

Figure 2. Calibration system using a compressed gas standard.

[75 FR 35593, June 22, 2010]

APPENDIX A-2 TO PART 50—REFERENCE METHOD FOR THE DETERMINATION OF SULFUR DIOXIDE IN THE ATMOSPHERE (PARAROSANILINE METHOD)

1.0 Applicability.

1.1 This method provides a measurement of the concentration of sulfur dioxide (SO₂) in ambient air for determining compliance with the primary and secondary national ambient air quality standards for sulfur oxides (sulfur dioxide) as specified in § 50.4 and § 50.5 of this chapter. The method is applicable to the measurement of ambient SO₂ concentrations using sampling periods ranging from 30 minutes to 24 hours. Additional quality assurance procedures and guidance are provided in part 58, appendixes A and B, of this chapter and in references 1 and 2.

2.0 Principle.

2.1 A measured volume of air is bubbled through a solution of 0.04 M potassium tetrachloromercurate (TCM). The SO₂ present in the air stream reacts with the

TCM solution to form a stable monochlorosulfonatomercurate(3) complex. Once formed, this complex resists air oxidation(4, 5) and is stable in the presence of strong oxidants such as ozone and oxides of nitrogen. During subsequent analysis, the complex is reacted with acid-bleached pararosanine dye and formaldehyde to form an intensely colored pararosanine methyl sulfonic acid.

(6) The optical density of this species is determined spectrophotometrically at 548 nm and is directly related to the amount of SO₂ collected. The total volume of air sampled, corrected to EPA reference conditions (25 °C, 760 mm Hg [101 kPa]), is determined from the measured flow rate and the sampling time. The concentration of SO₂ in the ambient air is computed and expressed in micrograms per standard cubic meter (µg/std m³).

3.0 Range.

3.1 The lower limit of detection of SO₂ in 10 mL of TCM is 0.75 µg (based on collaborative

test results).(7) This represents a concentration of $25 \mu\text{g SO}_2/\text{m}^3$ (0.01 ppm) in an air sample of 30 standard liters (short-term sampling) and a concentration of $13 \mu\text{g SO}_2/\text{m}^3$ (0.005 ppm) in an air sample of 288 standard liters (long-term sampling). Concentrations less than $25 \mu\text{g SO}_2/\text{m}^3$ can be measured by sampling larger volumes of ambient air; however, the collection efficiency falls off rapidly at low concentrations.(8, 9) Beer's law is adhered to up to $34 \mu\text{g}$ of SO_2 in 25 mL of final solution. This upper limit of the analysis range represents a concentration of $1.130 \mu\text{g SO}_2/\text{m}^3$ (0.43 ppm) in an air sample of 30 standard liters and a concentration of $590 \mu\text{g SO}_2/\text{m}^3$ (0.23 ppm) in an air sample of 288 standard liters. Higher concentrations can be measured by collecting a smaller volume of air, by increasing the volume of absorbing solution, or by diluting a suitable portion of the collected sample with absorbing solution prior to analysis.

4.0 Interferences.

4.1 The effects of the principal potential interferences have been minimized or eliminated in the following manner: Nitrogen oxides by the addition of sulfamic acid,(10, 11) heavy metals by the addition of ethylenediamine tetracetic acid disodium salt (EDTA) and phosphoric acid,(10, 12) and ozone by time delay.(10) Up to $60 \mu\text{g Fe}$ (III), $22 \mu\text{g V}$ (V), $10 \mu\text{g Cu}$ (II), $10 \mu\text{g Mn}$ (II), and $10 \mu\text{g Cr}$ (III) in 10 mL absorbing reagent can be tolerated in the procedure.(10) No significant interference has been encountered with $2.3 \mu\text{g NH}_3$.(13)

5.0 Precision and Accuracy.

5.1 The precision of the analysis is 4.6 percent (at the 95 percent confidence level) based on the analysis of standard sulfite samples.(10)

