Designation: D 2914 – 9501

An American National Standard

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] These test methods are under the jurisdiction of ASTM Committee D-22 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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1.3 The lower limit of ~~detection, corresponding to twice the standard deviation,~~ detection is 0.02~~7~~5 μg SO_2/mL **(1)**[2], representing an air concentration of ~~4 μg~~ 25 μg SO_2/m^3 (0.00~~9~~15 ppm(v)) in a ~~24-h~~ 30–min sample, or ~~7 μg~~ 13 μg SO_2/m^3 (0.00~~3~~5 ppm(v)) in a ~~1-h~~ 24–h sample.

1.4 These test methods incorporate sampling for ~~1 h~~ periods between 30 min and ~~for~~ 24 h.

1.5 These test methods describe ~~manual and automated determinations~~ the determination of the collected (impinged) samples. ~~Each method of determination has two submethods designated as Manual Methods~~ A Method A and ~~B and Automated Methods I and II. The automated methods can determine 30 impinged samples per hour or 40 impinged samples per hour, depending upon the choice of instruments.~~

~~1.6 Manual~~ a Method B are described.

1.6 Method A is preferred over ~~Manual~~ 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.

~~1.7 Automated Method II is preferred over Automated Method I, as it gives the better precision. However, choice of method will be dictated by availability of equipment.~~

NOTE 1—These test methods are applicable at concentrations below 25 μg/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 μg/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.~~8~~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.~~7~~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 complex ~~**(1, 2).**~~ **(2,3).**[9] Ethylenediaminetetraacetic acid disodium salt (EDTA) is added to this solution to complex heavy metals that interfere with this method **(3~~4~~).** Dichlorosulfonatomercurate, once formed, is stable to strong oxidants (for example, ozone and oxides of nitrogen) **(1~~2~~).** After the absorption is completed, any ozone in the solution is allowed to decay **(4).** ~~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~~ **(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

[2] *Annual Book of ASTM Standards*, Vol 05.0~~5~~6.
[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] ~~The boldface numbers in parentheses refer to the list~~
[8] Available from U.S Government Printing Office, Superintendent of ~~references at the end of this standard.~~ Documents, 732 North Capitol Street, NW, Mail Stop: SDE, Washington, DC 20401.
[9] ~~Gelman 37-mm in-line filters have been found satisfactory for~~
[9] The boldface numbers in parentheses refer to the list of references at the end of this ~~purpose.~~ standard.

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 **(12).** 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 **(45).**

4.2 Automated Method II is based on Manual Method A.

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 **(6) (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 **(78).**

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 The Manual Method

5.4 Method A has been designed to correspond to the EPA-Designated Reference Method **(67)** for the determination of sulfur dioxide, and Automated Methods I and II have been designed to correspond to the EPA-designed equivalent methods **(8, 9).** dioxide.

6. Interferences

6.1 The interferences of oxides of nitrogen are eliminated by sulfamic acid **(4,5,6),** of ozone by time delay **(45),** and of heavy metals by EDTA and phosphoric acid **(3, 4).(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 10 μg 2.3 μg of Cu(II) and 22 μg of V(V). NH_3(9).**

7. Apparatus

7.1 *For Sampling*:

7.1.1 *Absorber, 1-h Short–Term Sampling*—An all-glass midget impinger having a 25-mm outside diameter, a total solution capacity of 30 mL, mL and a 1-mm diameter orifice having a stem clearance of 4 ± 1 mm from the bottom of the impinger of 4 ± 1 mm. An impinger meeting these specifications vessel is commercially available from a number used for sampling periods of manufacturers. 30 min and 1 h (or any period considerably less than 24 h).

7.1.2 *Absorber, 24-h Sampling*—A glass or polypropylene absorption tube approximately 30 32 mm in diameter and 160 164 mm long, with a polypropylene two-port closure 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). The closure shall be fitted with Insert a 8-mm outside diameter, 6-mm glass impinger stem, 6 mm inside diameter glass orifice tube approximately 150 and 158 mm long, having into one port of the end drawn out absorber cap. Taper the tip of the stem to form an a small diameter orifice of 0.4 (0.4 ± 0.1 mm and positioned to allow mm) such that a c 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 f. Perform the orifice test before use to verify the bottom of orifice size. Permanently mark the t 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 tube with a polypropylene residence time less than 20 sec), used to transport ambient air to the sampling train location. Design or glass funnel at orient the end of the probe to preclude the sampling of precipitation, large particles, etc.

7.1.4 *Moisture Trap*—Glass or polypropylene tube equipped with a two-port closure. The entrance port of trap as shown in Fig. 1, placed between the closure is fitted with tubing that extends absorber tube and flow control device to prevent entrained liquid from reaching the bottom of flow control device. Pack the trap. The unit is loosely packed tube with 16-mesh activated coconut charcoal and glass wool to prevent moisture entrainment. The charcoal should be changed weekly. 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 *Filter*, membrane, of 0.8Cap Seals—Seal the absorber and moisture trap caps securely to 2.0-μm porosity, with filter holder.[9] prevent leaks during use, by using heat-shrink material to prevent the caps coming loose during sampling, shipment, or storage.

7.1.6 *PumpFilter*, capable membrane, of maintaining a vacuum greater than 70 kPa (0.7 atm) at 0.8 to 2.0 μm porosity, with filter holder, to protect the specified 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*:

7.1.78.1 *Flow Control Device*—Any device—A calibrated rotameter and needle valve combination capable of maintaining a constant and measuring air flow rate (±2%) to within ±2 percent is suitable for short-term sampling but shall not be used for

