Determination of Sulfur Dioxide
by the West-Gaeke Method

1. INTRODUCTION

The determination of sulfur dioxide in air is complicated by the presence of oxygen and the coexistence of other pollutants, such as the oxidants (ozone; oxides of nitrogen) or reductants (hydrogen sulfide; disulfide) that either react with the sulfur dioxide itself during sampling and storage or interfere with subsequent analytical processes. Acidic and/or basic substances in air further contribute to the complexity of the determination. The techniques employed for the determination include conductometry; polarography, iodimetry, acidimetry, gas chromatography, flame photometry, coulometry and spectrophotometry. Of all the methods proposed, the spectrophotometric method introduced by West and Gaeke in 1956 (12.1) remains the choice for critical studies because of its relative freedom from interferences, its sensitivity and its accuracy.

The spectrophotometric method has been subjected to exhaustive study by many laboratories and responsible agencies throughout the world. In general, collaborative studies have completely verified the reliability of the method. A number of minor modifications of the original procedure have been proposed mainly in the form of concentration changes of reagents. However, the modifications have generally introduced complications and have done little to improve the method. The procedure recommended is, therefore, the original one modified only in minor details.

2. SCOPE AND FIELD OF APPLICATION

This is the reference method for the determination of sulfur dioxide. It should be used for critical studies of air quality and, when suitably modified, it can be used for determining base-line values for "unpolluted" atmospheres. It is a preferred method for continuous air monitoring, provided the instrumentation employed is of sound design and construction.

The method can be used for spot checks, monitoring, field surveys, methods and instrument calibration and such other applications as require a sensitive, accurate and reliable method for the determination of sulfur dioxide.

3. PRINCIPLE OF THE METHOD

The West-Gaeke method is based on the absorption and stabilization of sulfur dioxide from air by a solution of sodium (or potassium) tetrachloro-

mercurate II, to form the dichlorosulfitomercurate II complex. The sulfito complex resists oxidation by atmospheric oxygen and is even stable in the presence of small amounts of strong oxidants such as ozone and the oxides of nitrogen.

Quantitative determinations of the collected sulfur dioxide is accomplished by adding acid-bleached pararosaniline hydrochloride and formaldehyde to the sulfito complex and measuring the intensely colored pararosaniline methylsulfonic acid so produced.

4. REACTIONS

4.1 Tetrachloromercurate II is produced by adding 2 moles of NaCl (or KCl) to 1 mole of $HgCl_2$

$$2NaCl + HgCl_2 \rightarrow 2Na^+ + [HgCl_4]^-$$
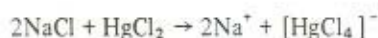
4.2 Sulfur dioxide is trapped and stabilized through complexation

$$SO_2 + [HgCl_4]^- + H_2O \rightarrow [HgCl_2 \, SO_3]^- + 2H^+ + 2Cl^-$$
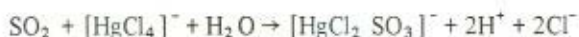
4.3 Formation of the color product, pararosaniline methylsulfonic acid. See 12.2.

5. REAGENTS

5.1 *Distilled water (or deionized water)*

Must be Cl_2 free.

5.2 *Tetrachloromercurate II, TCM, 0.1 M*

Dissolve 0.1 mole of mercury II chloride (27.2g) mole of sodium chloride (11.7g) in water and dilute to 1 liter.

5.3 *Formaldehyde, 0.2%*

Dilute 5ml of 37% formaldehyde to 1 liter with water. Prepare daily.

5.4 *Pararosaniline stock solution*

Mix 0.64g of pararosaniline hydrochloride with 240ml of concentrated hydrochloric acid, dilute to 1 liter with water and stir until dissolved. This solution is stable for at least 2 years and improves with age but a new calibration should be carried out at least once each year.

5.5 *Pararosaniline reagent*

Dilute stock solution 1:4 with water as needed. Stable at least 2 months.

5.6 *Sulfamic acid, 0.5%*

Dissolve 0.5g sulfamic acid in water and dilute to 100ml. Stable for several days at room temperature or several weeks if refrigerated.

6. APPARATUS

6.1 *Absorber*

A midget or other fritted bubbler should be used.

6.2 *Air monitoring equipment*

A suitable metering valve in conjunction with a wet or dry test gas meter or rotameter may be used to measure and control the air flow. With rotameters the metering valve should be placed downstream of the flowmeter. Alternatively calibrated hypodermic needles may be used as critical orifices with a pump that can maintain greater than a 0.5 atmospheric differential across the orifice. A membrane filter should be placed upstream of the critical orifice to protect the orifice from plugging and the filter should be changed at regular intervals.

A 22-gauge hypodermic needle will deliver a flow of about 1 liter/min while a 27-gauge needle 5/8in long will deliver a flow of 150 to 200ml/min (12.3).

7. SAMPLING AND SAMPLES

Add 10ml TCM to a midget bubbler. Insert the bubbler into the sampling system upstream of the air metering equipment. The sampling probe may consist of glass or TFE-Teflon and should be as short as possible. Collect about 30 liters of sample at a flow of between 0.5 and 2.5 liters/min typically 1 liter/min for 30 minutes. Twenty-four hour samples may be collected using 20ml of TCM and a flow rate of about 200ml/min. Water lost by evaporation should be replaced.