5.2 Collaborative test results(14) based on the analysis of synthetic test atmospheres (SO_2 in scrubbed air) using the 24-hour sampling procedure and the sulfite-TCM calibration procedure show that:

- The replication error varies linearly with concentration from $\pm 2.5 \mu\text{g}/\text{m}^3$ at concentrations of $100 \mu\text{g}/\text{m}^3$ to $\pm 7 \mu\text{g}/\text{m}^3$ at concentrations of $400 \mu\text{g}/\text{m}^3$.
- The day-to-day variability within an individual laboratory (repeatability) varies linearly with concentration from $\pm 18.1 \mu\text{g}/\text{m}^3$ at levels of $100 \mu\text{g}/\text{m}^3$ to $\pm 50.9 \mu\text{g}/\text{m}^3$ at levels of $400 \mu\text{g}/\text{m}^3$.
- The day-to-day variability between two or more laboratories (reproducibility) varies linearly with concentration from $\pm 36.9 \mu\text{g}/\text{m}^3$ at levels of $100 \mu\text{g}/\text{m}^3$ to $\pm 103.5 \mu\text{g}/\text{m}^3$ at levels of $400 \mu\text{g}/\text{m}^3$.
- The method has a concentration-dependent bias, which becomes significant at the 95 percent confidence level at the high concentration level. Observed values tend to be lower than the expected SO_2 concentration level.

6.0 Stability.

6.1 By sampling in a controlled temperature environment of $15^\circ \pm 10^\circ \text{C}$, greater than 98.9 percent of the SO_2 -TCM complex is retained at the completion of sampling.(15) If kept at 5°C following the completion of sampling, the collected sample has been found to be stable for up to 30 days.(10) The presence of EDTA enhances the stability of SO_2 in the TCM solution and the rate of decay is independent of the concentration of SO_2 .(16)

7.0 Apparatus.

7.1 Sampling.

7.1.1 *Sample probe:* A sample probe meeting the requirements of section 7 of 40 CFR part 58, appendix E (Teflon® or glass with residence time less than 20 sec.) is used to transport ambient air to the sampling train location. The end of the probe should be designed or oriented to preclude the sampling of precipitation, large particles, etc. A suitable probe can be constructed from Teflon® tubing connected to an inverted funnel.

7.1.2 *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 minutes and 1 hour (or any period considerably less than 24 hours). Such an impinger is shown in Figure 1. These impingers are commercially available from distributors such as Ace Glass, Incorporated.

7.1.3 *Absorber—24-hour sampling:* A polypropylene tube 32 mm in diameter and 164 mm long (available from Bel Art Products, Pequannock, NJ) is used as the absorber. The cap of the absorber must be a polypropylene cap with two ports (rubber stoppers are unacceptable because the absorbing reagent can react with the stopper to yield erroneously high SO_2 concentrations). A glass impinger stem, 6 mm in diameter and 158 mm long, is inserted into one port of the absorber cap. The tip of the stem is tapered 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 must be 6 ± 2 mm. Glass stems can be fabricated by any reputable glass blower or can be obtained from a scientific supply firm. Upon receipt, the orifice test should be performed to verify the orifice size. The 50 mL volume level should be permanently marked on the absorber. The assembled absorber is shown in Figure 2.

7.1.4 *Moisture trap:* A moisture trap constructed of a glass trap as shown in Figure 1 or a polypropylene tube as shown in Figure 2 is placed between the absorber tube and flow control device to prevent entrained liquid from reaching the flow control device. The tube is packed with indicating silica gel as shown in Figure 2. Glass wool may be substituted for silica gel when collecting short-term samples (1 hour or less) as shown in

Figure 1, or for long term (24 hour) samples if flow changes are not routinely encountered.

7.1.5 *Cap seals:* The absorber and moisture trap caps must seal securely to prevent leaks

during use. Heat-shrink material as shown in Figure 2 can be used to retain the cap seals if there is any chance of the caps coming loose during sampling, shipment, or storage.