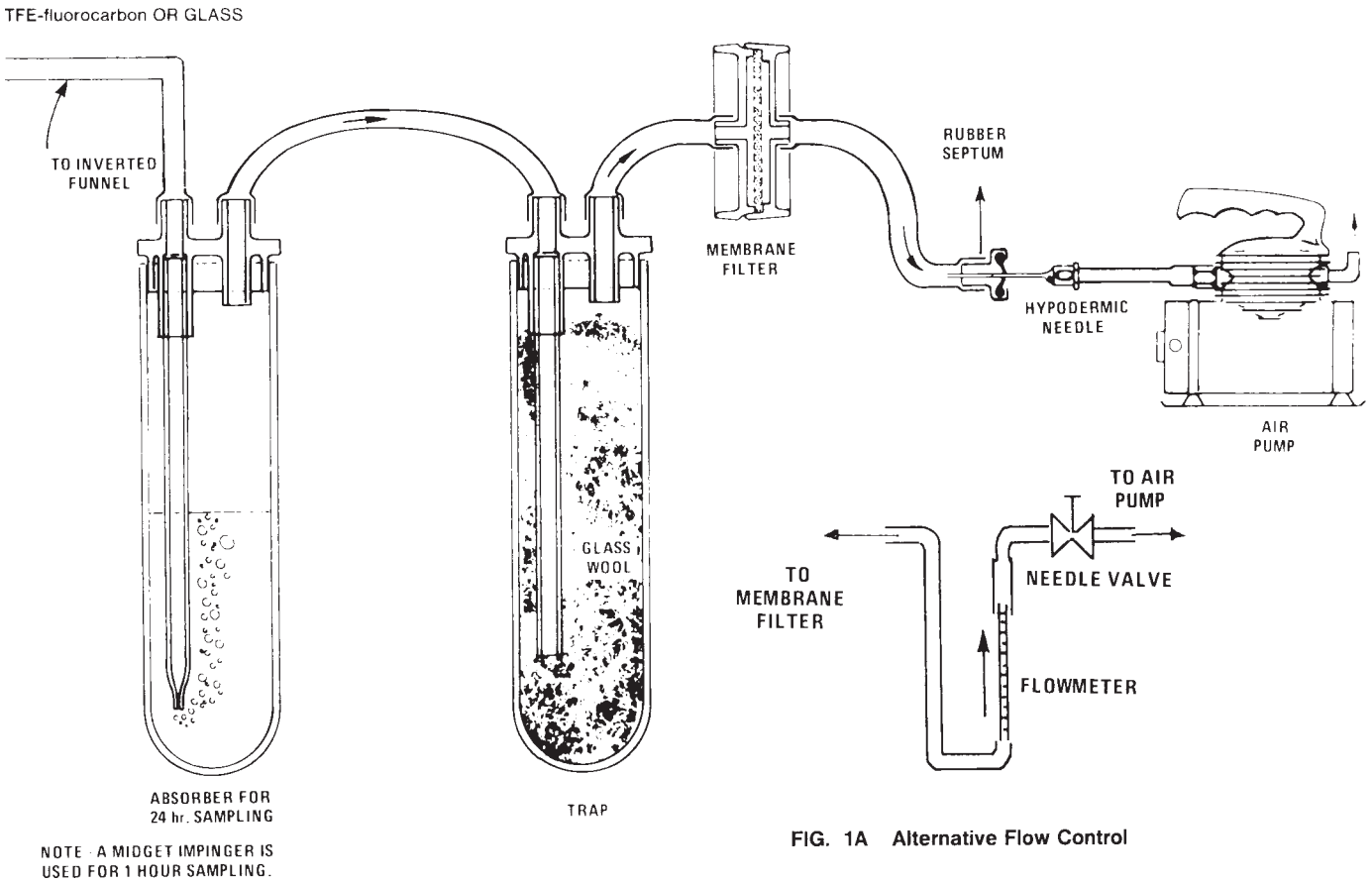

FIG. 1A Alternative Flow Control

FIG. 1 Sampling System

long-term sampling. A critical orifice can be ~~used. For 1-h sampling (0.5 L/min),~~ used for regulating flow rate for both long-term and short-term sampling. Use a 23-gage hypodermic needle ~~16~~ 25 mm long as a critical orifice **(10)** ~~or~~ to yield a ~~needle valve is suggested. For 24-h~~ flow rate of approximately 1 L/min for a 30–min sampling ~~(0.2 L/min),~~ period. When sampling for 1 h, use a 27-gage hypodermic needle ~~10~~ 16 mm ~~long is suggested. In either case, protect the~~ 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 ~~valve or~~ critical orifice ~~from particulate matter~~ 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 ~~moisture entrainment.~~

~~7.1.8~~ 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.

7.1.910 *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 ± 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. See Practice D 1605 for discussion of this apparatus.~~ 1.

7.2 ~~*For Manual Methods A and B*~~ *Shipping*:

7.2.1 ~~*Spectrophotometer or Colorimeter*— The instrument shall be suitable for measurement of color at 548 nm for Method A or 575 nm for Method B. With Method A, reagent blank problems may result with spectrophotometers or colorimeters~~

havingShipping Container—to maintain a spectral bandwidth greater than 10 nm. The wavelength calibration temperature of 5 ± 5°C while transporting the sample from the collectriopn site to the analytical laboratomry. Ice coolers or refrigerated shipping containers hallve been found to be verified in accordance with Practice E 275. satisfactory. The optical cell shall have a minimum path length use of 10 mm.

7.2.2 *Constant-Temperature Bath*, capable eutectic cold packs instead of controlling ice will give a more stable temperature to ±2°C. control.

7.3 *Automated Methods I and II*—The automated analytical system will generally consist of a series of modular units that will perform the functions of feeding samples to the system by means of a turntable, a pump to move the sample from the turntable to the analytical module and from the analytical module to a detection device such as a colorimeter. The pump also provides the means of adding reagents to the sample to develop a color, adjust the pH, or otherwise condition the sample for the analytical finish. A recorder or a printout device is used to record the data or the signal that is generated by the detection device. There are several pieces of equipment available to perform these functions. Two such systems will be presented, one of which is an older system

and is designated as Method I.[10] The other is a newer system and is designated as Method II.[11] Analysis:

7.3.1 *Automated System**Spectrophotometer or Colorimeter*—The instrument shall be suitable for Method I (see Fig. 2) consists measurement of the following:

7.3.1.1 *Turntable*,[10] set color at 548 nm for 30 samples per hour and a 1:4 ratio of sample to wash time.

7.3.1.2 *Sample Cups*, 10-mL capacity.

7.3.1.3 *Pump*,[10] capable of maintaining the flow rates in Table 1. Pump tubing shall be poly(vinyl chloride), Method A or other inert tubing 575 nm for sample and reagent.

7.3.1.4 *Sampler Probe*, made Method B. For Method A, an effective spectral bandwidth of polychlorotrifluoroethylene or glass. Because of less than 15 nm is required since reagent blank problems may otherwise result. Verify the corrosive properties wavelength calibration of the TCM absorbing reagent, no metal shall contact the sample solution.

7.3.1.5 *Pump Tubes*—The pump tubes are such that sample and reagent flow rates are as specified spectrophotometer in Table 1. The different flow rates are obtained by selecting pump tubing accordance with Practice E 275 upon initial receipt of the proper inside diameter. Deviation from these flow rates is acceptable only to the extent that a proper calibration curve instrument and acceptable quality control checks are obtained.

7.3.1.6 *Mixing Coils and Time Delay Coils*, as shown in Table 2.

7.3.1.7 *Aperture*—A No. 4 sample aperture and after each 160 h or normal use or every 6 months, whichever occurs first, using a No. 1 reference aperture shall be normally used. Some other combination of apertures can be used if the baseline cannot be obtained with the specified apertures.

7.3.1.8 *Colorimeter with a Phototube Colorimeter Control*,[10] with proper filters for measurement of transmittance at 570 nm. Interference filters shall have a spectral bandwidth not greater than 20 nm. The filters shall be checked with an accurate spectrophotometer, at least quarterly, standard wavelength filter traceable to assure maximum transmittance at the specified wavelength.

7.3.1.9 *Flow Cell*, 50-mm tubular.

7.3.1.10 *Voltage Stabilizer*.

7.3.1.11 *Strip Chart Recorder*. National Institute of Standards and Technology.

7.3.2 *Automated System for Method II* (see Fig. 3) consists of the following:

7.3.2.1 *Sampler Turntable*,Spectrophotometer Cells—A set for 40 samples per hour and a 6:1 ratio of sample to wash time.

7.3.2.2 *Sample Cups*, 10-mL volume.

7.3.2.3 *Proportioning Pump*, capable of maintaining the flow rates indicated in Table 1. Pump tubing 1–cm path length cells suitable for use in the proportioning pump shall be poly(vinyl chloride) or other inert tubing for sample and reagent. Silicone tubing shall be used for air injection.

7.3.2.4 *Sampler Probe*, made of polychlorotrifluoroethylene or glass. Because of visible region. If the corrosive properties of cells are unmatched, determine the TCM absorbing reagent, no metal shall contact matching correction factor according to 11.2.

7.3.3 *Temperature Control Device*—Conduct the sample solution.

7.3.2.5 *Pump Tubes*—The pump tubes are such color development steps during analysis in an environment that sample and reagent flow rates are as specified is in Table 1. The different flow rates are obtained by selecting pump tubing of the proper inside diameter. Deviation from these flow rates is acceptable only range of 20 to the extent that a proper 30°C and controlled to ±1°C. Perform both calibration curve and acceptable quality sample analysis under identical conditions (within 1°C). Adequate temperature control checks are obtained.

