Designation: D 2914 – 01

Standard Test Methods for Sulfur Dioxide Content of the Atmosphere (West-Gaeke Method)[1]

This standard is issued under the fixed designation D 2914; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 These test methods cover the bubbler collection and colorimetric determination of sulfur dioxide (SO_2) in the ambient or workplace atmosphere.

1.2 These test methods are applicable for determining SO_2 over the range from approximately 25 $\mu g/m^3$ (0.01 ppm(v)) to 1000 $\mu g/m^3$ (0.4 ppm(v)), corresponding to a solution concentration of 0.03 μg SO_2/mL to 1.3 μg SO_2/mL. Beer's law is followed through the working analytical range from 0.02 μg SO_2/mL to 1.4 μg SO_2/mL.

1.3 The lower limit of detection is 0.075 μg SO_2/mL **(1)**[2], representing an air concentration of 25 μg SO_2/m^3 (0.01 ppm(v)) in a 30–min sample, or 13 μg SO_2/m^3 (0.005 ppm(v)) in a 24–h sample.

1.4 These test methods incorporate sampling for periods between 30 min and 24 h.

1.5 These test methods describe the determination of the collected (impinged) samples. A Method A and a Method B are described.

1.6 Method A is preferred over Method B, as it gives the higher sensitivity, but it has a higher blank. Manual Method B is pH-dependent, but is more suitable with spectrometers having a spectral band width greater than 20 nm.

NOTE 1—These test methods are applicable at concentrations below 25 $\mu g/m^3$ by sampling larger volumes of air if the absorption efficiency of the particular system is first determined, as described in Annex A4.

NOTE 2—Concentrations higher than 1000 $\mu g/m^3$ can be determined by using smaller gas volumes, larger collection volumes, or by suitable dilution of the collected sample with absorbing solution prior to analysis.

1.7 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific precautionary statements, see 8.3.1, Section 9, and A3.1.1.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1071 Test Methods for Volumetric Measurement of Gaseous Fuel Samples[2]

D 1193 Specification for Reagent Water[3]

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres[4]

D 1357 Practice for Planning the Sampling of the Ambient Atmosphere[4]

D 1605 Practices for Sampling Atmospheres for Analysis of Gases and Vapors[5]

D 1914 Practice for Conversion Units and Factors Relating to Sampling and Analysis of Atmospheres[4]

D 3195 Practice for Rotameter Calibration[4]

D 3609 Practice for Calibration Techniques Using Permeation Tubes[4]

D 3631 Test Methods for Measuring Surface Atmospheric Pressure[4]

E 1 Specification for ASTM Thermometers[6]

E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near-Infrared Spectrophotometers[7]

2.2 *Other Standards:*

40 CFR Part 58 Probe and Monitoring Path Siting Criteria from Ambient Air Quality Monitoring, Appendix E[8]

3. Terminology

3.1 For definitions of terms used in this method, refer to Terminology D 1356.

4. Summary of Test Methods

4.1 Sulfur dioxide (SO_2) is absorbed by aspirating a measured air sample through a tetrachloromercurate (TCM) solution, resulting in the formation of a dichlorosulfonatomercurate

[1] These test methods are under the jurisdiction of ASTM Committee D22 on Sampling and Analysis of Atmospheres and are the direct responsibility of Subcommittee D22.03 on Ambient Atmospheres and Source Emissions.

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[2] *Annual Book of ASTM Standards*, Vol 05.06.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Annual Book of ASTM Standards*, Vol 11.03.

[5] *Discontinued*—See *1991 Annual Book of ASTM Standards*, Vol 11.03.

[6] *Annual Book of ASTM Standards*, Vol 14.03.

[7] *Annual Book of ASTM Standards*, Vol 03.06.

[8] Available from U.S Government Printing Office, Superintendent of Documents, 732 North Capitol Street, NW, Mail Stop: SDE, Washington, DC 20401.

complex **(2,3).**[9] Ethylenediaminetetraacetic acid disodium salt (EDTA) is added to this solution to complex heavy metals that interfere with this method **(4).** Dichlorosulfonatomercurate, once formed, is stable to strong oxidants (for example, ozone and oxides of nitrogen) **(2).** After the absorption is completed, any ozone in the solution is allowed to decay **(5).** The liquid is treated first with a solution of sulfamic acid to destroy the nitrite anion formed from the absorption of oxides of nitrogen present in the atmosphere **(6).** It is treated next with solutions of formaldehyde and specially purified acid-bleached pararosaniline containing phosphoric acid (H_3PO_4) to control pH. Pararosaniline, formaldehyde, and the bisulfite anion react to form the intensely colored pararosaniline methyl sulfonic acid which behaves as a two-color pH indicator **(2).** The pH of the final solution is adjusted to the desired value by the addition of prescribed amounts of 3 *N* H_3PO_4 to the pararosaniline reagent **(5).**

5. Significance and Use

5.1 Sulfur dioxide is a major air pollutant, commonly formed by the combustion of sulfur-bearing fuels. The Environmental Protection Agency (EPA) has set primary and secondary air quality standards **(7)** that are designed to protect the public health and welfare.

5.2 The Occupational Safety and Health Administration (OSHA) has promulgated exposure limits for sulfur dioxide in workplace atmospheres **(8).**

5.3 These methods have been found satisfactory for measuring sulfur dioxide in ambient and workplace atmospheres over the ranges pertinent in 5.1 and 5.2.

5.4 Method A has been designed to correspond to the EPA-Designated Reference Method **(7)** for the determination of sulfur dioxide.

6. Interferences

6.1 The interferences of oxides of nitrogen are eliminated by sulfamic acid **(5,6)**, of ozone by time delay **(5)**, and of heavy metals by EDTA and phosphoric acid **(4,5).** At least 60 μg of Fe(III), 10 μg of Mn(II), and 10 μg of Cr(III), 10 μg of Cu(II) and 22 μg of V(V) in 10 mL of absorbing reagent can be tolerated in the procedure. No significant interference was found with 2.3 μg of NH_3**(9)**.

7. Apparatus

7.1 *For Sampling*:

7.1.1 *Absorber, Short–Term Sampling*—An all-glass midget impinger having a solution capacity of 30 mL and a stem clearance of 4 ± 1 mm from the bottom of the vessel is used for sampling periods of 30 min and 1 h (or any period considerably less than 24 h).

7.1.2 *Absorber, 24-h Sampling*—A glass or polypropylene tube 32 mm in diameter and 164 mm long with a polypropylene two-port cap (rubber stoppers are unacceptable because the absorbing reagent can react with the stopper to yield erroneously high SO_2 concentrations, and cause high and variable blank values). Insert a glass impinger stem, 6 mm inside diameter and 158 mm long, into one port of the absorber cap. Taper the tip of the stem to a small diameter orifice (0.4 ± 0.1 mm) such that a No. 79 jeweler's drill bit will pass through the opening but a No. 78 drill bit will not. Clearance from the bottom of the absorber to the tip of the stem shall be 6 ± 2 mm. Perform the orifice test before use to verify the orifice size. Permanently mark the 50 mL volume level on the absorber. See Fig. 1.

7.1.3 *Air Sample Probe*—A sample probe meeting the requirements of Section 7 of 40 CFR Part 58, Appendix E, (TFE-fluorocarbon, polypropylene, or glass with a residence time less than 20 sec), used to transport ambient air to the sampling train location. Design or orient the end of the probe to preclude the sampling of precipitation, large particles, etc.

7.1.4 *Moisture Trap*—Glass or polypropylene trap as shown in Fig. 1, placed between the absorber tube and flow control device to prevent entrained liquid from reaching the flow control device. Pack the tube with coconut charcoal and glass wool or with indicating silica gel. Charcoal is preferred when collecting long-term samples (1 h or more) if flow changes are routinely encountered.

7.1.5 *Cap Seals*—Seal the absorber and moisture trap caps securely to prevent leaks during use, by using heat-shrink material to prevent the caps coming loose during sampling, shipment, or storage.

7.1.6 *Filter*, membrane, of 0.8 to 2.0 μm porosity, with filter holder, to protect the flow controller from particles during long-term sampling. This item is optional for short-term sampling.

