis is given in OSHA Method No. ID104. Samples were prepared by adding known amounts of a stock sodium sulfate solution to 25 ml of 0.3 N hydrogen peroxide. The concentrations evaluated corresponded to 6.03, 12.05 and 23.75 mg/m^3 of sulfur dioxide when sampled at 1.0 liter per minute for a period of 60 minutes.

2.1. Method of preparation of sulfate stock solution:

2.1.1. A 12,003 ppm sulfate stock solution was prepared by dissolving and diluting 1.7748 gram of anhydrous sodium sulfate (certified A.C.S. grade) to 100 ml with a 0.3 N hydrogen peroxide solution. On the day preceding the preparation of this stock solution, the sodium sulfate had been heated for approximately two hours at 110 degrees C in a drying oven and then allowed to cool overnight in a drying dessicator.

2.2. Preparation of known spiked samples.

2.2.1. Three sets of spiked samples were prepared by injecting 45.2, 90.3 and 178 ul, respectively, of the 12,003 ppm sulfate stock solution into 25-mL volumetric flasks. These solutions were then diluted to volume with 0.3 N hydrogen peroxide solution. The spikes were injected by means of a calibrated 200 ul micropipette. Each set consisted of six samples and a sample blank. The sulfate concentrations of the prepared sets were equivalent to 2.30, 4.60 and 9.06 ppm of sulfur dioxide at standard temperature and pressure. These values approximate 0.5, 1, and 2 times the OSHA PEL based on a 60 liter air volume.

2.3. Analysis by ion chromatography: each sample was analyzed twice.

2.4. Analytical method recovery (A.M.R.): the results of the analytical method recovery are presented in Table I. Also included in Table VI are the analytical method recoveries for the barium perchlorate titration determinations.

3. Sampling and Analysis

3.1. Preparation of known generated samples: test atmospheres of sulfur dioxide gas were dynamically generated at approximately 0.5, 1, and 2 times the OSHA PEL by diluting the gas from a 505 ppm certified gas cylinder of sulfur dioxide in nitrogen with purified humid house air. A diagram of the generation system is presented in Figure 1.

3.1.1. The certified sulfur dioxide gas was calibrated against an NBS primary standard to verify the concentration which was within ±2% of the stated value.[1]

3.1.2. The certified sulfur dioxide gas and the humid air were mixed together in a 7/16 inch i.d. Teflon mixing tee prior to entering the sampling chamber. The sampling chamber was a twelve port 7/16 inch i.d. Teflon sampling manifold. There were six sampling ports located on opposite sides of the sampling manifold. The sampling ports were spaced approximately 3 1/4 inches apart.

3.1.3. All of the other portions of the generation system such as the connecting tubing and fittings were made of stainless steel or Teflon to avoid any contamination problems.

3.1.4. The flow rate of the test atmosphere into the sampling manifold was approximately 2.2 times the total sampling flow rate.

3.1.5. The flow rate of the certified sulfur dioxide gas was monitored and controlled by means of a Tylan mass flow controller. The flow rate, temperature and relative humidity of the air was controlled by means of a Miller-Nelson Research Inc. Model HCS-201 Mass Flow-Temperature-Humidity Control System.

3.1.6. The flow rates of the certified sulfur dioxide gas and the air were measured at the 0.5 and 1 times test levels just prior to sampling. At twice the test level, the flow rates were measured just prior

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[1] The calibration was performed by the OSHA Health Response Team.

to and just after the sampling. The flow rate of the certified sulfur dioxide gas was measured by means of a Mast Development Co. Model 823-1 Electronic Bubble flowmeter. The flow rate of the humid air was measured by means of a dry test meter which had been calibrated against a primary standard.[1]

3.1.7. A calibrated Interscan Sulfur Dioxide Analyzer was used to continuously monitor the sulfur dioxide concentration of the test atmosphere in the sampling manifold during the sampling process at the 2X level.[1]

3.1.8. Test atmospheres at the 0.5X and 1X levels were generated at a temperature of 24 degrees C and a relative humidity of 75%. The test atmosphere at the 2X level was generated at 24 degrees C and 50% relative humidity.

