Collection and Determination of Sulfur Dioxide
Incorporating Permeation and the West-Gaeke Procedure

1. SCOPE AND FIELD OF APPLICATION

1.1 This method (9.1) provides a technique for sampling and determining the average concentration of sulfur dioxide (SO_2) in the ambient atmosphere for periods from 6 hours to 1 week. The method is selective, sensitive, reproducible and suitable for field use. Sampling is accomplished by permeation through a silicone membrane with subsequent determination by the West-Gaeke Method (9.2).

1.2 The lower limit of detection for a 24hr sampling period is $5\mu g/m^3$ (based on twice the standard deviation of the blank) while the analytical range is from 5 to $1,000\mu g/m^3$.

1.3 The precision is 2 to 3% when repetitive samples are run by the same operator under laboratory conditions. The accuracy under field conditions is primarily limited by variations of ambient temperature. Variations of $\pm 10°C$ will cause errors no greater than 5%.

1.4 The method is particularly well suited for taking 24hr averages which are often stipulated by various regulating bodies.

1.5 At concentrations of $600\mu g/m^3$ of hydrogen sulfide, $500\mu g/m^3$ ozone and $300\mu g/m^3$ nitrogen dioxide, no significant interferences occur. Particulates should not interfere since they cannot permeate the membrane. At $4,500\mu g/m^3$ of hydrogen sulfide darkening of the silicone membrane occurs. This is accompanied by the formation of yellow spots on the membrane and pinholes through which liquid may leak. Permeation devices with darkened membranes should, therefore, be discarded.

2. PRINCIPLE

2.1 Sampling is accomplished with a permeation device consisting of a glass tube with a silicone membrane across one end. Sodium tetrachloromercurate (II) is placed inside the tube in contact with the membrane. When the tube is exposed, SO_2 after permeating the silicone membrane is absorbed and stabilized as the dichlorosulfitomercurate (II) complex (9.3). The amount of SO_2 absorbed in a given amount of time can then be related to the average concentration because the rate of permeation of SO_2 is directly proportional to the concentration of SO_2 to which the device is exposed.

2.2 The absorbed sulfur dioxide is analyzed by the traditional West-Gaeke method by addition of acidified pararosaniline and formaldehyde. The absorbance of the magenta colored product is then read at 575nm and the amount of SO_2 in the absorbing solution is found on a calibration chart. The ambient concentration can be calculated from the amount of SO_2 absorbed by use of a calibration constant that has been previously determined for the particular permeation device used. The device is calibrated by exposing it to a known concentration of SO_2.

2.3 The dichlorosulfitomercurate (II) decomposes on exposure to direct sunlight. A light shielding box is used to mount the permeation device to protect the solution.

3. REAGENTS

3.1 Reagent grade chemicals shall be used in all tests and shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society,[1] where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

3.2 *Purity of water*

High quality deionized water should be used in all test solutions. Water must be free of oxidants.

3.3 *Sodium tetrachloromercurate (II), 1.0 M*

Dissolve 272g of mercuric chloride ($HgCl_2$) (*Caution:* Highly poisonous), and 117g sodium chloride (NaCl) in water and dilute to 1 liter.

3.4 *Pararosaniline hydrochloric solution*

Dissolve 0.7g of pararosaniline in 240ml of concentrated hydrochloric acid and water and dilute to 1 liter. Dilute 20ml of this concentrate to 100ml with water. This solution is stable for at least three months. The concentrate is stable for at least a year. The use of impure pararosaniline may result in high reagent blanks. Blanks (vs. water) of approximately 0.02 absorbance units should be obtained for 1cm cells if the reagent is of acceptable quality.

3.5 *Formaldehyde, 0.2%*

Dilute 0.5ml of 37% formaldehyde to 100ml with deionized water. This solution should be prepared daily.