7.1.7 *Pump*, equipped with vacuum gauge, capable of maintaining a vacuum greater than 70 kPa (0.7 atm) at the specified flow rate across the flow control device.

7.1.8 *Flow Control and Measurement Devices*:

7.1.8.1 *Flow Control Device*—A calibrated rotameter and needle valve combination capable of maintaining and measuring air flow to within ±2 percent is suitable for short-term sampling but shall not be used for long-term sampling. A critical orifice can be used for regulating flow rate for both long-term and short-term sampling. Use a 22-gage hypodermic needle 25 mm long as a critical orifice **(10)** to yield a flow rate of approximately 1 L/min for a 30–min sampling period. When sampling for 1 h, use a 23-gage hypodermic needle 16 mm in length to provide a flow rate of approximately 0.5 L/min. Provide a flow control for a 24–h sample by a 27–gage hypodermic needle critical orifice that is 9.5 mm in length so that the flow rate is in the range of 0.18 to 0.22 L/min.

7.1.8.2 *Flow Measurement Device*—calibrated as specified in 11.1.1, and used to measure sample flow rate at the monitoring site.

7.1.9 *Thermometer*—ASTM Thermometer 33C, meeting the requirements of Specification E 1 will meet the requirements of most applications in this method.

7.1.10 *Barograph or Barometer*, capable of measuring atmospheric pressure to ±0.5 kPa (5 torr).

7.1.11 *Temperature Control Device*—To maintain the temperature of the absorbing solution during sampling at 15 ± 10°C. Maintain the temperature of the collected sample at 5 ±

[9] The boldface numbers in parentheses refer to the list of references at the end of this standard.

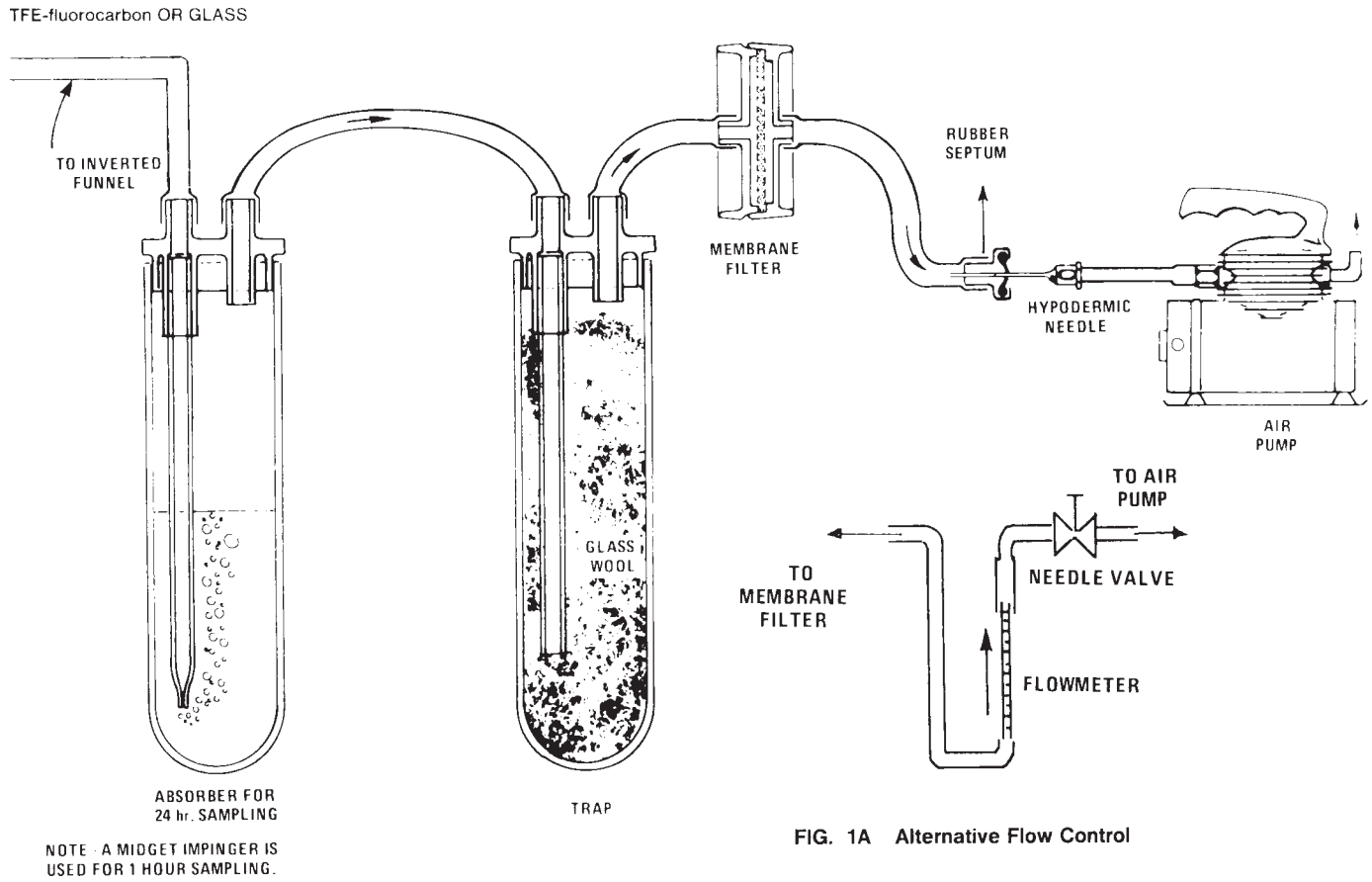

FIG. 1A Alternative Flow Control

FIG. 1 Sampling System

5°C, as soon as possible following sampling and until analysis. Where an extended period of time may elapse before the collected sample can be moved to the lower storage temperature, use a collection temperature near the lower limit of the 15 ± 10°C range to minimize losses during this period. Thermoelectric coolers specifically designed for this temperature control are available commercially and normally operate in the range of 5 to 15°C. Small refrigerators can be modified to provide the required temperature control; however, insulate the inlet lines from the lower temperatures to prevent condensation when sampling under humid conditions. A small heating pad may be necessary when sampling at low temperatures (<7°C) to prevent the absorbing solution from freezing **(11)**.

7.1.12 *Sampling Train Container*—a light-proof box to shield the absorbing solution from light during and after sampling.

7.1.13 *Timer*—to initiate and to stop sampling for the 24–h sampling period. This is not a required piece of equipment; however, without the timer it will be necessary to manually start and stop the sampling. An elapsed time meter may also be used to determine the sampling period.

7.1.14 The arrangement of the component parts for sampling is shown in Fig. 1.

7.2 *Shipping*:

7.2.1 *Shipping Container*—to maintain a temperature of 5 ± 5°C while transporting the sample from the collection site to the analytical laboratory. Ice coolers or refrigerated shipping containers have been found to be satisfactory. The use of eutectic cold packs instead of ice will give a more stable temperature control.

7.3 *Analysis*:

7.3.1 *Spectrophotometer or Colorimeter*—The instrument shall be suitable for measurement of color at 548 nm for Method A or 575 nm for Method B. For Method A, an effective spectral bandwidth of less than 15 nm is required since reagent blank problems may otherwise result. Verify the wavelength calibration of the spectrophotometer in accordance with Practice E 275 upon initial receipt of the instrument and after each 160 h or normal use or every 6 months, whichever occurs first, using a standard wavelength filter traceable to the National Institute of Standards and Technology.

7.3.2 *Spectrophotometer Cells*—A set of 1–cm path length cells suitable for use in the visible region. If the cells are unmatched, determine the matching correction factor according to 11.2.

7.3.3 *Temperature Control Device*—Conduct the color development steps during analysis in an environment that is in the range of 20 to 30°C and controlled to ±1°C. Perform both calibration and sample analysis under identical conditions (within 1°C). Adequate temperature control may be obtained by means of constant temperature baths, water baths with manual temperature control, or temperature controlled rooms.

7.3.4 *TCM Waste Receptacle*—A glass waste receptacle for the storage of spent TCM solution. Store the vessel stoppered in a hood at all times.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. All reagents shall conform to the specification of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[10] 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.