3.2. Collection of generated samples:

3.2.1. Six samples were collected simultaneously for sixty minutes at a flow rate (with one exception) of approximately 1.0 liter per minute at each of the three test levels.

3.2.2. Samples were collected in midget bubblers containing 15 ml of 0.3 N hydrogen peroxide by means of E.I. Dupont De Nemours and Co. Model P-4000 constant flow sampling pumps.

3.2.3. Midget bubblers were connected to the sampling ports of the manifold with Teflon tubing and fittings without use of a prefilter and to the sampling pumps with a short piece of Tygon tubing. Sampling port positions one, three and five on one side of the manifold were used for the collection of three samples and port positions two, four and six on the other side of the manifold were used for the collection of the other three samples. The six unused sampling ports were plugged during the sampling process.

3.2.4. At each test level, the flow rates of the sampling pumps were calibrated during the sampling process by means of a 1000 ml soap bubble flowmeter.

3.2.5. After sampling, the samples were transferred to clean 25 ml volumetrics. The bubbler base and stem were rinsed with 4-8 ml of unused 0.3 N hydrogen peroxide and the rinsings were added to the 25 ml volumetrics which were then diluted to volume with 0.3 N hydrogen peroxide.

3.3. Analysis of known generated samples: the generated samples were analyzed by ion chromatography. Each sample was analyzed twice. The results of sampling and analysis are shown in Table II.

4. Collection Efficiency and Breakthrough[2]

4.1. Two midget bubblers were connected in series to each other with a short piece of Tygon tubing. Fifteen ml of 0.3 N hydrogen peroxide was added to each bubbler.

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[2] Sampling was performed by the OSHA Health Response team. Analysis was performed by the Inorganic Service Branch of the OSHA laboratory.

4.2. Five samples were collected at a concentration of approximately twice the OSHA PEL from 240 to 270 minutes at approximately 1.0 liter per minute as described in section 3.

4.3. After sampling, the samples were transferred to clean glass 20 ml scintillation vials. The bubbler base and stem were rinsed with 2-3 ml of unused 0.3 N hydrogen peroxide and the rinsings were added to the glass vials.

4.4. The amount of sulfur dioxide collected in each bubbler was then measured. The collection efficiency of the first bubbler was calculated by dividing the amount of sulfur dioxide collected in the first bubbler by the total amount of sulfur dioxide collected in the first and second bubblers. The breakthrough was calculated by dividing the amount of sulfur dioxide collected in the second bubbler by the total amount of sulfur dioxide collected in the first and second bubblers. The results are reported in Table III. The collection efficiency was found to be 100%. No breakthrough occurred.

5. Storage Stability: a study was conducted to assess the stability of sulfur dioxide air samples when stored in midget bubblers containing 0.3 N hydrogen peroxide.

5.1. The six samples at the OSHA - PEL level which were generated and analyzed in the Sampling and Analysis Study (see section 3) were used in the storage stability study.

5.2. Twenty five ml volumetric flasks containing the samples were closed tightly and stored in the light at ambient laboratory temperature. The samples were analyzed after 1, 24, and 31 day storage periods.

5.3. Results of the storage stability study are shown in Table IV. These results indicate that samples may be stored under the conditions found at the OSHA laboratory for a period of at least 31 days.

6. Detection limit

6.1. The Wilcoxon's Rank Sum Test was used for the determination of the qualitative detection limit of sulfur dioxide analysis by ion chromatography. The test is a non-parametric or a distribution-free test. A detailed description of this test is explained in the formaldehyde backup report (11.2.). The results of using the Wilcoxon's Rank Sum Test are shown in Table V. As shown in Table V, the qualitative detection limit is 0.013 ug of sulfur dioxide per injection at the 95% confidence level or 1.0 ug of sulfur dioxide in a 15 ml sample volume for a 200 ul sample injection volume. This corresponds to 0.017 mg/m^3 of sulfur dioxide for 260 liter air volume.