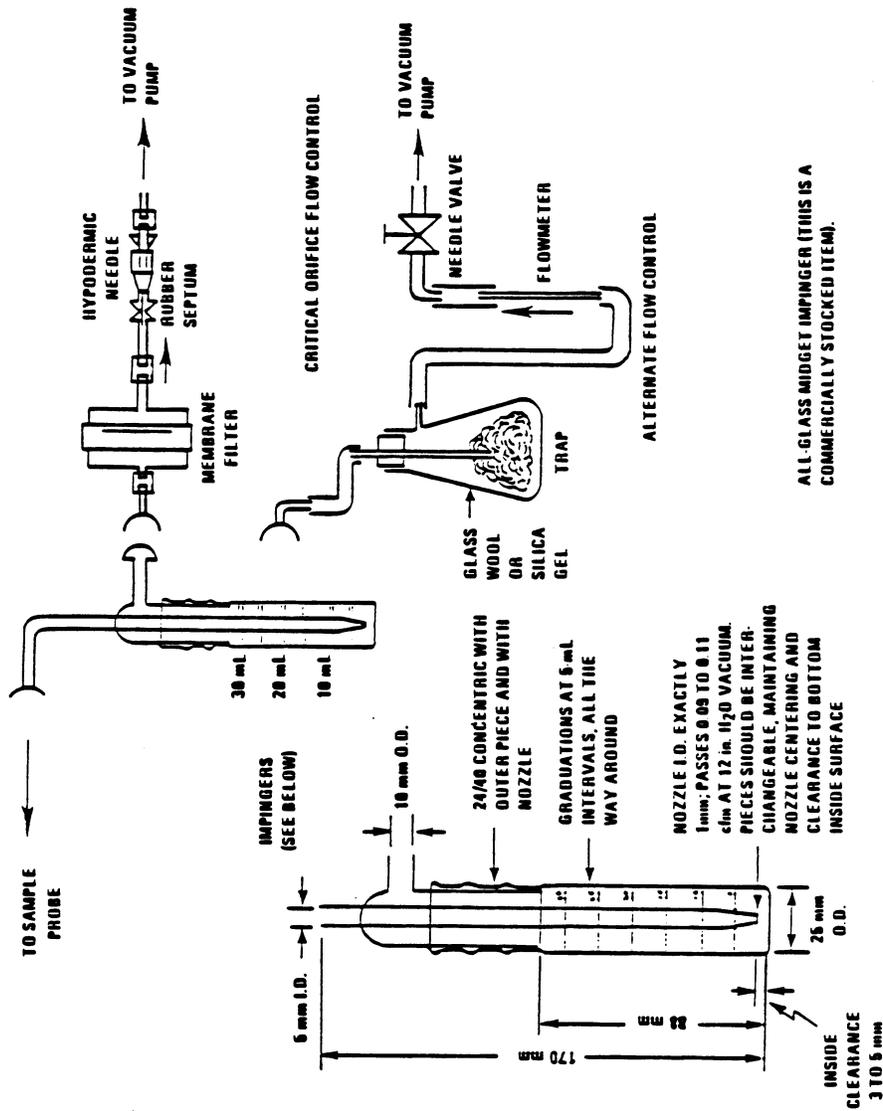


Figure 1. Short-term sampling train.