8.2 *Purity of Water*—Unless otherwise indicated, water shall be Type II distilled water in accordance with Specification D 1193. Water shall be free of oxidants.

8.2.1 Verify the purity of the distilled water as follows:

8.2.1.1 Place 0.20 mL of potassium permanganate solution (0.316 g/L), 500 mL of distilled water, and 1 mL of concentrated sulfuric acid in a chemically resistant glass bottle, stopper the bottle, and allow to stand.

8.2.1.2 If the permanganate color (pink) does not disappear completely after a period of 1 h at room temperature, the water is suitable for use.

8.2.1.3 If the permanganate color does disappear, the water can be purified by redistilling with one crystal each of barium hydroxide and potassium permanganate in an all glass still.

8.3 *Sampling Reagents*:

8.3.1 *Absorbing Reagent (0.04 M potassium tetrachloromercurate [TCM])*—Dissolve 10.86 g $HgCl_2$, 0.066 g EDTA, and 6.0 g KCl in distilled water and dilute to volume with distilled water in a 1000–mL volumetric flask. The pH of this reagent should be between 3.0 and 5.0 **(5).** Check the pH of the absorbing solution by using pH indicating paper or a pH meter. If the pH of the solution is not between 3.0 and 5.0, dispose of the solution according to the disposal technique described in Annex A3. The absorbing reagent is normally stable for 6 months. If a precipitate forms, dispose of the reagent according to Annex A3. (**Warning—**Mercuric chloride and TCM are very poisonous, particularly when concentrated. Avoid contact with skin and especially, with eyes. Avoid generating or breathing dust. Keep away from food. Wash hands after use. Do not ingest.)

8.3.1.1 Ethylenediaminetetraacetic acid disodium salt (EDTA).

8.3.1.2 Mercuric chloride, $HgCl_2$.

8.3.1.3 Potassium chloride, KCl.

8.3.2 *Acetate Buffer* (1 *M*)—Dissolve in a 100 mL volumetric flask, 13.61 g of sodium acetate trihydrate ($NaC_2H_5O_2 \cdot 3H_2O$) in 50 mL of water. Add 5.7 mL of glacial acetic acid (CH_3COOH) and dilute to 100 mL. The pH should be 4.74.

8.3.3 *1-Butanol*—Certain batches of 1-butanol contain oxidants that create a sulfur dioxide (SO_2) demand. Check by shaking 20 mL of 1-butanol with 5 mL of 15 % potassium iodide (KI) solution. If a yellow color appears in the alcohol phase, redistill the 1-butanol from silver oxide.

8.3.4 *Formaldehyde* (0.2 %)—Dilute 5 mL of 36 to 38 % formaldehyde (HCHO) to 1 L. Prepare this solution daily.

8.3.5 *Hydrochloric Acid* (1 *N*)—Slowly and while stirring, add 86 mL of concentrated hydrochloric acid to 500 mL of distilled water. Allow to cool and dilute to 1000 mL with distilled water. This is stable for one year.

8.3.6 *Pararosaniline, Stock Solution (PRA),* 0.2 %—Dissolve 0.2 g of pararosaniline in 100 mL of water. The stock pararosaniline solution shall meet the following specifications:

8.3.6.1 The solution shall have a wavelength of maximum absorbance at 540 nm for Method A or at 575 mn for Method B, in a buffered solution of 0.01 M sodium acetate-acetic acid.

8.3.6.2 The absorbance of the reagent blank, which is temperature-sensitive (0.015 absorbance units/°C) shall not exceed 0.170 absorbance units at 22°C with a 10-mm optical path length where the blank is prepared as specified and at the specified concentration of the stock pararosaniline solution.

NOTE 3—This specification is applicable only in the case of Method A.

8.3.6.3 The calibration curve (Annex A2) shall have a slope of 0.030 ± 0.002 absorbance units/μg SO_2, at the same optical path length, when the sulfite solution is properly standardized.

NOTE 4—This specification is applicable only in the case of Method A.

8.3.6.4 A specially purified (99 to 100 % pure) solution which meets the above specifications is commercially available in the required 0.20 % solution.

8.3.6.5 Alternatively, the dye may be purified as indicated in Annex A1.

8.3.7 *Pararosaniline Reagent*

8.3.7.1 Pipet 1.0 mL of stock pararosaniline solution into a 100 mL volumetric flask, and dilute to volume. Pipet 5.0 mL of that solution into a 50 mL volumetric flask. Add 5.0 mL of acetate buffer solution, and dilute to the mark. After 1 h, determine the absorbance at 540 nm for Method A or at 575 mn for Method B, with a spectrophotometer having a spectral bandwidth of less than 11 μm, using 1-cm optical path length. Determine the assay of PRA as follows:

$$M = \frac{A \times 21.3}{W} \quad (1)$$

where:

M = % PRA in sample,
A = absorbance of solutions,
W = the mass in g of the PRA dye used in the assay to prepare 50 mL of stock solution (that is, 0.1 g of dye was used to prepare 50 mL of the solution in the purification procedure described in Annex A1) (see Note 5), and
21.3 = constant to convert absorbance to mass.

NOTE 5—When commercial concentrate is used, use the stated purity to compute *w*. For example, if the stated purity is 98 %, *W* will be 0.098 g.

8.3.7.2 *Pararosaniline Reagent for Method A*—To a 1 L flask, add 80 mL of stock PRA, plus 0.8 mL of stock for each

[10] *Reagent Chemicals, American Chemical Society Specifications,* American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

percent the stock assays below 100 %. Add 100 mL of 3 *M* phosphoric acid and dilute to volume. This is stable for 9 months when stored at 25°C or below.

8.3.7.3 *Pararosaniline Reagent for Method B*—To a 1 L flask, add 80 mL of stock PRA, plus 0.8 mL of stock for each percent the stock assays below 100 %. Add 800 mL of 3 *M* phosphoric acid and dilute to volume. This is stable for 9 months when stored away from light at 25°C or below.

8.3.8 *Phosphoric Acid (3.0 M)*—Dilute 205 mL of concentrated phosphoric acid (H_3PO_4, sp gr 1.69) to 1 L by pouring the acid into 700 mL of water while stirring, then dilute to volume. This is stable for one year.

8.3.9 *Potassium Hydroxide Solution* (6 *N)*—Dissolve 33.67 g of potassium hydroxide (KOH) in 100 mL of water.

8.3.10 *Potassium Iodate Solution*—Accurately weigh to the nearest 0.1 mg, 1.5 g (record weight) of primary standard grade potassium iodate, KIO_3, that has been previously dried at 180°C for at least 3 h and cooled in a dessicator. Dissolve, then dilute to volume in a 500 mL volumetric flask with distilled water.

8.3.11 *Sulfamic Acid* (0.6 %)—Dissolve 0.6 g of sulfamic acid (NH_2SO_3H) in 100 mL of water. Prepare fresh daily.

8.4 *Calibration Reagents*:

8.4.1 *Iodine Solution, Stock* (0.1 *N*)—Dissolve 12.7 g of resublimed iodine (I_2) and 40 g of potassium iodide (KI) in 25 mL of water, and dilute to 1 L in a volumetric flask.

8.4.2 *Iodine Solution, Working (0.01 N)*—Dilute 50 mL of stock iodine solution (0.1 *N*) to 500 mL in a volumetric flask.

8.4.3 *Potassium Iodate Solution*—Accurately weigh to the nearest 0.1 mg, 1.5 g (record weight) of primary standard grade potassium iodate (KIO_3) that has been previously dried at 180°C for at least 3 h and cooled in a dessicator. Dissolve, then dilute to volume in a 500 mL volumetric flask with distilled water.

8.4.4 *Starch Indicator Solution*—Triturate 0.4 g of soluble starch and 2 mg of mercuric iodide (HgI_2) (preservative) with a little water and add the paste slowly to 200 mL of boiling water. Boil until clear; cool and transfer to a glass-stoppered bottle.

8.4.5 *Sodium Thiosulfate, Stock Solution (0.1 N)*—Dissolve 24.82 g of sodium thiosulfate ($Na_2S_2O_3 \cdot 5\ H_2O$) in freshly boiled, cooled water, add 0.1 g of sodium carbonate (Na_2CO_3), and dilute to 1 L. Allow the solution to stand for a day before standardizing.