6.2. The quantitative determination limit is 0.033 ug of sulfur dioxide per injection or 2.5 ug of sulfur dioxide in a 15 ml sample volume for a 200 ul sample injection volume. This corresponds to 0.042 mg/m^3 of sulfur dioxide for a 60 liter air volume. The relative standard deviation of replicate determinations of standards at this level was less than 0.10.

7. Comparison of method: the barium perchlorate titration (BPT) procedure was chosen as the "reference" method to which the results of the "candidate" ion chromatography method were compared. The three sets of sodium sulfate spiked samples at 0.5, 1, and 2 times the OSHA PEL level

which were prepared and analyzed in the analysis study (see section 2.2.1) were used in this comparison of method study. The NIOSH BPT procedure was used with slight modifications (11.3.).

7.1. Reagents

7.1.1. Isopropanol, Mallinckrodt nanograde.

7.1.2. Hach Chemical Co. 0.00521 M-Barium Perchlorate.

7.1.3. Thorin Indicator Solution (0.15% in deionized water).

7.1.4. Perchloric Acid (1.8%): twenty five ml of Baker Analyzed reagent grade perchloric acid (70-72%) was diluted to one liter with deionized water.

7.2. Analytical procedure

7.2.1. Transfer an aliquot (4.6 - 9.5 ml) of the sulfate spiked sample to a clean 250 ml Erlenmeyer flask.

7.2.2. Add 100 ml of isopropanol to the flask.

7.2.3. Adjust the pH of the sample to 3.2 - 3.5 with 1.8% perchloric acid.

7.2.4. Add eight drops of the Thorin indicator to the flask and then titrate the sample with the 0.00521 M barium perchlorate solution with a 10 ml burette to a pink colored end point. A fluorescent lamp may be used to aid in identifying the end point.

7.2.5. Calculate the amount of sulfur dioxide found in the sample from the volume (ml) of barium perchlorate solution needed to titrate the sample. Blank corrections must be made.

7.3. Results: the comparison data of the BPT (reference) and IC (candidate) methods for 0.5, 1, and 2 times the OSHA PEL standard are shown in Table VI. This data will be used in estimating the different types of errors from which valid judgments on the acceptability of the method may be made. The statistical analysis of the method comparison will be described in detail in the next section, "Precision and Accuracy."

8. Precision and Accuracy

8.1. The precision and accuracy data based on the NIOSH statistical protocol (11.4) are presented in Table I and II. The pooled coefficients of variation for spiked (CV_1) and generated (CV_2) samples and the overall CV_T are as follows:

$$CV_1 = 0.018, \quad CV_2 = 0.010, \quad CV_T = 0.012$$

The average recovery of the generated samples over all levels was 95.4%. Any variation from 100% recovery was probably related to difficulties in generating the atmosphere containing the sulfur dioxide at a given concentration rather than the true bias in the method.

8.2. Method comparison: see reference (11.2.) for the detailed description about procedures, calculations, and discussions.

8.2.1. A summary of the data from the computer calculations follows:

$N = 18$	number of measurement
$X_{av} = 0.8306$ mg	average value for all "reference" measurements
$Y_{av} = 0.8263$ mg	average value for all "candidate" measurements
$S_b = 0.0102$	standard deviation for the slope, b
$S_a = 0.00956$	standard deviation for the intercept, a
$df = 17$	degrees of freedom

$P = 0.05$	probability
$t = -0.9139$	observed t-value
$t_c = 2.11$	critical t-value
$F = 1.038$	observed F-value
$F_c = 2.30$	critical F-value
$b = 1.018$	slope
$a = -0.01919$ mg	intercept
$S_{y/x} = 0.01882$ mg	standard error
bias = -0.00429 mg	the difference between the means of the two methods
$S_d = 0.01994$ mg	standard deviation of differences
$r = 0.9992$	correlation coefficient

8.2.2. Conclusions

8.2.2.1. The calculated value for the slope is 1.018 which indicates a proportional error of 1.8%. The 95% confidence interval for the slope is:

$$b \pm t_c S_b = 1.018 \pm 2.11 \times 0.0102$$
$$= 0.997 \text{ to } 1.040$$

The calculated value for the slope is therefore not significantly different from the ideal value of 1.000.