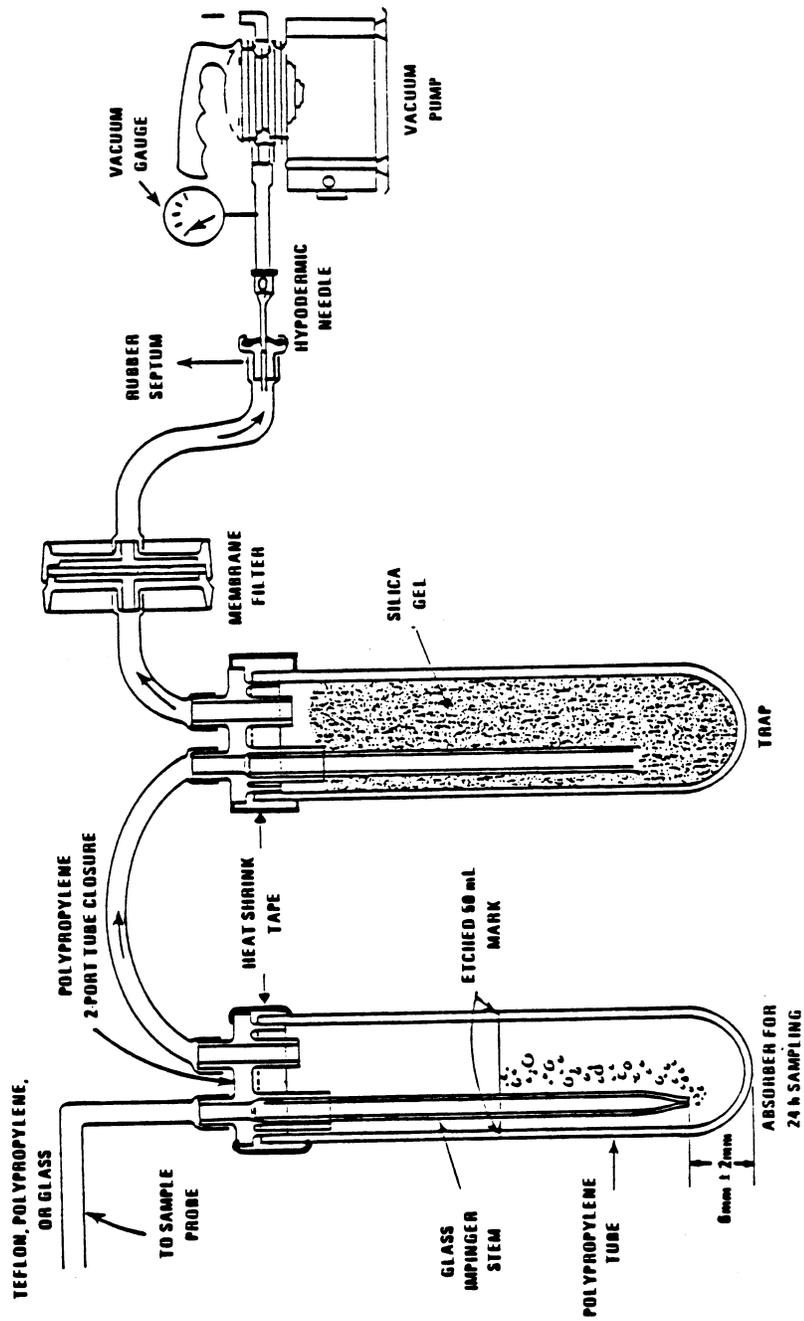


Figure 2. 24-Hour sampling system.

7.1.6 *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 may 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. A 22-gauge hypodermic needle 25 mm long may be used as a critical orifice to yield a flow rate of approximately 1 L/min for a 30-minute sampling period. When sampling for 1 hour, a 23-gauge hypodermic needle 16 mm in length will provide a flow rate of approximately 0.5 L/min. Flow control for a 24-hour sample may be provided by a 27-gauge hypodermic needle critical orifice that is 9.5 mm in length. The flow rate should be in the range of 0.18 to 0.22 L/min.

7.1.7 *Flow measurement device*: Device calibrated as specified in 9.4.1 and used to measure sample flow rate at the monitoring site.

7.1.8 *Membrane particle filter*: A membrane filter of 0.8 to 2 μm porosity is used to protect the flow controller from particles during long-term sampling. This item is optional for short-term sampling.

7.1.9 *Vacuum pump*: A vacuum pump equipped with a vacuum gauge and capable of maintaining at least 70 kPa (0.7 atm) vacuum differential across the flow control device at the specified flow rate is required for sampling.