7.3.2.6 *Mixing Coils*, as described in Table 2.

7.3.2.7 *Heating Bath*, 45°C heated coil, total volume 5.4 mL.

7.3.2.8 *Colorimeter and Voltage Stabilizer*,[10] may be obtained by means of constant temperature baths, water baths with manual temperature control, or temper filature controlled rooms.

7.3.4 *TCM Waste Receptacle*—A glass waste receptacle for measurement the storage of absorbance at 560 nm. Interference filters shall have spent TCM solution. Store the vessel stoppered in a spectral bandwidth not greater than 20 nm. The filters shall be checked with an accurate spectrophotometer, hood at least quarterly, to assure maximum transmittance at the specified wavelength.

7.3.2.9 *Flow Cell*, 15-mm long with an inside diameter of 2 mm.

7.3.2.10 *Readout Device*—An mv strip chart recorder or digital voltmeter of proper range. 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 ~~*Reagents Common to Manual Methods A and B and Automated Methods I and H*~~*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.

8.3.23 *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.

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

8.3.45 *Hydrochloric Acid* (1 *N*) ~~—Dilute~~)—Slowly and while stirring, add 86 mL of concentrated hydrochloric acid ~~(HCl, sp gr 1.19)~~ to ~~1 L by pouring the acid into 800~~ 500 mL of ~~water while stirring, then~~ distilled water. Allow to cool and dilute to ~~volume.~~ 1000 mL with distilled water. This is stable for one year.

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

8.3.56.1 The solution~~s~~ shall have a wavelength of maximum absorbance at 540 ~~μm~~ nm for Method A or at 575 mn for Method B, in a buffered solution of ~~the acetate buffer.~~

~~8.3.5.2 The~~ 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 ~~Manual~~ Method A.

8.3.56.3 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 ~~Manual~~ Method A.

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

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

~~8.3.6 *Potassium Hydroxide Solution* (6 *N*)—Dissolve 33.67 g of potassium hydroxide (KOH) in 100 mL of water.~~

~~8.3.7 *Potassium TCM Absorbing Reagent* (0.04 *M*)—Dissolve 10.86 g of mercuric chloride ($HgCl_2$), 5.96 g of potassium chloride (KCl), 0.066 g of EDTA in water, and dilute to 1 L in a volumetric flask. The pH of this reagent should be 4.0 ± 1.0. Adjust the solutions to the correct value by the dropwise addition of 6 *N* potassium hydroxide (KOH) solution. This is normally stable for 6 months, but should be discarded if a precipitate is formed.~~

~~NOTE 5—**Caution:** 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.~~

~~8.4 *Reagents Common to Manual Methods A and B*:~~

~~8.4.1 *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.~~

~~8.4.2 *Sulfamic Acid* (0.6 %)—Dissolve 0.6 g of sulfamic acid (NH_2SO_3H) in 100 mL of water. Prepare fresh daily.~~

~~8.5 *Reagents Common to Automated Methods I and II*:~~

~~8.5.1 *Phosphoric Acid, concentrated*, (H_3PO_4, sp gr 1.69).~~

~~8.5.2 *Sulfamic Acid* (0.17 %)—Dissolve 1.7 g of sulfamic acid (NH_2SO_3H) in 1 L of water. Prepare fresh daily.~~

~~8.6 *Pararosaniline Reagent*:~~

~~8.6.1 *PRA Assay*—~~Pipet

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 ~~6),~~ 5), and
21.3 = constant to convert absorbance to mass.

NOTE 65—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.

8.63.7.2 *Pararosaniline Reagent for ~~Manual~~ Method A*—To a ~~1-L~~ 1 L flask, add 80 mL of stock PRA, plus 0.8 mL of stock for each 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.

8.63.7.3 *Pararosaniline Reagent for ~~Manual~~ 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.

8.6.4 *Pararosaniline Reagent for Automated Method I*

8.3.8 *Phosphoric Acid (3.0* —To a 1-L flask add 80*M)*—Dilute 205 mL of stock PRA plus 0.8 mL of stock for each percent the stock assays below 100 %. Add 800 mL of concentrated phosphoric acid and (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 9 months when stored at 25°C or below.

8.6.5 *Pararosaniline Reagent for Automated Method II one year.*

8.3.9 *Potassium Hydroxide Solution* —To a 1-L flask add 80 mL (6 *N)*—Dissolve 33.67 g of stock PRA plus 1.0 potassium hydroxide (KOH) in 100 mL of stock for each percent water.

8.3.10 *Potassium Iodate Solution*—Accurately weigh to the stock assays below 100 %. Add 125 mL nearest 0.1 mg, 1.5 g (record weight) of concentrated phosphoric acid 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. This reagent is stable for 9 months when stored at 25°C or below.

8.7 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 Standards Reagents*:

8.74.1 *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.

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

8.74.3 *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.

8.7.4

8.4.5 *Sodium Thiosulfate, Stock Solution (0.1* (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.

8.7.4.5.1 To standardize, weigh 1.5 g to an accuracy of 0.1 mg of potassium iodate (KIO_3) that had been dried at 180°C for 2 h and cooled. Add to a 500-mL volumetric flask and dilute to volume.

8.7.4.2 Pipet accurately pipet 50 mL of this potassium iodate solution into a 500- mL iodine flask. A and add 2.0 g of potassium iodide (KI) and 10 mL of a 1 + 10 dilution of concentrated hydrochloric acid (HCl). 1 N HCI. Stopper the flask and after waiting allow to stand for 5 min, titrate with min. Titrate the solution with stock sodium thiosulfate solution to a pale yellow color. Add 5 mL of starch indicator solution and complete titrate until the titration. blue color just disappears. Repeat this procedure three times.

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

$$N = \frac{W \times 10^3 \times 0.1}{V \times 35.67} \tag{2}$$

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

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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.

8.7.5

8.4.6 *Sodium Thiosulfate, Working Solution (0.01N)*—Dilute 5 100 mL of stock sodium thiosulfate solution to 500 mL in into a 1000 mL volumetric flask. This is not stable flask and should be prepared fresh daily by dilution dilute to volume with freshly boiled, cooled, distilled water. Calculate the normality of the stock solution.

8.7.6 working sodium thiosulfate titrant (NT) as follows:

$$N_T = N_s\ x\ 0.100 \tag{3}$$

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.

8.7.6.1 Standardize the sulfite solution by back titration in the following manner: Add 25 mL of distilled water (treated as described in 8.7.6) to a 500- mL iodine flask and

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

8.4.7.2 *Working Sulfite-TCM Solution*—Pipet 5 mL of the blue color. standard sulfite solution into a 250 mL volumetric flask and dilute to volume with 0.04 M TCM. Calculate the equivalent concentration of SO_2 sulfur dioxide in the standard working solution as follows:

$$C_s = \frac{(B - S)NK}{V} \tag{4}$$

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

A NT 32,000 25

where:

C_{sTCM/SO_2} = equivalent concentration of SO_2 in solution, μg/mL,
SA = volume, mLvolume of thiosulfate solution titrant required for titration of the sample, blank, mL,
B = volume, mLvolume of thiosulfate solution titrant required for titration of the blank, sample, mL,
NT = normality of the thiosulfate solution, titrant, from Eq 3,
K 32,000 = microlliequivalent weight for SO_2 = 32 030 μg, and , μg,
V 25 = volume, mLvolume of sample taken, mL. standard sulfite solution, mL, and
0.02 = dilution factor.