8.4.5.1 To standardize, accurately pipet 50 mL of potassium iodate solution into a 500 mL iodine flask and add 2.0 g of potassium iodide and 10 mL of 1 N HCI. Stopper the flask and allow to stand for 5 min. Titrate the solution with stock sodium thisulfate solution to a pale yellow color. Add 5 mL of starch solution and titrate until the blue color just disappears. Repeat this procedure three times.

8.4.5.2 Calculate the normality of the sodium thiosulfate solution as follows:

$$N_s = \frac{W \times 10^3 \times 0.1}{V \times 35.67} \quad (2)$$

where:

N_s = normality of the sodium thiosulfate solution,
V = volume of thiosulfate solution taken, mL,
W = mass, g, of the KIO_3,
10^3 = conversion factor, mL to L,
0.1 = dilution factor, and
35.67 = gram equivalent weight of KIO_3.

Average the normality found from the three determinations.

8.4.6 *Sodium Thiosulfate, Working Solution (0.01N)*—Dilute 100 mL of stock sodium thiosulfate solution into a 1000 mL volumetric flask and dilute to volume with freshly boiled, cooled, distilled water. Calculate the normality of the working sodium thiosulfate titrant (NT) as follows:

$$N_T = N_s\, x\, 0.100 \quad (3)$$

8.4.7 *Sulfite Solution, Standard*—Dissolve 0.4 g of sodium sulfite (Na_2SO_3) or 0.3 g of sodium metabisulfite ($Na_2S_2O_5$) in 500 mL of recently boiled and cooled water (preferably doubly distilled deaerated water). This solution contains from 320 to 400 μg/mL as SO_2. The actual concentration in the standard solution is determined by adding a known excess of iodine and back titrating with sodium thiosulfate that has been standardized against the potassium iodate solution (primary standard). As sulfite solution is unstable, prepare fresh daily.

8.4.7.1 To back-titrate, pipet 50 mL of the 0.01 N iodine solution into each of two 500 mL iodine flasks (A and B). To flask A (blank) add 25 mL distilled water, and to flask B (sample) pipet 25 mL sulfite solution. Stopper the flasks and allow to stand for 5 min. Prepare the working sulfite-TCM solution immediately prior to adding the iodine solution to the flasks. Using the standardized 0.01 N thiosulfate titrant, titrate the solution in each flask to a pale yellow color. Then add 5 mL starch solution and continue the titration until the blue color just disappears.

8.4.7.2 *Working Sulfite-TCM Solution*—Pipet 5 mL of the standard sulfite solution into a 250 mL volumetric flask and dilute to volume with 0.04 M TCM. Calculate the concentration of sulfur dioxide in the working solution as follows:

$$C_{TCM/SO_2} = \frac{(A - B)\,(NT)\,(32{,}000)}{25} \times 0.02 \quad (4)$$

where:

C_{TCM/SO_2} = equivalent concentration of SO_2 in solution, μg/mL,
A = volume of thiosulfate titrant required for the blank, mL,
B = volume of thiosulfate titrant required for the sample, mL,
NT = normality of the thiosulfate titrant, from Eq 3,
32,000 = milliequivalent weight for SO_2, μg,
25 = volume of standard sulfite solution, mL, and
0.02 = dilution factor.

This solution is stable for 30 days if kept at 5°C **(12)**. Prepare fresh daily if not kept at 5°C.

8.4.7.3 *Dilute Working Sulfite-TCM Solution*—Prepare a dilute working sulfite-TCM solution by diluting 10 mL of the working sulfite-TCM solution to 100 mL with TCM absorbing reagent.

8.4.8 *Sulfur Dioxide Permeation Tube*—Permeation devices may be prepared or purchased and in both cases shall be traceable either to a National Institute of Standards and Technology (NIST) Standard Reference Material (SRM 1625, SRM 1626, SRM 1627) or to an NBS/EPA-approved commercially available Certified Reference Material (CRM). See Reference **(13)** for a description of CRM's and a list of CRM sources. A recommended protocol for certifying a permeation device to an NIST SRM or CRM is given in Practice D 3609. Device permeation rates of 0.2 to 0.4 μg/min, inert gas flows of about 50 mL/min, and dilution air flow rates from 1.1 to 15 L/min conveniently yield standard atmospheres in the range of 25 to 600 μg SO_2/m^3(0.010 to 0.230 ppm(v)).

9. Precautions

9.1 *Safety Precautions*:

9.1.1 *Mercury Compounds*—The absorbing solution contains mercury salts. Precautions to its use are shown in 8.3.1.

9.2 *Sampling and Transporting Precaution*—Maintain the temperature of the impinging solution below 25°C during sampling, transporting to the laboratory, and storage prior to analysis, to avoid loss of SO_2. Do not expose to light.

10. Sampling

10.1 See Practice D 1357 for general sampling guidelines.

10.2 Sampling procedures are described for short-term (30 min) and for long-term (24 h) sampling. Select different combinations of sampling rate and time to meet special needs, but adjust sample volumes and air flow rates so that the linearity is maintained between absorbance and concentration over the dynamic range.

10.3 See 12.1 for detailed sampling procedures.

10.3.1 *Determination of Flow Rate at Sampling Site*:

For short-term samples, determine the standard flow rate at the sampling site at the initiation and completion of sample collection with a calibrated flow measuring device connected to the inlet of the absorber. For 24 h samples, determine the standard flow rate at the time the absorber is placed in the sampling train and again when the absorber is removed from the train for shipment to the analytical laboratory with a calibrated flow measuring device connected to the inlet of the sampling train. Determine the flow rate with all components of the sampling system in operation (for example, the absorber temperature controller and any sample box heaters must also be operating). Use Eq 5 to determine the standard flow rate when a calibrated positive displacement meter is used as the flow measuring device. Other types of calibrated flow measuring devices may also be used to determine the flow rate at the sampling site provided that the user applies any appropriate corrections to devices for which output is dependent on temperature or pressure.

$$Q_{std} = Q_{act} \times \frac{P_a\,(1 - RH)\,P_{H_2O}}{P_{std}} \times \frac{298.16}{T_{meter} + 273.16} \quad (5)$$

where:

Q_{std} = flow rate at standard conditions, std L/min (25°C and 101.3 kPa,

Q_{act} = flow rate at monitoring site conditions, L/min,

P_b = barometric pressure at monitoring site conditions, kPa,

RH = fractional relative humidity of the air being measured,

P_{H_2O} = vapor pressure of water at the temperature of the air in the flow or volume standard, in the same units as P_b, (for wet volume standards only, that is, bubble flowmeter or wet test meter; for dry standards, that is, dry test meter, $P_{H_2O} = 0$),

P_{std} = standard barometric pressure, in the same units as P_b(101.3 kPa), and

T_{meter} = temperature of the air in the flow or volume standard, °C (for example, bubble flowmeter).

If a barometer is not available, the following equation may be used to determine the barometric pressure:

$$P_b = 101.3 - .01(H)kP_a \quad (6)$$

where:

H = sampling site elevation above sea level in meters.

10.4 If the initial flow rate (Q_i) differs from the flow rate of the critical orifice or the flow rate indicated by the flowmeter in the sampling train (Q_c) by more than 5 percent as determined by Eq 7, check for leaks and redetermine Q_i.

$$\%\,Diff = \frac{Q_i - Q_c}{Q_c} \times 100 \quad (7)$$

Invalidate the sample if the difference between the initial (Q_i) and final (Q_f) flow rates is more than 5 percent as determined by Eq 8:

$$\%\,Diff = \frac{Q_i - Q_f}{Q_f} \times 100 \quad (8)$$

11. Calibration and Standardization

11.1 *Sampling*:

11.1.1 *Flowmeter or Hypodermic Needle*—Calibrate the flowmeter in accordance with Practice D 3195. Repeat this calibration monthly. Calibrate the hypodermic needle with a flowmeter calibrated in accordance with Practice D 3195 before and after sampling.