4. APPARATUS

4.1 *Permeation device*

The permeation device is prepared by sealing a 0.0025cm thick film of single backed (polyester) silicone rubber[2] to the end of a 41mm O.D x 80mm long glass tube using silicone rubber cement. The membrane backing should be on the exterior of the finished device. For calibration, the device is inserted into a rubber stopper. After calibration, the glass tube is wrapped with tape to help protect absorbed SO_2 from sunlight. A one hole rubber stopper with an 8cm long 1mm I.D. capillary inserted into it is installed in the top of the device to eliminate internal pressures.

4.2 *Shelter*

A light shielding box is used to mount the permeation device. There should be free movement of air through the box and the permeation device should be mounted near the top of the center of the box.

4.3 *Flowmeters*

Dry test meters or rotameters with an accuracy of ±2% should be used for calibrating membranes.

4.4 *Calibration chamber*

A calibration chamber into which the permeation device can be placed must be used.

4.5 *Photometer*

Most spectrophotometers, colorimeters and filter photometers are satisfactory. The precision of the photometric readout should be better than 2% between 0.3 and 0.5 absorbance units.

5. SAMPLING

5.1 *Collection of sample*

Place 10ml of 1 M sodium tetrachloromercurate (II) in the permeation device. Expose the device to the ambient atmosphere in the shelter designed for the device. Normal exposures vary from 6 hours to 7 days (see clause 8.1). If more than half the solution evaporates during the exposure period, the loss should be made up with deionized water.

5.2 At the end of the exposure period transfer the sample to a container suitable for transporting the sample. During this step, and succeeding steps, the sodium tetrachloromercurate (II) must be protected from sunlight.

6. PROCEDURE

6.1 *Safety precautions*

If solutions containing sodium tetrachloromercurate (II) are spilled on skin, flush with water immediately. Mercury wastes should be recovered when possible by addition of 100g of zinc to 1 liter of the spent sodium tetrachloromercurate (II) solution or by other procedures (9.7, 9.8) and sent to a reprocessor (9.8).

6.2 *Determination*

Adjust the volume of the trapped sample to 10.0ml by adding an appropriate amount of water. Add 1ml each of the pararosaniline and formaldehyde solutions and stir vigorously. Read the absorbance at 575nm after 40 ± 10 minutes versus a reagent blank treated identically as the sample and find the total μg (w) of SO_2 in the sample from a calibration plot. Samples above the range of calibration can be diluted several times with the reagent blank to obtain absorbance readings on scale, but this exercise should be carried out only to save a sample.

6.3 *Calibration and standards*

6.3.1 Preparation of standard sulfur dioxide concentrations

Calibrate permeation tubes that contain liquified SO_2 gravimetrically and use to prepare standard concentrations of SO_2 in air (9.4, 9.5, 9.6). Use these standard concentrations of SO_2 to calibrate the permeation device and prepare known solutions of SO_2 in sodium tetrachloromercurate (II).

Prepare or obtain[3] an FEP fluorocarbon tube that emits at a rate of 3 to $6\mu g/min$. Larger tubes or a group of tubes may be used for calibration of several of the permeation devices at one time. Maintain the tube under a stream of clean dry air or nitrogen (100ml/min) with the temperature controlled to $\pm 0.1°C$. The permeation tube may then be immersed in a constant temperature bath. Calibrate the tube (to a precision of $\pm 2\%$) by weighing the tube about every four days. The tube should be weighed to $\pm 0.1mg$ and the time recorded to the nearest 10min. The rate of permeation will be given by the equation.

$$Rate = \frac{Weight\ Loss\ (\mu g)}{Time\ (min)}$$

For use as a standard source of SO_2 increase the flow rate to between 1 and 2 l/min and allow to equilibrate for 5min. A concentration of about $3,000\mu g/m^3$ should be produced.

6.3.2 Calibration curves for sodium tetrachloromercurate (II)

Absorb $500\mu g$ of SO_2 from the standard source into 150ml of 1 M sodium tetrachloromercurate (II) using a 250ml bubbler equipped with an extra coarse frit. After collection, transfer the sample quantitatively to a 250ml volumetric flask using two 10ml portions of unexposed sodium tetrachloromercurate (II) and dilute to volume with this same reagent. This solution is stable for 1 month if refrigerated.