The TCM solution should be shielded from sunlight during and after sampling and extended exposure to temperatures above $30°-35°C$ should be avoided. If stored for more than 1 to 2 days the sample should be refrigerated. At $25°$, $30°$ and $40°C$, losses of sulfur dioxide occur at the respective rates of 1.0, 2.5 and 12% per day.

8. PROCEDURE

If a precipitate is observed in the sample, it should be removed by centrifugation or filtration. Allow 20 minutes between sampling and analysis to ensure decomposition of any ozone that may be present. To the sample and a 10.0ml TCM blank add 1.0ml each of the pararosaniline and the formaldehyde solutions and mix. Allow to stand for 30 minutes and read the absorbance relative to the blank at 560nm. If shortly after the addition of formaldehyde and pararosaniline an absorbance value above the analytical range appears likely, the sample should be diluted with an additional 10ml of TCM together with 1.0ml portions of pararosaniline and formaldehyde.

9. CALIBRATION CURVES

Permeation tubes containing liquid sulfur dioxide may be used (12.4) to prepare calibration curves (available from the U.S. Bureau of Standards, also Metronics, Inc., 3201 Porter Drive, Palo Alto, California, 94304 and Polyscience Corp., P.O. Box 791, Evanston, Illinois 60204). The permeation tube should be maintained under a stream of clean dry air or nitrogen ($\approx$100ml/min) with the temperature controlled to $\pm0.1°C$. Conveniently, the permeation tube may be placed in a 250ml bubbler and the bubbler may then be immersed in a constant temperature bath. Calibrate the tube gravimetrically at the intended operating temperature (to a precision of $\pm2\%$) by weighing the tube about every four days. The tube which should emit sulfur dioxide at a rate of 2 to 5μg/min should be weighed to ±0.1mg. Note the time to the nearest 5 minutes. The rate of permeation will be given by the equation.

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

Increase the flow rate over the tube to 1 liter/min and allow to equilibrate for 5 minutes. Absorb the emitted sulfur dioxide in 10 to 15ml TCM with a midget bubbler while maintaining the same flow rate. Remove the bubbler after absorbing 250μg of sulfur dioxide. Quantitatively transfer the solution to a 100ml volumetric flask. Rinse the bubbler twice with unexposed TCM and dilute to volume with this reagent. Dilute 2, 4, 6 and 8ml aliquots of this standard which contains 2.5μg/ml sulfur dioxide to 10ml with fresh TCM. Also take 10ml of the undiluted standard. Analyse the solutions by the method given in the procedure section (8) and plot μg sulfur dioxide per 10ml solution versus absorbance. Alternatively, anhydrous reagent grade sodium sulfite may be used to standardize the method.

190

10. EXPRESSION OF RESULTS

Convert the volume of air sampled to the volume at standard conditions of $25°C$, 760mm Hg;

$$V_R = V \times \frac{P}{760} \times \frac{298}{(t + 273)}$$

V_R = volume of air at $25°C$ and 1 atmosphere
V = volume of air sampled, liters
P = barometric pressure, mm Hg
t = temperature of air sampled, $°C$
    Ordinarily, the correction for pressure
    is slight and may be neglected.

Determine the concentration of sulfur dioxide in the sample by the following formula:

$$SO_2, \mu g/m^3 = \frac{W}{V_R}$$

Where $W = \mu g \, SO_2/10ml$ found from calibration curve
    10^3 = Conversion of liters to m^3.
Where desired, values may be reported in ppm,
    ppm $SO_2 = \mu g \, SO_2/m^3 \times 3.82 \times 10^{-4}$.

11. SPECIAL CASES

If high levels of nitrogen oxides (2 ppm or above) are expected 1ml of sulfamic acid may be added to the sample 10 minutes prior to analysis (12.5, 6). Large amounts of some heavy metal may interfere, these interferences may be eliminated by the addition of 0.07g of EDTA (ethylenediaminetetraacetate, tetrasodium salt) per liter of TCM prior to sampling (12.7, 8). If these modifications are to be used, calibration curves employing them should also be made.

12. REFERENCES

12.1 West, P. W. and Gaeke, G. C. *Anal. Chem.*, **28**, 1,816, 1956.
12.2 Nauman, R. V., West, P. W., Tron, F. and Gaeke, G. C. *Anal. Chem.*, **32**, 1,307, 1960.
12.3 Lodge, J. P. Jr., Pate, J. B., Ammons, B. E. and Swanson, G. A. *J. Air Pol. Control Assoc.*, **16**, 197, 1966.
12.4 O'Keeffe, A. E. and Ortman, G. C. *Anal. Chem.*, **38**, 760, 1966.

12.5 West, P. W. and Ardevesa, F. *Anal. Chem.*, **34**, 1,324, 1962.

12.6 Pate, J. B., Ammons, B. E., Swanson, G. A. and Lodge, J. P. Jr. *Anal. Chem.*, **37**, 942, 1956.

12.7 Zurlo, N. and Griffini, A. M. *Med. Lavoro.*, **53**, 330, 1962.

12.8 Scaringelli, F. P., Saltzman, B. E. and Frey, S. A. *Anal. Chem.*, **39**, 1,709, 1967.