8.2.2.2. The constant error is estimated at -0.01919 mg by the y intercept. The 95% confidence interval for the intercept is:

$$a \pm t_c S_a = -0.0192 \pm 2.11 \times 0.00956 \text{ mg}$$
$$= -0.0394 \text{ to } 0.0010 \text{ mg}$$
$$= -39.4 \text{ to } 1.0 \text{ ug}$$

The calculated value for the intercept is therefore not significantly different from the ideal value of 0.0000.

8.2.2.3. The random error is estimated to be 18.8 ug by the standard error.

8.2.2.4. The correlation coefficient is 0.9992 which means that the range of data studied is wide enough.

8.2.2.5. For a sulfur dioxide value of 831 ug by the barium perchlorate titration method, the IC method will on the average give a result of 826 ug (the same value to two significant figures). Since $S_{y/x}$ is 18.8 ug, the uncertainty in the value of sulfur dioxide by the IC method at the 95% confidence interval will be between ± 39.7 ug.

8.2.2.6. The fact that t is less than t_c and F is less than F_c indicates, respectively, that a systematic error has not been shown to exist and that the random error of the "candidate" IC method is not different from the random error of the "reference" method. However, the t and F values should not be used as indicators of acceptability of the performance of the "candidate" IC method.

9. Interferences

9.1. Particulate sulfate and sulfuric acid interferences can be removed by use of a 37 mm diameter cellulose ester membrane prefilter (Millipore Type AA or equivalent) supported by a cellulose backup pad. Sulfur dioxide is not adsorbed onto the prefilter at low and high relative humidity (11.5). Studies made by the OSHA Health Response

Team indicate that the use of a cellulose backup pad to support the prefilter and that particulate matter collected on the prefilter will not hinder the collection of sulfur dioxide.

9.2. Sulfur trioxide gas (SO_3), if present in a dry atmosphere, gives a positive bias in the SO_2 determination.

10. Additional Information

10.1. Comparison of collecting techniques for sampling sulfur dioxide: A study of midget impinger vs bubbler samplers made by the OSHA Health Response Team indicates no significant difference between the collection efficiency or breakthrough.

11. References

11.1. OSHA Method No. ID104 for Sulfur Dioxide in Workplace Atmospheres, Inorganic Methods Evaluation Branch, OSHA Analytical Laboratory, 1981.

11.2. Backup Data Report No. ID101 for Formaldehyde, Inorganic Methods Evaluation Branch, OSHA Analytical Laboratory, 1981.

11.3. Taylor, D.G. Ed. "NIOSH Manual of Analytical Methods," 2nd ed.; DHEW (NIOSH) Publication No. 78-175; U.S. Government Printing Office: Washington, D.C., 1978; Vol. 4, Method No. S308.

11.4. Taylor, D.G.; Kupel, R.E.; Bryant, J.M. "Documentation of the NIOSH Validation Tests," DHEW (NIOSH) Publication No. 77-185; U.S. Government Printing Office: Washington, D.C., 1977.

11.5. Backup Data Report No. S308 for Sulfur Dioxide, U.S. Department of Health, Education and Welfare, NIOSH, Cincinnati, OH, July 8, 1977.

Sulfur Dioxide Backup Data Report

PRECISION AND ACCURACY DATA (PAD)
TABLE I
DATA SHEET: SULFUR DIOXIDE
ANALYSIS

LEVEL 0.5S (OSHA-PEL)			1S			2S		
MG TAKEN	MG FOUND	AMR	MG TAKEN	MG FOUND	AMR	MG TAKEN	MG FOUND	AMR
0.362	0.351	0.970	0.723	0.698	0.965	1.425	1.430	1.004
0.362	0.355	0.981	0.723	0.717	0.992	1.425	1.428	1.002
0.362	0.353	0.975	0.723	0.679	0.939	1.425	1.396	0.980
0.362	0.355	0.981	0.723	0.685	0.947	1.425	1.425	1.000
0.362	0.364	1.006	0.723	0.721	0.997	1.425	1.410	0.989
0.362	0.366	1.011	0.723	0.710	0.982	1.425	1.432	1.005
N =		6			6			6
MEAN		0.987			0.970			0.997
STD DEV		0.017			0.024			0.010
CV_1		0.017			0.025			0.010