8.7.7 *Sulfite Solution, Dilute Standard for Manual Methods A and B*—Immediately after standardization of the sulfite solution, pipet 2 mL of the freshly standardized

This solution into a 100-mL volumetric flask containing approximately 10 mL of 0.04 *M* TCM and then bring to mark with 0.04 *M* TCM. This solution is stable for 30 days if stored kept at 5°C. Concentration of SO_2 in the 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 is as follows:

SO_2, μg/mL = 0.02 × concentration of standard solution (4)

8.7.8 *Sulfite Solution, Dilute Standard for Automated Methods I and II*—Immediately after standardization of the sulfite solution, pipet 25 by diluting 10 mL of the freshly standardized working sulfite-TCM solution into a 500-mL flask containing approximately 50 mL of 0.04 *M* TCM, and fill to the mark 100 mL with 0.04 *M* TCM. This is stable for 30 days if stored at 5°C. The concentration of the SO_2 in the dilute solution is as follows:

SO_2, μg/mL = 0.05 × concentration of standard solution (5)

8.8 TCM absorbing reagent.

8.4.8 *Sulfur Dioxide Permeation Tube*—TPermeation 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 8.3.7.

9.1.1.1 Disposal procedures for the mercury salts are described in Annex A3. 8.3.1.

9.2 *Sampling and Transporting Precautions*—TMaintain the temperature of the impinging solution should be maintained 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 ~~(1 h)~~ (30 min) and for long-term (24 h) sampling. ~~One can select different~~ Select different combinations of sampling rate and time to meet special needs, but adjust sample volumes and air flow rates ~~must be adjusted~~ so that the linearity is maintained between absorbance and concentration over the dynamic range.

~~10.2 See Practices D 1357~~

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 ~~D 1605~~ 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 ~~g~~ 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. ~~This should be repeated~~ Repeat this calibration monthly. Calibrate the hypodermic needle with a flowmeter calibrated in accordance with ~~Recommended~~ Practice D 3195 before and after sampling.

11.1.2 ~~T~~ Maintain the pressure drop of the flow-measuring devices ~~must be maintained~~ 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 8.7 or 8.4, as described in Annex A2.

11.2.1 For Manual Methods A and B, repeat this determination A2, when new stock PRA solution is prepared, or every three months, whichever is first.

11.2.2 For Automated Methods I and II, prepare a calibration curve at the beginning, near the middle, and at the end of each run.

11.2.3 For

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

12. Procedure

12.1 *Sampling*:

12.1.1 *One-Hour Sampling*—Add 10 mLGeneral Considerations—Procedures are described for short-term sampling (30 min and 1 h) and for long-term sampling (24 h). Select different combinations of TCM solution absorbing reagent volume, sampling rate, and sampling time to meet special needs. For combinations other than those specifically dgescribed, adjust the conditions so that linearity is mpaingtained between absorbance and insert it into 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 system (Fig. 1). Collect 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 approximately 0.5 L/min the time the absorber is placed in the sampling train and again when the absorber is removed from the train for 1 h, shipment to the analytical laboratory, using either 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 needle valve 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 tr;ain as shown, makin Fg sure that all connections between the various components are leak tight. 1 Greaseless ball joint fittings, heat shrinkable TFE-fluorocarbon tubing, or Fig. 1a, TFE-fluorocarbon tube fittings may be used to attain leakfree conditions for polrtions of the sampling train that come into contact with air containing SO_2. Shield the absorbing reagent from direct sunlight during and after sampling by covering the impinger to prevent deterioration. Keep with aluminum foil or by enclosing the temperature of the absorbing solution below 25°C. sampling train in a light-proof box. Determine the volume of air sampled by multiplying the average flow rate, measured before and after sampling, by 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 minutes and record min, as the atmospheric pressure, in accordance with Practice D 3631, and temperature. Discard the sample if volume will later be determined using the needle or restricting orifice does not meet the requirements of 7.1.7.1. Remove sampling flow rate and stopper the impinger. If sampling time. Record the sample must be stored before analysis, maintain the temperature at 5°C in a refrigerator.

12.1.2 atmospheric pressure and temperature.

12.1.4 *Twenty-Four-Hour Sampling*—Place 50 mL of TCM absorbing solution in a large absorber, close the absorber cap, and collect sample if needed, apply the heat shrink material. Verify that the reagent level is at 0.2 L/min for 24 h, usually from midnight 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 midnight. Make sure no entrainment of solution occurs. 15 ± 10°C. During collection and storage, protect sampling, control the sample from direct sunlight. Keep the absorber temperature to prevent decomposition of the collected complex. From the onset of sampling until analysis, protect the absorbing solution below 25°C. from direct sunlight. Determine the total air volume by multiplying the average air flow rate, measured before and after sampling, by rate according to 10.3. Collect the sampling time in minutes. Discard the sample if the needle or restricting orifice does not meet the requirements for 24 h from midnight to midnight at a flow rate of 7.1.7.1. The correction of 24-h measurements 0.200 ± 0.020 L/min. A start/stop timer is helpful for temperature initiating and pressure may be difficult stopping sampling and is not ordinarily done; however, the accuracy of the measurement an elapsed time meter will be improved if meaningful corrections can be applied. Measure pressure in accordance with Practice D 3631. If storage is necessary, refrigerate at 5°C. useful for determining the sampling time.

12.2 *Transporting Impinged Samples*— Keep the temperature of the samples below 25°C by using refrigerated shipping containers to transport them from the field.[10] Avoid—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 ~~when analysis~~ stopper immediately. Verify that the temperature of the ~~samples~~ absorber is ~~delayed for any appreciable time without refrigeration and protection from light,~~ not above 25°C. Mark the ~~r~~ 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 ~~corrected~~ 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 ~~*Sampling*~~*Sample Preparation*—Remove the samples from the shipping container ~~M~~. If the shipment period exceeded 12 h from the completion of sampling, verify that the temperature is below 10°C. Also, compare the sol ~~M~~ution 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 s ~~A~~hipping, make an appropriate notation in the record and ~~B:~~ invalidate the sample. Prepare the samples for analysis as follows:

12.3.1.1 ~~*One-Hour*~~*For 30 min or 1 h Samples*—~~After collection,~~—Quantitatively transfer the ~~sample quantitatively~~ entire 10 mL amount of absorbing solution to a ~~25-mL volumetric flask, using about 5~~ 25 mL volumetric flask and rinse with a small amount (<5 mL) of ~~water for rinsing. Delay analysis for 20 min to allow any ozone to decompose.~~ distilled water.

12.3.1.2 *Twenty-Four-Hour Samples*—~~Dilute~~—If the ~~entire~~ 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 wa~~b~~ter to compensate for ~~b~~ water lost to evaporation during sampling. If the final volume is greater than the original volume, measure the volume with a graduated cylinder. ~~P~~ To analyze, pipet ~~5~~ 10 mL of the solution into a ~~25-mL flask. Add 5-mL absorbing solution. Delay analysis for 20 min to allow any ozone to decompose.~~ 25 mL volumetric flask.

12.3.1.3 ~~*Determination*~~*Sample Analysis*—For each set of determinations, prepare a reagent blank by adding 10 mL ~~(or 20 mL if~~ TCM absorbing solution to a 25 mL volumetric flask, and two congtrol standuards 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 ~~was taken) of~~ to stand 20 min after the ~~unexposed absorbing reagent plus 5 mL~~ completion of ~~water~~ sampling to ~~a 25-mL volumetric flask.~~ 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 to destroy the nitrite from oxides of nitrogen.~~ min.