11.1.2 Maintain the pressure drop of the flow-measuring devices the same during sampling as during calibration.

11.2 *Spectrophotometer Cell Matching*—If unmatched spectrophotometer cells are used, determine an absorbance correction factor as follows:

11.2.1 Fill all cells with distilled water and designate the one that has the lowest absorbance at 548 nm for Method A or at 575 mn for Method B, as the reference. Mark this reference cell as such and continually use it for this purpose throughout all future analyses.

11.2.2 Zero the spectrophotometer with the reference cell.

11.2.3 Determine the absorbance of the remaining cells (A_c) in relation to the reference cell and record these values for future use. Mark all cells in a manner that adequately identifies the correction.

11.2.4 Determine the corrected absorbance during future analyses using each cell as follows:

$$A = A_{obs} - A_c \quad (9)$$

where:
A = corrected absorbance,
A_{obs} = uncorrected absorbance, and
A_c = cell correction.

11.3 *Analysis*—Prepare a calibration curve of the colorimetric method using the standards prepared in 8.4, as described in Annex A2, when new stock PRA solution is prepared, or every three months, whichever is first.

11.3.1 For detailed calibration procedures see Annex A2 or Annex A4.

12. Procedure

12.1 *Sampling*:

12.1.1 *General Considerations*—Procedures are described for short-term sampling (30 min and 1 h) and for long-term sampling (24 h). Select different combinations of absorbing reagent volume, sampling rate, and sampling time to meet special needs. For combinations other than those specifically described, adjust the conditions so that linearity is maintained between absorbance and concentration over the dynamic range. Do not use absorbing reagent volumes less than 10 mL. The collection efficiency is above 98 percent for the conditions described; however, the efficiency may be substantially lower when sampling concentrations below 25 μg SO_2/m^3 **(14,15)**.

12.1.2 For short-term samples, determine the standard flow rate at the sampling site at the initiation and completion of sample collection with a calibrated flow measuring device connected to the inlet of the absorber. For 24 h samples, determine the standard flow rate at the time the absorber is placed in the sampling train and again when the absorber is removed from the train for shipment to the analytical laboratory, using a calibrated flow measuring device connected to the inlet of the sampling train. Make the flow rate determination with all components of the sampling system in operation (for example, the absorber temperature controller and any sample box heaters).

12.1.3 *Short-Term Sampling*—Place 10 mL of TCM absorbing reagent in a midget impinger and seal the impinger with a thin film of silicon stopcock grease (around the ground glass joint). Insert the sealed impinger into the sampling train as shown, making sure that all connections between the various components are leak tight. Greaseless ball joint fittings, heat shrinkable TFE-fluorocarbon tubing, or TFE-fluorocarbon tube fittings may be used to attain leakfree conditions for portions of the sampling train that come into contact with air containing SO_2. Shield the absorbing reagent from direct sunlight by covering the impinger with aluminum foil or by enclosing the sampling train in a light-proof box. Determine the flow rate according to 10.3. Collect the sample at 1 ± 0.10 L/min for 30 min sampling or 0.500 ± 0.05 L/min for 1 h sampling. Record the exact sampling time in min, as the sample volume will later be determined using the sampling flow rate and the sampling time. Record the atmospheric pressure and temperature.

12.1.4 *Twenty-Four-Hour Sampling*—Place 50 mL of TCM absorbing solution in a large absorber, close the cap, and if needed, apply the heat shrink material. Verify that the reagent level is at the 50 mL mark on the absorber. Insert the sealed absorber into the sampling train. At this time verify that the absorber temperature is controlled to 15 ± 10°C. During sampling, control the absorber temperature to prevent decomposition of the collected complex. From the onset of sampling until analysis, protect the absorbing solution from direct sunlight. Determine the flow rate according to 10.3. Collect the sample for 24 h from midnight to midnight at a flow rate of 0.200 ± 0.020 L/min. A start/stop timer is helpful for initiating and stopping sampling and an elapsed time meter will be useful for determining the sampling time.

12.2 *Transporting Impinged Samples*—Avoid exposure to light. Solutions of dichlorosulfonatomercurate are relatively stable. When stored at 5°C for 30 days, no detectable losses of SO_2 occur. At 25°C losses of SO_2 in solution occur at a rate of 1.5 %/day. These losses of SO_2 follow a first-order reaction, and the reaction rate is independent of concentration. Actual field samples containing EDTA have similar decay curves. When sampling is complete, remove the impinger or absorber from the sampling train and stopper immediately. Verify that the temperature of the absorber is not above 25°C. Mark the level of the solution with a temporary (for example, grease pencil) mark. If the sample will not be analyzed within 12 h of sampling, store it at 5° ± 5°C until analysis. Analysis must occur within 30 days. If the sample is transported or shipped for a period exceeding 12 h, it is recommended that thermal coolers using eutectic ice packs, refrigerated shipping containers, etc., be used for periods up to 48 h **(11)**. Measure the temperature of the absorber solution when the shipment is received. Invalidate the sample if the temperature is above 10°C. Store the sample at 5° ± 5°C until it is analyzed.

12.3 *Analysis*:

12.3.1 *Sample Preparation*—Remove the samples from the shipping container. If the shipment period exceeded 12 h from the completion of sampling, verify that the temperature is below 10°C. Also, compare the solution level to the temporary level mark on the absorber. If either the temperature is above 10°C or there was significant loss (more than 10 mL) of the sample during shipping, make an appropriate notation in the record and invalidate the sample. Prepare the samples for analysis as follows:

12.3.1.1 *For 30 min or 1 h Samples*—Quantitatively transfer the entire 10 mL amount of absorbing solution to a 25 mL volumetric flask and rinse with a small amount (<5 mL) of distilled water.

12.3.1.2 *Twenty-Four-Hour Samples*—If the volume of the sample is less than the original 50 mL volume (permanent mark on the absorber), adjust the volume back to the original volume with distilled water to compensate for water lost to evaporation during sampling. If the final volume is greater than the original volume, measure the volume with a graduated cylinder. To analyze, pipet 10 mL of the solution into a 25 mL volumetric flask.

12.3.1.3 *Sample Analysis*—For each set of determinations, prepare a reagent blank by adding 10 mL TCM absorbing solution to a 25 mL volumetric flask, and two control standards containing approximately 5 and 15 μg SO_2, respectively. The control standards are described in 13.5. Perform the analysis as follows:

(a) Allow the sample to stand 20 min after the completion of sampling to allow any ozone to decompose (if applicable).

(b) To each 25 mL volumetric flask containing reagent blank, sample, or control standard, add 1 mL of 0.6 % sulfamic acid and allow to react for 10 min.

(c) Accurately pipet 2 mL of 0.2 % formaldehyde solution and then 5 mL of pararosaniline solution into each flask. Start a laboratory timer set at 30 min.

(d) Bring each flask to volume with recently boiled and cooled distilled water and mix thoroughly.

(e) Keep the solutions in a temperature controlled environment in the range of 20° to 30°C, maintained to ±1°C during the 30 min. This temperature must also be within 1°C of that used during calibration.

(f) After 30 min and before 60 min, determine the corrected absorbances (Eq 9) of each solution at 548 nm for Method A or at 575 mn for Method B, using 1 cm optical path length cells against a distilled water reference.

NOTE 6—Distilled water is used as a reference instead of the reagent blank because of the sensitivity of the reagent blank to temperature.

(g) Do not allow the colored solution to stand in the cells because a film may be deposited. Clean the cells with isopropyl alcohol after use.

(h) Ensure the reagent blank is within 0.03 absorbance units of the intercept of the calibration (Eq 12).

NOTE 7—*Absorbance range.* If the absorbance of the sample solution ranges between 1.0 and 2.0, the sample can be diluted 1:1 with a portion of the reagent blank and the absorbance redetermined within 5 min. Solutions with higher absorbances can be diluted up to sixfold with the reagent blank in order to obtain scale readings of less than 1.0 absorbance unit. However, it is recommended that a smaller portion (<10 mL) of the original sample be reanalyzed (if possible) if the sample requires a dilution greater 1:1.