CV_1 (POOLED) = 0.018

TABLE II
DATA SHEET: SULFUR DIOXIDE
SAMPLING AND ANALYSIS

TEST LEVEL-------------FOUND-----------------------TAKEN
(OSHA-PEL)

	SMPL NO.	ug	Corr ug	LITERS	mg/m^3	mg/m^3	RECOVERY
0.5S							
	1	300.300	300.300	59.300	5.064	5.451	92.902
	2	308.000	308.000	59.200	5.203	5.451	95.445
	3	481.500	481.500	91.900	5.239	5.451	96.118
	4	301.700	301.700	57.700	5.229	5.451	95.923
	5	281.700	281.700	55.200	5.103	5.451	93.621
	6	312.300	312.300	60.500	5.162	5.451	94.698
				N =	6		
				MEAN	5.167		94.784
				STD DEV	0.0707		1.2975
				CV_2	0.0137		
1S							
	1	608.400	608.400	59.700	10.191	10.610	96.050
	2	607.900	607.900	59.500	10.217	10.610	96.294
	3	601.300	601.300	59.000	10.192	10.610	96.056
	4	585.700	585.700	58.600	9.995	10.610	94.202
	5	564.500	564.500	56.300	10.027	10.610	94.502
	6	619.700	619.700	61.100	10.142	10.610	95.593
				N =	6		
				MEAN	10.127		95.450
				STD DEV	0.0939		0.8850
				CV_2	0.0093		
2S							
	1	1268.700	1268.700	59.300	21.395	22.090	96.852
	2	1256.900	1256.900	59.100	21.267	22.090	96.276
	3	1238.000	1238.000	58.900	21.019	22.090	95.150
	4	1217.600	1217.600	57.700	21.102	22.090	95.529
	5	1173.400	1173.400	55.700	21.066	22.090	95.366
	6	1300.600	1300.600	61.200	21.252	22.090	96.205
				N =	6		
				MEAN	21.183		95.896
				STD DEV	0.1440		0.6520
				CV_2	0.0068		

CV_1(Pooled) = 0.018
CV_2(Pooled) = 0.01
CV_T(Pooled) = 0.012
Avg Mean Recovery = 95.377

TABLE III
COLLECTION EFFICIENCY AND BREAKTHROUGH

Sample no.	Time,min	mg/m^3 found 1st bubbler	mg/m^3 found 2nd bubbler	Collection Efficiency (%)	Breakthrough (%)
1	270	19.6	ND	100.0	0.0
2	270	19.4	ND	100.0	0.0
3	270	19.2	ND	100.0	0.0
4	240	19.3	ND	100.0	0.0
5	240	19.1	ND	100.0	0.0
			Average	100.0%	0.0%

ND - DET LIM = 56.8 ug SO_2 in a 16.7 ml sample volume or
= 0.210 mg/m^3 based on a 270 liter air volume;
1 liter per minute flow rate for 270 minutes.