(c) Accurately pipet ~~in~~ 2 mL of ~~the~~ 0.2 % formaldehyde~~,~~ solution and then 5 mL of pararosaniline ~~reagent described in Methods A or B, and mix well.~~ solution into each flask. Start a laboratory timer ~~that has been~~ set ~~for~~ at 30 min.

(d) Bring ~~all~~ each flask to volume with ~~freshly~~ 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 ~~(using 10-mm optical path length cells),~~ and before 60 min, determine the corrected absorbances (Eq 9) of ~~the sample and of the blank~~ each solution at ~~the wavelength of maximum absorbance~~, 548 nm for Method A or at 575 ~~nm~~ mn for Method ~~B. Use~~ 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) in~~ blank because of the ~~reference cell.~~ sensitivity of the reagent blank to temperature.

(g) Do not allow the colored solution to stand in ~~absorbance cell;~~ the cells because a film ~~of dye would~~ may be ~~deposited thereon. The dye can be removed~~ deposited. Clean the cells with ~~HCl (1 + 1) prior to cleaning. If~~ isopropyl alcohol after use.

(h) Ensure the reagent blank ~~differs by more than~~ is within 0.03 absorbance units ~~from that found in~~ of the intercept of the calibration ~~curve, prepare a new curve.~~

~~12.3.1.4 If~~ (Eq 12).

NOTE 7—*Absorbance range.* If the absorbance of the sample solution ranges between 1.0 and 2.0, ~~dilute~~ the sample ~~1 + 1~~ can be diluted 1:1 with a portion of the reagent blank and ~~r~~ the absorbance redetermined within ~~a few minutes.~~ 5 min. Solutions with higher absorbances can be diluted up to sixfold with the reagent blank in order to obtain ~~on-scale~~ scale readings ~~within 10 %~~ of ~~the true~~ less than 1.0 absorbance ~~value.~~

~~12.3.2 *Preparation for Automated Methods I and II*—After collection, if a precipitate is observed in the sample, remove~~ unit. However, it ~~by centrifugation.~~

~~12.3.2.1 *One-Hour Samples*—If sample has lost water due to evaporation, bring sample back to 10 mL with distilled water. Delay analyses for 20 min to allow any ozone to decompose.~~

~~12.3.2.2 *Twenty-Four-Hour Samples*—If sample has lost water due to evaporation, bring sample back to 50 mL with distilled water. Delay analyses for 20 min to allow any ozone to decompose. Fill the test cups with standards as described in 10.2 and samples and place on the turntable. One quality control sample,~~ is recommended that a ~~1.0 µg SO_2 /mL calibration standard, shall be included after every 10 samples, followed by enough test cups filled with unreacted absorbing reagent to provide a baseline check. If ten or less samples are run, include three quality control standards. The quality control sample shall produce a net response (Baseline % T − Sample % T) within ±2.3 % T~~ smaller portion (<10 mL) of the ~~value indicated by the day's calibration~~

curve for Automated Method I, or a response within ±3.9 scale % of the value indicated by the day's calibration for the Automated Method II, for the analysis to be valid.

12.3.2.3 Start up the analyzer and start the reagents flowing through the system. The original sample in the flow cell shall be free of bubbles during operation. Refer to reanalyzed (if possible) if the manufacturer's instructions for general operating procedure. Position the sample probe so it samples from near the bottom of the sample cups. If the presence of SO_2 is suspected in the air about the analyzer, bubble the air used to segment the sampler through requires a solution of TCM.

12.3.3 *Procedure for Automated Method I*:

12.3.3.1 With the proper apertures in the colorimeter and unreacted absorbing reagent passing through the flow cell, set the baseline at 100 % transmittance with the 100 % *T* control.

12.3.3.2 Set full-scale response by placing a blank or zero aperture in the sample side of the colorimeter and adjusting the zero control to obtain a response of zero percent transmittance. Once the zero is set, remove the blank aperture.

12.3.3.3 Offset the baseline by adjusting the 100 % *T* control to obtain a baseline at 96 to 99 % *T*, in order to observe baseline drift.

12.3.3.4 Introduce the calibration standards as described in 10.2.

12.3.3.5 Introduce the samples.

12.3.4 *Procedures for Automated Method II*:

12.3.4.1 Set the electronic zero by turning the display rotary switch to the zero position and adjusting the zero control (screwdriver adjustment) for 0 % of scale.

12.3.4.2 Set the electronic full scale by turning the display rotary switch to the full-scale position and adjusting the fullscale control (screwdriver adjustment) for 100 % of scale.

12.3.4.3 Set the display rotary switch to the normal oper ation mode. With unreacted absorbing reagent flowing through the flow cell, adjust the baseline to 0 % of full scale.

12.3.5 *Procedure for Automated Method I and II*:

12.3.5.1 Once a stable baseline is obtained, span the colorimeter by introducing a 1.0 µg SO_2/mL calibration standard and adjusting the standard calibration control so that a recorder response of 71.4 % of full scale is obtained (when using the specified range from 0 to 1.4 µg SO_2/mL). Repeat several times to verify the setting. If the calibration standard concentration is not exactly 1.0, the recorder response should be adjusted proportionately.

12.3.5.2 Introduce the calibration standards as described in 11.2.

12.3.5.3 Introduce the samples.

12.4 *Maintenance of Automated Analytical Systems*:

12.4.1 Cleaning of the apparatus after each use is necessary to prevent contamination of subsequent analyses. Consult manufacturer's instructions for cleaning procedures. Alkaline materials should not be used because of the formation of a precipitate with TCM. dilution greater 1:1.

13. Calculations

13.1 *Sample Air Volume*:

13.1.1 *Calculationeen of Flow Ratre at Samplieng Site*—DEq 6 may be used to determine the e 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.

$$Q_{SO}P_{std} \times \frac{298.16}{T_{meter} + 273.16} \tag{10}$$

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

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_2} = vapor pressure of water at the impinged sample from temperature of the calibration curve, as described air in Annex

in_O A2.

13.2 *Air Volume*—Convert 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 sampled to in the flow or volume standard, °C (for example, bubble flowmeter).

13.1.2 *Total Sample Volume*—Determine the sampling volume at standard conditions of 25°C and 101.3 kPa (1 atm) as follows:

$$V_R = V \times \frac{P}{101.3} \times \frac{298.15}{T} \tag{11}$$

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

QiQf101.3 t

where:

V_{Rstd} = volume of airsampling volume at standard conditions, L,
$V Q_i$ = volumeflow rate determined at the initiation of air, L, sampling in std L/min,
$P Q_f$ = average atmospheric pressure, kPa, flow rate determined at the completion of sampling in std L/min, and
$T t$ = average temperature oftotal sampling time, min.