13. Calculations

13.1 *Sample Air Volume*:

13.1.1 *Calculation of Flow Rate at Sampling Site*—Eq 6 may be used to determine the standard flow rate when a calibrated positive displacement meter is used as the flow measuring device. Other types of calibrated flow measuring devices may also be used to determine the flow rate at the sampling site provided that the user applies any appropriate corrections to devices for which output is dependent on temperature or pressure.

$$Q_{STD} = Q_{ACT} \times \frac{P_b(1 - RH)\,P_{H_2O}}{P_{std}} \times \frac{298.16}{T_{meter} + 273.16} \quad (10)$$

WHERE:

Q_{std} = flow rate at standard conditions, std L/min (25°C and 101.3 kPa,
Q_{act} = flow rate at monitoring site conditions, L/min,
P_b = barometric pressure at monitoring site conditions, kPa,
RH = fractional relative humidity of the air being measured,
P_{H_2O} = vapor pressure of water at the temperature of the air in the flow or volume standard, in the same units as P_b, (for wet volume standards only, that is, bubble flowmeter or wet test meter; for dry standards, that is, dry test meter, $P_{H_2O} = 0$),
P_{std} = standard barometric pressure, 101.3 kPa, and
T_{meter} = temperature of the air in the flow or volume standard, °C (for example, bubble flowmeter).

13.1.2 *Total Sample Volume*—Determine the sampling volume at standard conditions as follows:

$$V_{std} = \frac{Q_i + Q_f}{2} \times t \quad (11)$$

where:

V_{std} = sampling volume at standard conditions, L,
Q_i = flow rate determined at the initiation of sampling in std L/min,
Q_f = flow rate determined at the completion of sampling in std L/min, and
t = total sampling time, min.

13.2 *Sulfur Dioxide Concentration in the Air Sample*—Calculate the SO_2 concentration in the air sample at standard conditions as follows:

13.2.1 Plot the absorbance against the total concentration in μg/mL SO_2 for the corresponding solution. A linear relationship should be obtained, and the *y*-intercept should be with 0.03 absorbance units of the zero standard absorbance.

13.2.2 *Calibration Slope, Intercept, and Correlation Coefficient*—Use the method of least squares to calculate a calibration equation in the form of:

$$y = mx + b \quad (12)$$

where:

y = corrected absorbance,
m = slope, absorbance unit/μg SO_2,
x = mass of SO_2, in μg, and
b = y intercept (absorbance units).

13.2.3 Calculate the slope (m), intercept (b), and correlation coefficient (r) as follows:

$$m = \frac{n\Sigma xy - (\Sigma x)(\Sigma y)}{n\Sigma x^2 - (\Sigma x)^2} \quad (13)$$

$$b = \frac{\Sigma y - m\Sigma x}{n} \quad (14)$$

$$r = \sqrt{\frac{m(\Sigma xy - \Sigma x\Sigma y/n)}{\Sigma y^2 - (\Sigma y)^2/n}} \quad (15)$$

where:

n = number of calibration points.

13.3 *Sulphur Dioxide Concentration*—Determine the concentration of SO_2 in each sample as follows:

$$C = \frac{(A - A_o)\,(B_x)\,(10^3)}{V_{std}} \frac{V_a}{V_b} \quad (16)$$

where:

C = concentration of SO_2 in air sample at standard conditions, μg/m^3,
A = corrected absorbance of the sample solution, from Eq 9,
A_o = corrected absorbance of the reagent blank, using Eq 9,
B_x = calibration factor equal to B_s, B_g, or B_t depending on the calibration procedure used, the reciprocal of the slope of the calibration equation,

V_a = volume of absorber solution analyzed, mL,
V_b = total volume of solution in absorber, mL, and
V_{std} = standard air volume sampled, std L.

13.4 *Control Standards*—Calculate the analyzed mass of SO_2 in each control standard as follows:

$$C_q = (A - A_O) \times B_x \quad (17)$$

where:
C_q = analyzed mass of SO_2 in each control standard, μg,
A = corrected absorbance of the control standard, and
A_o = corrected absorbance of the reagent blank.

The difference between the true and analyzed values of the control standards must not be greater than 1 μg. If the difference is greater than 1 μg, identify and correct the source of the discrepancy.

13.5 To convert $\mu g/m^3$ to ppm(v), refer to Practice D 1914.

14. Quality Assurance Procedures

14.1 See References **(16,17)** for additional quality assurance procedures for performing these test methods.

15. Precision and Bias

15.1 *Precision*:

15.1.1 *Method A*:

15.1.1.1 *Repeatability (Single-Analyst)*—The standard deviation of results obtained by a single analyst on separate samples **(18)** from the same flowing air stream is shown in Fig. 2 as a function of the mean value of SO_2 determined. Duplicate analyses should be considered suspect (95 % confidence level) if they differ by more than 2.77 times the standard deviation of repeatability.

15.1.1.2 *Reproducibility (Multilaboratory)*—The standard deviation of single analyses, obtained by analysts from different laboratories **(16)** taking separate samples from the same flowing air stream, is plotted in Fig. 3 against the mean value of SO_2 determined. Two such values should be considered suspect (95 % confidence level) if they differ by more than 2.77 times the standard deviation of reproducibility.

15.1.2 *Method B*—No precision data are available for Method B.

15.2 *Bias*:

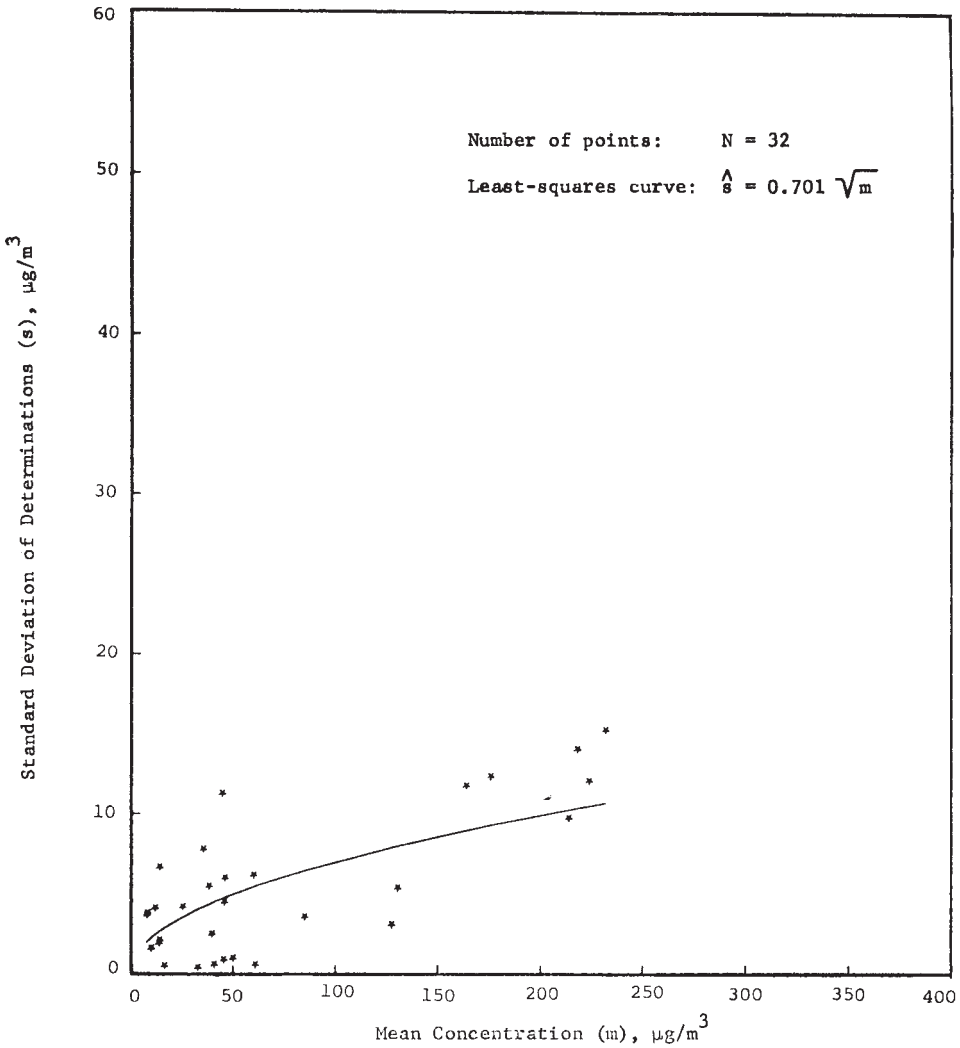

FIG. 2 Scatter Diagram and Least-Squares Curve Relating Within-Laboratory Standard Deviation (Repeatability) to Concentration of Sulfur Dioxide