Sulfur Dioxide Backup Data Report

PRECISION AND ACCURACY DATA (PAD)
TABLE IV
DATA SHEET: SO_2
STABILITY TEST

TEST LEVEL (OSHA-PEL)				FOUND		TAKEN	
1	SMPL NO.	ug	CORR ug	LITERS	MG/CU M	MG/CU M	RECOVERY
	1	608.400	608.400	59.700	10.191	10.610	96.050
	2	607.900	607.900	59.500	10.217	10.610	96.294
	3	601.300	601.300	59.000	10.192	10.610	96.056
	4	585.700	585.700	58.600	9.995	10.610	94.202
	5	564.500	564.500	56.300	10.027	10.610	94.502
	6	619.700	619.700	61.100	10.142	10.610	95.593
				N =	6		
				MEAN	10.127		95.450
				STD DEV	0.0939		0.8850
				CV_2	0.0093		
24	DAYS						
	1	586.900	586.900	59.700	9.831	10.610	92.656
	2	601.200	601.200	59.500	10.104	10.610	95.233
	3	595.900	595.900	59.000	10.100	10.610	95.193
	4	593.100	593.100	58.600	10.121	10.610	95.393
	5	567.200	567.200	56.300	10.075	10.610	94.954
	6	631.800	631.800	61.100	10.340	10.610	97.459
				N =	6		
				MEAN	10.095		95.148
				STD DEV	0.1620		1.5269
				CV_2	0.0160		
31	DAYS						
	1	596.700	596.700	59.700	9.995	10.610	94.203
	2	597.700	597.700	59.500	10.045	10.610	94.678
	3	593.000	593.000	59.000	10.051	10.610	94.730
	4	583.500	583.500	58.600	9.957	10.610	93.849
	5	556.300	556.300	56.300	9.881	10.610	93.129
	6	621.400	621.400	61.100	10.170	10.610	95.855
				N =	6		
				MEAN	10.017		94.407
				STD DEV	0.0979		0.9231
				CV_2	0.0098		

TABLE V
Wilcoxon's Rank Sum Test
(ns = nb = 6)

Rank	Sample	pk ht (mm)
1	RB1	1.2
2	RB1	1.2
3	RB1	1.2
4	RB1	1.7
5	RB1	1.8
6	RB1	1.9
7	Std	2.6
8	Std	2.8
9	Std	3.4
10	Std	3.7
11	Std	4.0
12	Std	4.2

RB = 21

C = 99.99%

Detection Limit = 0.013 ug SO_2 per injection

Notes (1) Injection volume of both reagent blank and standard was 200 ul.

(2) Standard is 0.013 ug SO_2.

TABLE VI

Comparison Study of Sulfur Dioxide Analysis
in 0.3N Hydrogen Peroxide Solution
Barium Perchlorate Titration (BPT) vs Ion Chromatography (IC)

PEL = 13 mg/m^3

Level 0.5S PEL

mg taken	mg found (IC)	AMR (IC)	mg found (BPT)	AMR (BPT)
0.362	0.351	0.970	0.345	0.952
0.362	0.355	0.981	0.380	1.050
0.362	0.353	0.975	0.360	0.995
0.362	0.355	0.981	0.356	0.984
0.362	0.364	1.006	0.363	1.002
0.362	0.366	1.011	0.353	0.974
n	=	6		6
mean	=	0.987		0.993
std dev	=	0.017		0.033
CV_1	=	0.017		0.034

Level 1.0S PEL

mg taken	mg found (IC)	AMR (IC)	mg found (BPT)	AMR (BPT)
0.723	0.698	0.965	0.734	1.016
0.723	0.717	0.992	0.744	1.028
0.723	0.679	0.939	0.715	0.989
0.723	0.685	0.947	0.689	0.953
0.723	0.721	0.997	0.728	1.006
0.723	0.710	0.982	0.738	1.021
n =		6		6
mean =		0.970		1.002
std dev =		0.024		0.028
CV_1 =		0.025		0.028

Level 2.0S PEL

mg taken	mg found (IC)	AMR (IC)	mg found (BPT)	AMR (BPT)
1.425	1.430	1.004	1.394	0.978
1.425	1.428	1.002	1.425	1.000
1.425	1.396	0.980	1.394	0.978
1.425	1.425	1.000	1.407	0.987
1.425	1.410	0.989	1.414	0.992
1.425	1.432	1.005	1.413	0.992
n	=	6		6
mean	=	0.997		0.988
std dev	=	0.010		0.010
CV_1	=	0.010		0.009

The average AMR BPT at each level is 0.994
The average AMR IC at each level is 0.985

OSHA

ANALYTICAL METHODS
MANUAL

OSHA ANALYTICAL LABORATORY
SALT LAKE CITY, UTAH
1985