7.1.10 *Temperature control device*: The temperature of the absorbing solution during sampling must be maintained at $15^\circ \pm 10^\circ \text{C}$. As soon as possible following sampling and until analysis, the temperature of the collected sample must be maintained at $5^\circ \pm 5^\circ \text{C}$. Where an extended period of time may elapse before the collected sample can be moved to the lower storage temperature, a collection temperature near the lower limit of the $15 \pm 10^\circ \text{C}$ range should be used 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, inlet lines must be insulated from the lower temperatures to prevent condensation when sampling under humid conditions. A small heating pad may be necessary when sampling at low temperatures ($< 7^\circ \text{C}$) to prevent the absorbing solution from freezing. (17)

7.1.11 *Sampling train container*: The absorbing solution must be shielded from light during and after sampling. Most commercially available sampler trains are enclosed in a light-proof box.

7.1.12 *Timer*: A timer is recommended to initiate and to stop sampling for the 24-hour period. The timer is not a required piece of equipment; however, without the timer a technician would be required to start and stop the sampling manually. An elapsed time

meter is also recommended to determine the duration of the sampling period.

7.2 Shipping.

7.2.1 *Shipping container*: A shipping container that can maintain a temperature of $5^\circ \pm 5^\circ \text{C}$ is used for 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. Such equipment is available from Cole-Parmer Company, 7425 North Oak Park Avenue, Chicago, IL 60648.

7.3 Analysis.

7.3.1 *Spectrophotometer*: A spectrophotometer suitable for measurement of absorbances at 548 nm with an effective spectral bandwidth of less than 15 nm is required for analysis. If the spectrophotometer reads out in transmittance, convert to absorbance as follows:

$$A = \log_{10}(1/T) \quad (1)$$

where:

A = absorbance, and

T = transmittance ($0 < T < 1$).

A standard wavelength filter traceable to the National Bureau of Standards is used to verify the wavelength calibration according to the procedure enclosed with the filter. The wavelength calibration must be verified upon initial receipt of the instrument and after each 160 hours of normal use or every 6 months, whichever occurs first.

7.3.2 *Spectrophotometer cells*: A set of 1-cm path length cells suitable for use in the visible region is used during analysis. If the cells are unmatched, a matching correction factor must be determined according to Section 10.1.

7.3.3 *Temperature control device*: The color development step during analysis must be conducted in an environment that is in the range of 20° to 30°C and controlled to $\pm 1^\circ \text{C}$. Both calibration and sample analysis must be performed 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 *Glassware*: Class A volumetric glassware of various capacities is required for preparing and standardizing reagents and standards and for dispensing solutions during analysis. These included pipets, volumetric flasks, and burets.

7.3.5 *TCM waste receptacle*: A glass waste receptacle is required for the storage of spent TCM solution. This vessel should be stoppered and stored in a hood at all times.

8.0 Reagents.

8.1 Sampling.

8.1.1 *Distilled water*: Purity of distilled water must be verified by the following procedure:⁽¹⁸⁾

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

8.1.2 *Absorbing reagent* (0.04 M potassium tetrachloromercurate [TCM]): Dissolve 10.86 g mercuric chloride, 0.066 g EDTA, and 6.0 g potassium chloride in distilled water and dilute to volume with distilled water in a 1,000-mL volumetric flask. (*Caution*: Mercuric chloride is highly poisonous. If spilled on skin, flush with water immediately.) The pH of this reagent should be between 3.0 and 5.0 (10) 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 one of the disposal techniques described in Section 13.0. The absorbing reagent is normally stable for 6 months. If a precipitate forms, dispose of the reagent according to one of the procedures described in Section 13.0.

8.2 Analysis.

8.2.1 *Sulfamic acid* (0.6%): Dissolve 0.6 g sulfamic acid in 100 mL distilled water. Prepare fresh daily.

8.2.2 *Formaldehyde* (0.2%): Dilute 5 mL formaldehyde solution (36 to 38 percent) to 1,000 mL with distilled water. Prepare fresh daily.

8.2.3 *Stock iodine solution* (0.1 N): Place 12.7 g resublimed iodine in a 250-mL beaker and add 40 g potassium iodide and 25 mL water. Stir until dissolved, transfer to a 1,000 mL volumetric flask and dilute to volume with distilled water.