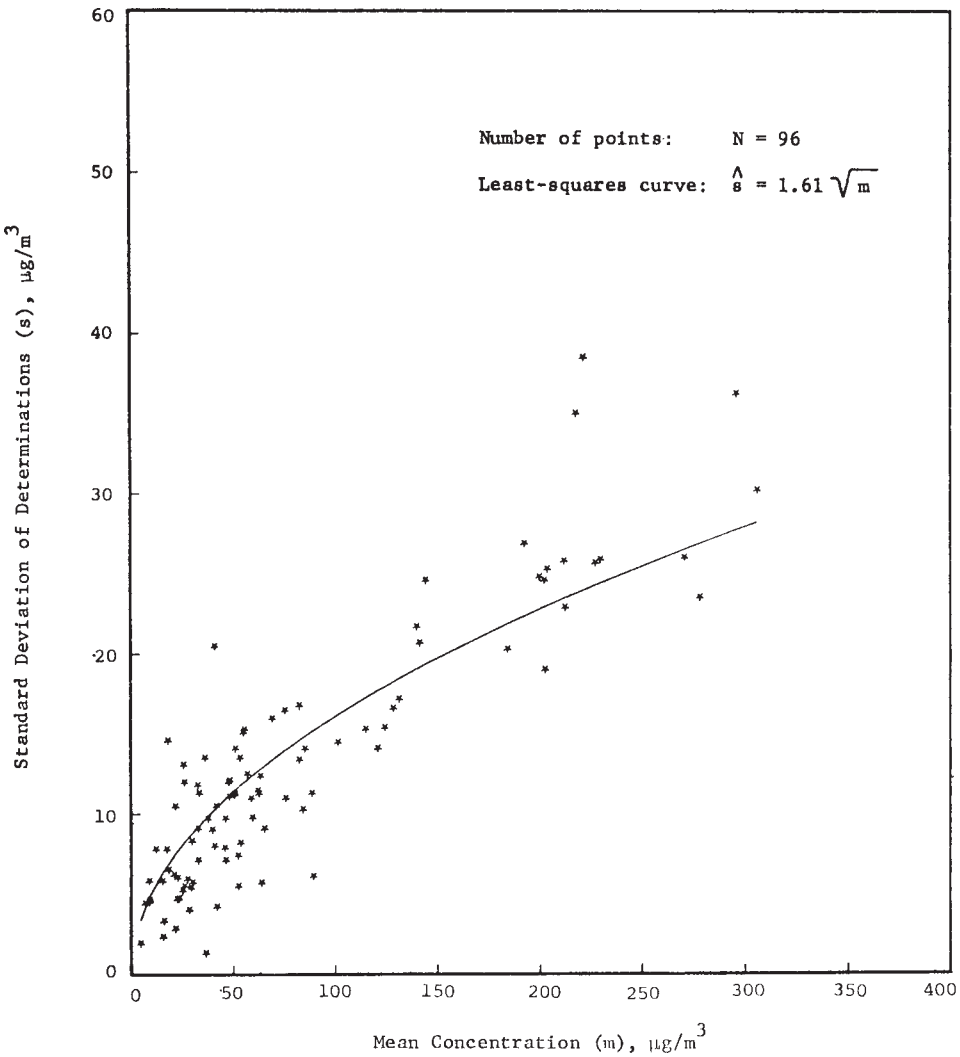

FIG. 3 Scatter Diagram and Least-Squares Curve Relating Between-Laboratory Standard Deviation (Reproducibility) to Concentration of Sulfur Dioxide

15.2.1 *Method A*—The results of an interlaboratory cooperative study **(16)** of this method at three locations showed an average of 11 % less SO_2 than when the spiked amount was measured. The biases of the measurements of the sulfur dioxide recovered from spiked-ambient samples were −22, +6, and −4 % at Los Angeles, CA, Bloomington, IL, and Manhattan, NY respectively. The biases do not appear to be dependent on concentration.

15.2.2 No bias statement can be made for Method B.

16. Keywords

16.1 ambient atmospheres; analysis; colorimetric analysis; EPA reference method; pararosanaline method; sampling; sulfur dioxide; West-Gaeke procedure

ANNEXES

(Mandatory Information)

A1. METHOD OF PURIFICATION OF PRA DYE

A1.1 In a large separatory funnel (250 mL), equilibrate 100 mL each of 1-butanol and 1 *M* HCl.

A1.2 Weigh 0.1 g of pararosaniline hydrochloride (PRA) in a beaker. Add 50 mL of the equilibrated acid and let stand for several minutes.

A1.3 To a 125 mL separatory funnel add 50 mL of the equilibrated 1-butanol.

A1.4 Transfer the acid solution containing the dye to the funnel and extract. The violet impurity will transfer to the organic phase.

A1.5 Transfer the lower (aqueous) phase into another separatory funnel and add 20 mL portions of 1- butanol. This is usually sufficient to remove almost all the violet impurity which contributes to the reagent blank. If violet impurity still appears in 1-butanol phase after five extractions, discard this lot of dye.

A1.6 After the final extraction, filter the aqueous phase through a cotton plug into a 50 mL volumetric flask and bring to volume with 1 *N* HCl. This stock reagent will be yellowish red.

A2. PREPARATION OF CALIBRATION CURVE

A2.1 Following Table A2.1, accurately pipet the indicated volumes of the indicated sulfite-TCM solutions into a series of 25–mL volumetric flasks. Add TCM absorbing reagent as indicated to bring the volume in each flask to 10 mL.

A2.2 To each volumetric flask, add 1 mL 0.6% sulfamic acid, accurately pipet 2 mL 0.2 % formaldehyde solution, then add 5 mL pararosaniline solution. Start a laboratory timer that has been set for 30 min. Bring all flasks to volume with recently boiled and cooled distilled water and mix thoroughly. The color must be developed (during the 30 min period) in a temperature environment in the range of 20° to 30°C, which is controlled to +1°C. For increased precision, a constant temperature bath is recommended during the color development step. After 30 min, determine the corrected absorbance of each standard at 548 nm, for Method A, or at 575 mn for Method B, against a distilled water reference. Denote this absorbance as (A). Distilled water is used in the reference cell rather than the reagent blank because of the temperature sensitivity of the reagent blank. Calculate the total mass of SO_2 in each solution, as follows:

$$M_{SO_2} = V_{TCM/SO_2} \times C_{TCM/SO_2} \times D \quad \text{(A2.1)}$$

where:

V_{TCM/SO_2} = volume of sulfite-TCM solution used, mL,
C_{TCM/SO_2} = concentration of sulfur dioxide in the working sulfite-TCM, μg SO_2/mL (from Eq 4), and
D = dilution factor (D = 1 for the working sulfite-TCM solution; D = 0.1 for the diluted working sulfite-TCM solution).

TABLE A2.1 Preparation of SO_2 Working Standards

Sulfite-TCM Solution	Vol. of Indicated Sulfite-TCM Solution, mL	Vol. of TCM, mL	Approximate Mass of SO_2[A], μg
Working (see 8.4.7.2)	4.0	6.0	28.8
Working (see 8.4.7.2)	3.0	7.0	21.6
Working (see 8.4.7.2)	2.0	8.0	14.4
Dilute Working (see 8.4.7.3)	10.0	0.0	7.2
Dilute Working (see 8.4.7.3)	5.0	5.0	3.6
	0.0	10.0	0.0

[A]Based on working sulfite-TCM solution concentration of 7.2 μg SO_2/mL; calculate the actual mass of SO_2 calculated using Eq A2.1.