13.2 *Sulfur Dioxide Concentration in the Air Sample*—Calculate the SO_2 concentration in the air sample, K, 101.3 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 = pressure of standard atmosphere, kPa, and 298.15*corrected absorbance,*
m = temperatureslope, absorbance unit/μg SO_2,
x = mass of standard atmosphere, K. 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 *Sulfphur Dioxide Concentration*—Determine the Air Sample —Calculate the concentration of SO_2 concentration in the air each sample at standard conditions as follows:

$$C = \frac{C_s \times V_s \times 1000}{VR} \times D \quad (7)$$

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

AAoBxVaVbVstd

where:

C = concentration of SO_2 in air sample at standard conditions, μg/m^3,
C_sA = concentrationcorrected absorbance of SO_2 in impinged sample, μg/mL, the sample solution, from Eq 9,
$D A_o$ = dilution factor to samples exceeding 1.4 μg/mL, corrected absorbance of the reagent blank, using Eq 9,
$D B_x$ = 1 if sample was not diluted. 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_{sa} = volume of impinged sample, absorber solution analyzed, mL,
V_{Rb} = total volume of air sampled at standard conditions, L, solution in absorber, mL, and 1000
V_{std} = factor to convert L to m^3.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 ~~μg/m^3~~ μg/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

145.1 *Precision*:

~~14.1.1 *Manual*~~

15.1.1 *Method A*:

145.1.1.1 *Repeatability (Single-Analyst)*—The standard deviation of results obtained by a single analyst on separate samples **(118)** from the same flowing air stream is shown in Fig. ~~4~~ 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.

145.1.1.2 *Reproducibility (Multilaboratory)*—The standard deviation of single analyses, obtained by analysts from different laboratories **(116)** taking separate samples from the same flowing air stream, is plotted in Fig. ~~5~~ 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.

~~14.1.2 *Manual*~~

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

~~14.1.3 *Automated Method I*—An estimate of the relative standard deviation **(8)** for 1-h samples at a concentration of 1000 μg SO_2/m^3 (0.38 ppm) is 5.0 %. Estimates of the relative standard deviation for 24-h samples at concentrations of 80, 350, and 900 μg SO_2/m^3 (0.03, 0.13, and 0.34 ppm, respectively) are 4.6, 3.1, and 2.6 %, respectively.~~

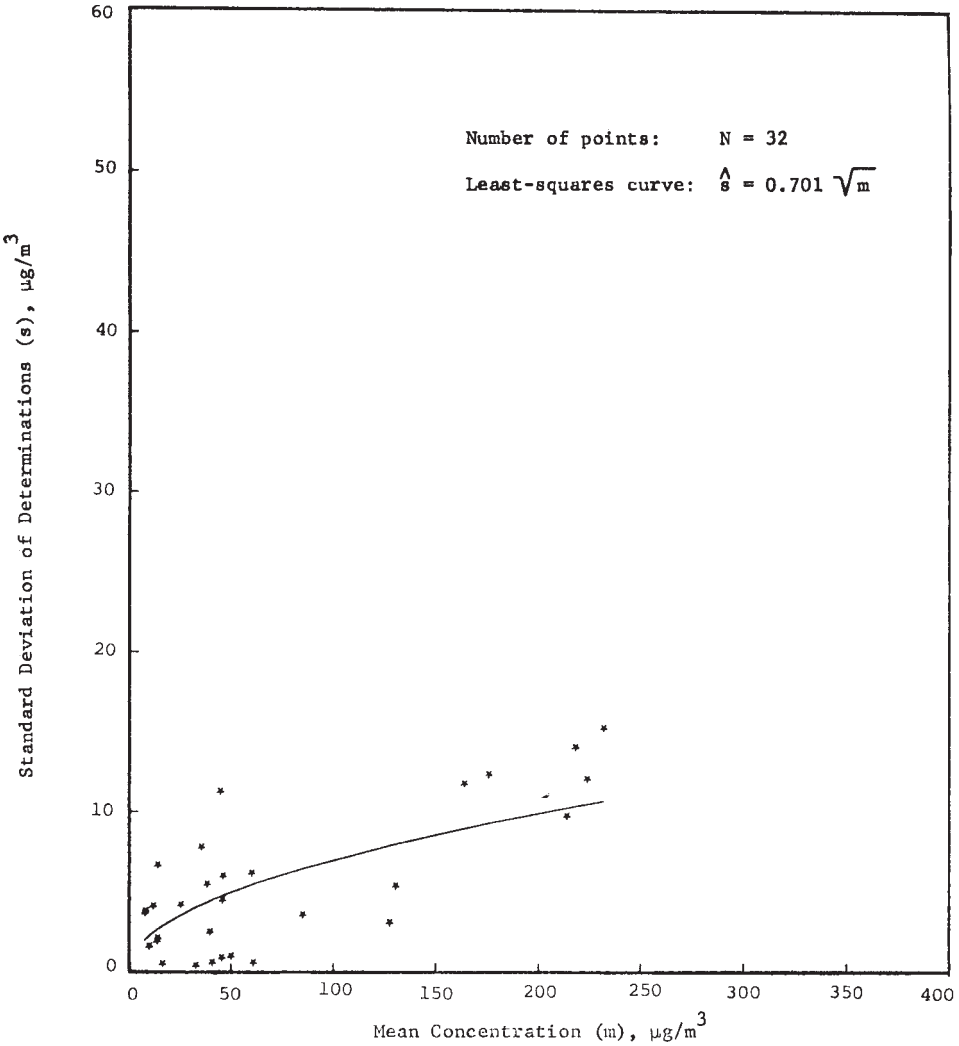

FIG. ~~4~~ 2 Scatter Diagram and Least-Squares Curve Relating Within-Laboratory Standard Deviation (Repeatability) to Concentration of Sulfur Dioxide

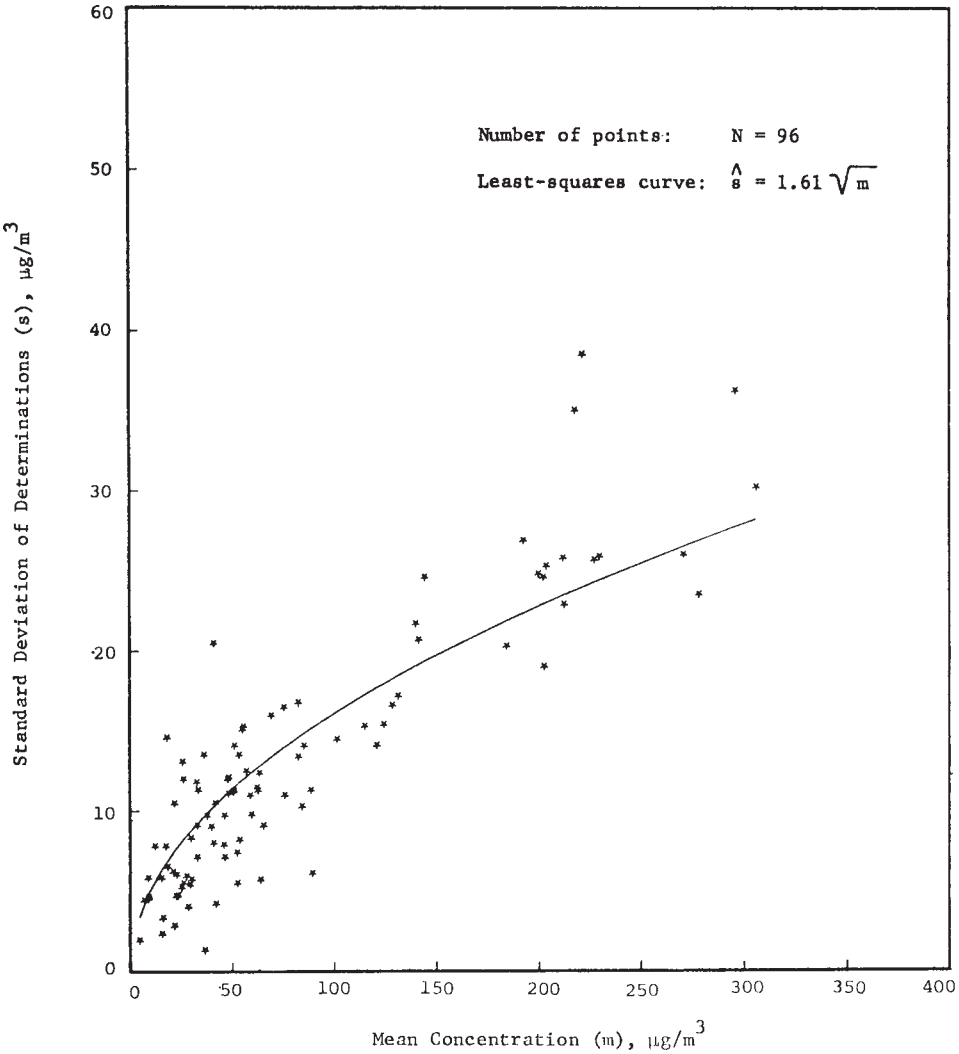

FIG. 5 3 Scatter Diagram and Least-Squares Curve Relating Between-Laboratory Standard Deviation (Reproducibility) to Concentration of Sulfur Dioxide