Pipet graduated amounts (such as 0, 2, 4, 6, 8, and 10ml) of the above standard and corresponding amounts of unexposed tetrachloromercurate (II) into a series of 25ml Erlenmeyer flasks or test tubes to give a total volume of 10ml. Then add the remaining reagents as described in the procedure (see clause 6.2) and plot absorbance (vs. blank) against the total micrograms of SO_2. The plot is not linear above about $8\mu g$ SO_2.

6.3.3 Calibration of permeation device

Flow standard SO_2 in air through the calibration chamber for 5 minutes. Add 10ml of sodium tetrachloromercurate (II) to the permeation device. Insert the device into the calibration chamber and note the time. Remove after 2 hours and analyze as described in the procedure (see clause 6.2).

7. EXPRESSION OF RESULTS

7.1 *Calculation of calibration constant*

Calculate the calibration constant as follows:

$$k = \frac{Pt}{rw}$$

where: k = calibration constant.

t = exposure time, hr.

w = weight of SO_2 absorbed, μg.

P = rate of emission SO_2 by permeation tube $\mu g/min$.

r = flow rate of air at calibration temperature and pressure.

7.2 *Calculation of results*

Calculate the concentration of SO_2 in air as follows:

$$SO_2, \mu g/m^3 = \frac{wk}{t}$$

where: t = exposure time, hr.
w = weight of SO_2 absorbed, μg.
k = calibration constant.

The constant k, increases 0.5% for a 1°C increase in temperature, therefore, if the average temperature that the device is exposed to varies greatly from the temperature that the calibration was carried out it should be corrected for temperature. A compensation to relate data to the standard 760mm of Hg may also be made by the following equation:

$$k_p = \frac{760\ k}{p}$$

where: k_p = calibration constant at pressure, p.
p = average atmospheric pressure at sampling location.

8. NOTES ON PROCEDURES

8.1 *Solution containing SO₂*

Sampling solutions of dichlorosulfitomercurate (II) are somewhat unstable when stored at elevated temperatures. Therefore, long exposure periods at high temperatures should be avoided. A 24-hour sampling period can, in general, be tolerated except under extremely harsh conditions (temperatures greater than 40°C). At 40° and 30° the losses of sulfur dioxide are 3.0 and 0.5% per day. At lower temperatures the rate of SO_2 loss is practically neglibible. For extended storage (more than 1 week) the samples should be refrigerated.

8.2 *Precision and accuracy*

The precision is 2 to 3% when repetitive samples are run by the same operator under laboratory conditions. The accuracy under field conditions is primarily limited by variations of ambient temperature. Variations of ±10°C will cause errors no greater than 5%.

9. REFERENCES

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9.3   Nauman, R. V., West, P. W. and Tron, F. *Anal. Chem.*, **32**, 1,307, 1960.
9.4   O'Keeffe, A. E. and Ortman, G. C. *Anal. Chem.*, **38**, 760, 1966.

9.5   Scaringelli, F. P., Frey, S. A. and Saltzman, B. E. *Amer. Ind. Hyg. Assoc. J.*, **28**, 260, 1967.

9.6   Thomas, M. D. and Amtower, R. E. *J. Air Pol. Control Assoc.*, **16**, 618, 1966.

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9.8   Dean, R. B., Williams, R. T. and Wise, R. H. *Envir. Sci. and Tech.*, **5**, 1,044, 1971.

FOOTNOTES

1. "Reagent Chemicals, American Chemical Society Specifications", Am. Chemical Soc., Washington, D.C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards", by Joseph Rosin, D. Van Nostrand Co., Inc., New York, N.Y., and the "United States Pharmacopeia".

2. Silicone rubber film obtained from General Electric Co. has been found to be satisfactory.

3. Permeation tubes are available from the U.S. Bureau of Standards, Metronics, Inc., 3201 Porter Drive, Palo Alto, California, 94304 and Polyscience Corp., P.O. Box 791, Evanston, Illinois, 60204.