A2.3 Determine the calibration equation using the method of linear least squares. The total mass of SO_2 contained in each solution is the *x* variable, and the corrected absorbance (Eq 10) associated with each solution is the *y* variable. For the calibration to be valid, for method A, the slope must be in the range of 0.030 + 0.002 absorbance unit/μg SO_2, the intercept as determined by the least squares method must be equal to or less than 0.170 absorbance unit when the color is developed at 22°C (add 0.015 to this 0.170 specification for each °C above 22°C) and the correlation coefficient must be greater than 0.998. If these criteria are not met, it may be the result of an impure dye and/or an improperly standardized sulfite-TCM solution. Determine a calibration factor (B_s) by calculating the reciprocal of the slope, which is subsequently used for calculating the sample concentration.

A3. WASTE DISPOSAL

A3.1 Since the absorbing solution contains mercury, waste solution from the analysis should be treated prior to disposal or shipment for reclamation. The following procedure **(16)** is suggested:

A3.1.1 To each litre of waste solution, add sodium carbonate (Na_2CO_3) (about 10 g) until neutral and 10 g of granular zinc or magnesium.

A3.1.2 Sodium hydroxide (NaOH) may have to be added if a neutral solution is not obtained with sodium carbonate.

A3.1.3 Stir the solution for 24 h in a hood. (**Warning—** Hydrogen gas will be released during this process.)

A3.1.4 After 24 h, the solid material (mercury amalgam) will have separated. Decant and discard the supernatant liquid.

A3.1.5 Quantitatively transfer the solid material to a convenient container and allow to dry.

A3.1.6 This procedure removes more than 99 % of the mercury from the absorbing solution.

A4. ALTERNATIVE PROCEDURE FOR PREPARATION OF CALIBRATION STANDARDS WITH SO_2 PERMEATION DEVICES

A4.1 *Dynamic Calibration Procedures*—Atmospheres containing accurately known concentrations of sulfur dioxide are prepared using permeation devices. In the systems for generating these atmospheres, the permeation device emits gaseous SO_2 at a known, low, constant rate, provided the temperature of the device is held constant (+0.1°C) and the device has been accurately calibrated at the temperature of use. The SO_2 permeating from the device is carried by a low flow of dry carrier gas to a mixing chamber where it is diluted with SO_2-free air to the desired concentration and supplied to a vented manifold. A typical system is shown schematically in Fig. A4.1 and this system and other similar systems have been described in detail in **(19-23)**.

A4.1.1 *Procedure for 30 min and 1 h Samples*—Generate a series of six standard atmospheres of $S0_2$ (for example, 0, 50, 100, 200, 350, 500, 750, $\mu g/m^3$) by adjusting the dilution flow rates appropriately. The concentration of SO_2 in each atmosphere is calculated as follows:

$$C_a = \frac{P_r \times 10^3}{Q_d + Q_p} \quad \text{(A4.1)}$$

where:

C_a = concentration of SO_2 at standard conditions, μ/m^3,
P_r = permeation rate, μ/min,
Q_d = flow rate of dilution air, L/min, and
Q_p = flow rate of carrier gas across permeation device, L/min.

Ensure that the total flow rate of the standard exceeds the flow demand of the sample train, with the excess flow vented at atmospheric pressure. Sample each atmosphere using similar

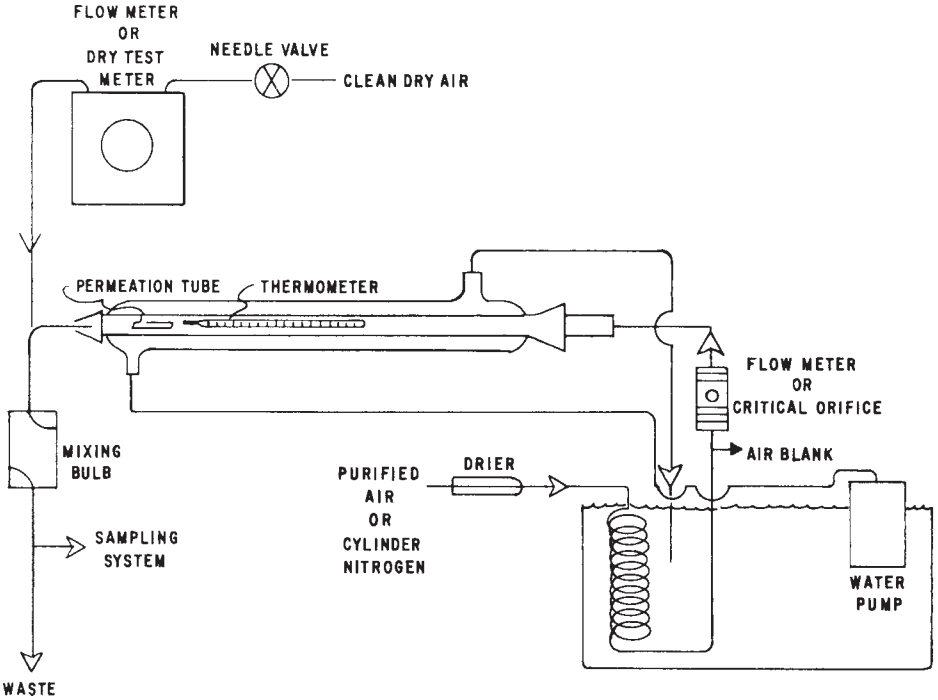

FIG. A4.1 Gas Dilution System for Preparation of Standard Concentrations of Sulfur Dioxide for Laboratory Use by the Permeation Tube Method

apparatus under the same conditions as field sampling (that is, use the same absorbing reagent volume and sample the same volume of air at an equivalent flow rate). Due to the length of the sampling periods required, this method is not recommended for 24 h sampling. At the completion of sampling, quantitatively transfer the contents of each impinger to one of a series of 25 mL volumetric flasks (if 10 mL of absorbing solution was used) using small amounts of distilled water for rinse (<5mL). If >10 mL of absorbing solution was used, bring the absorber solution in each impinger to original volume with distilled H_2O and pipet 10 mL portions from each impinger into a series of 25 mL volumetric flasks. If the color development steps are not to be started within 12 h of sampling, store the solutions at 5° ± 5°C. Calculate the total mass of SO_2 in each solution as follows:

$$M = \frac{C_a \times Q_s \times t \times V_a \times 10^{-3}}{V_b} \quad \text{(A4.2)}$$

where:

M = mass of SO_2 in each solution, in μg,
C_a = concentration of SO_2 in the standard atmosphere, μg/m^3,
s = sampling flow rate, L/min,
t = sampling time, min,
V_a = volume of absorbing solution used for color development (10 mL), and
V_b = volume of absorbing solution used for sampling, mL.

Add the remaining reagents for color development in the same manner as in Annex A2 for static solutions. Calculate a calibration equation and a calibration factor (B_g) according to Annex A2, adhering to all the specified criteria.

A4.1.2 *24 h Samples*—Generate a standard atmosphere containing approximately 1,050 μg SO_2/m^3 and calculate the exact concentration according to Eq A4.1. Set up a series of six absorbers according to Fig. 1 and connect to a common manifold for sampling the standard atmosphere. Be sure that the total flow rate of the standard exceeds the flow demand at the sample manifold, with the excess flow vented at atmospheric pressure. Sample the standard atmosphere for varying time periods to yield solutions containing 0, 0.2, 0.6, 1.0, 1.4, 1.8, and 2.2 μg SO_2/mL solution. Calculate the sampling times required to attain these solution concentrations as follows:

$$t = \frac{V_b \times C_s}{C_a \times Q_s \times 10^{-3}} \quad \text{(A4.3)}$$

where:

t = sampling time, min,
V_b = volume of absorbing solution used for sampling (50 mL),
C_s = desired concentration of SO_2 in the absorbing solution, μg/mL,
C_a = concentration of the standard atmosphere calculated according to equation A4.1, μg SO_2/m^3, and
Q_s = sampling flow rate, L/min.

At the completion of sampling, bring the absorber solutions to original volume with distilled water. Pipet a 10 mL portion from each absorber into one of a series of 25 mL volumetric flasks. If the color development steps are not to be started within 12 h of sampling, store the solutions at 5° ± 5°C. Add the remaining reagents for color development in the same manner as in 10.2 for static solutions. Calculate the mass of SO_2 in each standard, using Eq A4.2.

Calculate a calibration equation and a calibration factor (B_t) according to Annex A2 adhering to all the specified criteria.

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