14.1.4 *Automated Method II*—An estimate of the relative standard deviation **(9)** for 1-h samples at a concentration of 980 µg SO_2/m^3 (0.37 ppm) is 5.0 %. Estimates of the relative standard deviation for 24-h samples at concentrations of 100, 350, and 900 µg SO_2/m^3 (0.037, 0.13, and 0.34 ppm, respectively) are 4.2, 0.4, and 0.8 %, respectively.

14.2

15.2 *Bias*:

14.2.1 *Manual*

15.2.1 *Method A*—The results of an interlaboratory cooperative study **(11 6)** 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.

14 5.2.2 No bias statement can be made for Manual Method B or Automated Methods I or II.

15. B.

16. Keywords

15 6.1 ambient atmospheres; analysis; caolorimetric analysis; EPA equivalent method; 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 Manual Method A and B**~~

~~A2.1.1 Accurately~~

A2.1 Following Table A2.1, accurately pipet ~~graduated amounts~~ the indicated volumes of the ~~dilute standard sulfite solution (8.7.7)~~ indicated sulfite-TCM solutions into a series of 25–mL volumetric ~~flasks (such as 0.5, 1, 2, 3, 4, and 5-mL). Prepare standards in duplicate.~~

~~A2.1.2 Add sufficient~~ flasks. Add TCM ~~solutions~~ absorbing reagent as indicated to bring the volume in each flask to ~~about~~ 10 mL.

~~A2.1.3 Add~~

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

TABLE A2.1 Preparation of ~~TCM Abs~~ SO_2 Worbking ~~Re~~ Stagentdards

Sulfitae-TCM Solutiondard, µg ~~SO_2/mL~~	Volume. of Indicated Sulfitae-TCM Solutiondard, mL	~~Di~~Voluted. of TCM, ~~to,~~ mL	Approximate ~~Concentr~~ Matiss on,~~f~~ µg SO_2/mL[A], µg
~~20~~	~~7.0~~	~~100~~	~~1.4~~
Working (see 8.4.7.2)	7.0	6.0	28.8
~~20~~	~~5.0~~	~~100~~	~~1.0~~
Working (see 8.4.7.2)	5.0	7.0	21.6
~~20~~	~~2.0~~	~~100~~	~~0.4~~
Working (see 8.4.7.2)	2.0	8.0	14.4
~~1.0~~	~~10.0~~	~~100~~	~~0.10~~
Dilute Working (see 8.4.7.3)	10.0	0.0	7.2
~~1.0~~	~~4.0~~	~~100~~	~~0.04~~
Dilute Working (see 8.4.7.3)	4.0	5.0	3.6
~~1.0~~	~~2.0~~	~~100~~	~~0.02~~
	2.0	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.

and cooled distilled water and mix thoroughly. The color must be developed (during the remaining reagents described 30 min period) in 12.1 and proceed as described therein.

A2.1.4 Use a constant-temperature bath maintained ±1°C, temperature environment in the range from 20 of 20° to 30°C. T, 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 calibration and that reference cell rather than the reagent blank because of the analysis shall be within 2°C.

A2.1.5 Plot temperature sensitivity of the absorbance against reagent blank. Calculate the total concentration in µg/mL mass of SO_2 for the corresponding solution. A linear rela tionship should be obtained, and the *y*-intercept should be within 0.03 absorbance units of the zero standard absorbance. For maximum precision, determine the line of best fit using regression analysis by the method of least squares.

A2.1.6 Determine the slope of the line; calculate its reciprocal; and denote this in each solution, as the calibration factor, follows:

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

B

where: *s*. This can be used for calculating the results

V_{TCM/SO_2} = volume of samples, provided there are no changes in temperature or pH. Analyze at least one control sample containing a known amount sulfite-TCM solution used, mL,

C_{TCM/SO_2} = concentration of sulfur dioxide in the working sulfite-TCM, µg SO_2 during each series of determinations.

A2.2 Automated Methods I and II

A2.2.1 Prepare calibration standards by dilution of/mL (from Eq 4), and

D = dilution factor (D = 1 for the dilute standard sulfite solutions (8.7.8) and working sulfite-TCM solution; D = 0.1 for the 1.0 µg/mL diluted working sulfite-TCM solution).

A2.3 Determine the calibration standard, equation using TCM absorbing reagent as shown in Table A2.1.

A2.2.2 Run the standards in decreasing order method of concentrations, in duplicate, as described in Section 12.

A2.2.3 Plot absorbance (for Method I) or net response in percent linear least squares. The total mass of full scale (for Method II) for all three calibrations (*y*-axis) versus the corresponding concentration in mg SO 2/mL ($_2$ contained in each solution is the *x*-axis).

A2.2.4 For maximum precision, determine 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 best fit using regression analysis 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 subsequaently 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 **(116)** 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. **Caution: (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 ~~This annex contains an alternative procedure for the preparation of calibration standards. It is not recommended for routine use because the precision and error have not been determined. It may be used to determine the efficiency of sampling~~*Dynamic Calibration Procedures*—Atmospheres containing accurately known concentrations ~~below the range~~ of sulfur dioxide are prepared using permeation devices. In the ~~method mentioned in Note 1.~~

~~A4.2 *Procedure:*~~

~~A4.2.1 Calibrated~~ systems for generating these atmospheres, the permeation ~~tubes that contain liquefied~~ device emits gaseous SO_2 ~~can be used to prepare standard concentrations~~ at a known, low, constant rate, provided the temperature of ~~SO_2 in air~~ **~~(12, 13, 14)~~**. ~~See Practice D 3609 for details. Analyses of these known concentrations give calibration curves that simulate all~~ the ~~operational conditions performed during the sampling~~ device is held constant (+0.1°C) and ~~chemical procedures. This calibration curve includes~~ the ~~important correction for collection efficiency~~ device has been accurately calibrated at ~~various concentrations~~ 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)**.

~~A4.2.2 Prepare or obtain~~

A4.1.1 *Procedure for 30 min and 1 h Samples*—Generate a ~~TFE-fluorocarbon permeation tube that emits SO~~ series of six standard atmospheres of $S0_2$ ~~at a rate of 0.1 to 0.2 µg/min (0.04 to 0.08 µg/min at standard conditions of 25°C and 101.3 kPa (1 atm)). A permeation tube with an effective length of 10 to 20 mm and a wall thickness of 0.75 mm (0.030 in.) will yield the desired permeation rate if held at a constant temperature of 20°C.~~

~~A4.2.3 Calibrate permeation tubes containing SO_2 under a stream of dry nitrogen to prevent the formation of blisters in the walls.~~

~~A4.2.4 To prepare standard concentrations of SO_2, assemble the apparatus, as shown in Fig. A4.1, consisting of a water-cooled condenser; constant-temperature water bath maintained at 20°C; cylinders containing pure dry nitrogen and pure dry air, with appropriate pressure regulators; needle valves and flowmeters for the nitrogen and dry air diluent gas streams. Bring the diluent gases to temperature~~ (for example, 0, 50, 100, 200, 350, 500, 750, $\mu g/m^3$) by ~~passage through a 2-m long copper coil immersed in~~ adjusting the ~~water bath. Insert a calibrated permeation tube into the central tube of the condenser maintained at 20°C by circulating water from the constant-temperature bath and pass a stream of nitrogen over the tube at a fixed rate of approximately 50 mL/min. Dilute this gas stream to the desired concentration by varying the~~ dilution flow ~~rate of the "clean dry air." This flow rate can normally be varied from 0.2 to 15 L/min. The flow rate of the sampling system determines the lower limit for the flow~~

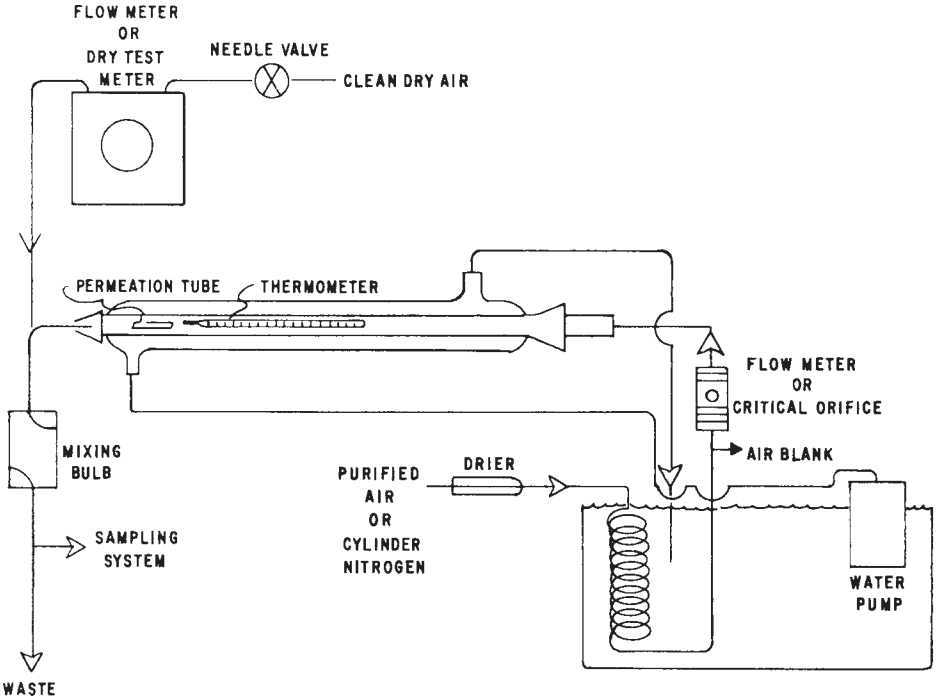

FIG. A4.1 Gas Dilution System for Preparation of Standard Concentrations of Sulfur Dioxide for Laboratory Use by the Permeation Tube Method

rate of diluent gases. The flow rates of the nitrogen and the diluent air must be measured to an accuracy of 1 to 2 %. With a tube permeating SO_2 at a rate of 0.1 µL/min (0.26 µg/min), the range of concentration of SO_2 will be between 20 to 1000 µg/m^3 (0.007 to 0.04 ppm), a generally satisfactory range for ambient air conditions. When higher concentrations are desired, calibrate and use longer permeation tubes.

A4.2.5 *Procedure for Preparing Simulated Calibration Curves*—Obviously, one can prepare a multitude of curves by selecting different combinations of sampling rate and sampling time. appropriately. The following description represents a typical procedure for ambient air sampling of short duration, with a brief mention of a modification for 24-h sampling. The system is designed to provide an accurate measure concentration of SO_2 in the 20 to 3000 µg/m^3 (0.01 to 0.5 ppm) range. It can easily be modified to meet special needs.

A4.2.6 The dynamic range of the colorimetric procedure fixes the total volume of the sample at 30 L; then to obtain linearity between the absorbance of the solution and the concentration of SO_2 in parts per million, select a constant sampling time. This fixing of sampling time each atmosphere is also desirable from a practical standpoint. In this case, select a sampling time of 30 min. Then, to obtain a 30-L sample requires a flow rate of 1 L/min. A22-gage hypodermic needle, operating calculated as a critical orifice, will control air flow at this approximate desired rate. Calculate the concentration of standard SO_2 in air as follows: follows:

$$C = \frac{P(1000)}{R + r} \tag{A4.1}$$

$$C_a = \frac{P_r \times 10^3}{Q_d + Q_p} \tag{A4.1}$$

PrQd1000

where:

C_a = concentration of SO_2 at standard conditions, µg/m^3,
P_r = permeation rate, µg/min,
R = flow rate of diluent dilution air, L/min, and
Q_d
r = flow rate of diluent nitrogen, L/min, and
Q_p
1000 = conversion factor to convert L to m^3. carrier gas across permeation device, L/min.

A4.2.7 A plot

Ensure that the total flow rate of the concentration standard exceeds the flow demand of SO the sample train, with the excess flow vented at atmospheric pressure. Sample each atmosphere using similar 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_2 in µg/m^3 (*x*-axis) against absorbance of the final solution (*y*-axis) will yield a straight line, the slope of which is the factor for conversion of absorbance toµ g/m^3. This factor includes the correction for collection efficiency. Any deviationO and pipet 10 mL portions from linearity at the lower concentration range indicates each impinger into a change in collection efficiency series of the sampling system. Actually, the standard concentration of 20 µg/m^3 is slightly below the dynamic range of the method. 25 mL volumetric flasks. If this is the range of interest, the total volume of air collected should be increased to obtain sufficient color development steps are not to be started within the dynamic range 12 h of sampling, store the colorimetric procedure. Also, once solutions at 5° ± 5°C. Calculate the calibration factor has been established under simulated conditions, the conditions can be modified so that the concentration total mass of SO_2 is a simple multiple of the absorbance of the colored solution.

A4.2.8 For long-term sampling of 24-h duration, the conditions can be fixed to collect 300 L of sample in a larger volume of TCM. For example, for 24 h at 0.2 L/min, approximately 288 L of air are collected. An aliquot representing 0.1 of the entire amount of the sample is taken for the analysis. The remainder of the analytical procedure is the same each solution as described in Section 12.

A4.2.9 *Calculations*— Calculate the concentration of SO_2 in the sample as follows: follows:

$$C = \frac{(A - A')10^3(B)}{V} \tag{A4.2}$$

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

CastVaVb

where:

~~C~~ M = mass of SO_2 in each solution, in μg,
C_a = concentration of SO_2 in the standard atmosphere, $\mu g/m^3$,
~~A~~ s = ~~sample absorbance,~~ sampling flow rate, L/min,
~~A'~~ t = ~~reagent blank absorbance,~~ sampling time, min,
~~B~~ V_a = ~~calibration factor, µg/absorbance unit,~~ volume of absorbing solution used for color development (10 mL), and
V_b = ~~sample volume, L, corrected to 25°C~~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 ~~101.3 kPa, and~~
~~10~~ 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 ~~correct L to m~~ 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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