8.2.4 *Iodine solution* (0.01 N): Prepare approximately 0.01 N iodine solution by diluting 50 mL of stock iodine solution (Section 8.2.3) to 500 mL with distilled water.

8.2.5 *Starch indicator solution*: Triturate 0.4 g soluble starch and 0.002 g mercuric iodide (preservative) with enough distilled water to form a paste. Add the paste slowly to 200 mL of boiling distilled water and continue boiling until clear. Cool and transfer the solution to a glass stoppered bottle.

8.2.6 *1 N hydrochloric acid*: Slowly and while stirring, add 86 mL of concentrated hydrochloric acid to 500 mL of distilled water. Allow to cool and dilute to 1,000 mL with distilled water.

8.2.7 *Potassium iodate solution*: Accurately weigh to the nearest 0.1 mg, 1.5 g (record weight) of primary standard grade potassium iodate that has been previously dried at 180 °C for at least 3 hours and cooled in a desiccator. Dissolve, then dilute to volume in a 500-mL volumetric flask with distilled water.

8.2.8 *Stock sodium thiosulfate solution* (0.1 N): Prepare a stock solution by dissolving 25 g sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) in 1,000 mL freshly boiled, cooled, distilled water and adding 0.1 g sodium carbonate to the solution. Allow the solution to stand at least 1 day before standardizing. To standardize, accurately pipet 50 mL of potassium iodate solution (Section 8.2.7) into a 500-mL iodine flask and add 2.0 g of potassium iodide and 10 mL of 1 N HCl. Stopper the flask and allow to stand for 5 minutes. Titrate the solution with stock sodium thiosulfate solution (Section 8.2.8) to a pale yellow color. Add 5 mL of starch solution (Section 8.2.5) and titrate until the blue color just disappears. Calculate the normality (N_s) of the stock sodium thiosulfate solution as follows:

$$N_s = \frac{W}{M} \times 2.80 \quad (2)$$

where:

M = volume of thiosulfate required in mL, and

W = weight of potassium iodate in g (recorded weight in Section 8.2.7).

$$2.80 = \frac{10^3(\text{conversion of g to mg}) \times 0.1(\text{fraction iodate used})}{35.67(\text{equivalent weight of potassium iodate})}$$

8.2.9 *Working sodium thiosulfate titrant* (0.01 N): Accurately pipet 100 mL of stock sodium thiosulfate solution (Section 8.2.8) into a 1,000-mL volumetric flask and dilute to volume with freshly boiled, cooled, distilled water. Calculate the normality of the working sodium thiosulfate titrant (N_T) as follows:

$$N_T = N_s \times 0.100 \quad (3)$$

8.2.10 *Standardized sulfite solution for the preparation of working sulfite-TCM solution*: Dissolve 0.30 g sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) or 0.40 g sodium sulfite (Na_2SO_3) in 500 mL of recently boiled, cooled, distilled water. (Sulfite solution is unstable; it is therefore important to use water of the highest purity to minimize this instability.) This solution contains the equivalent of 320 to 400 $\mu\text{g SO}_2/\text{mL}$. The actual concentration of the solution is determined by adding excess iodine and back-titrating with standard sodium thiosulfate solution. To back-titrate, pipet 50 mL of the 0.01 N iodine solution (Section 8.2.4) 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 minutes. Prepare the working sulfite-TCM solution (Section 8.2.11) immediately prior to adding the iodine solution to the flasks. Using a buret containing standardized 0.01 N thiosulfate titrant (Section 8.2.9), titrate the solution in each flask to a pale yellow color. Then add 5 mL starch solution (Section 8.2.5) and con-

tinue the titration until the blue color just disappears.

8.2.11 *Working sulfite-TCM solution:* Accurately pipet 5 mL of the standard sulfite solution (Section 8.2.10) 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:

$$C_{\text{TCM}/\text{SO}_2}(\mu\text{g SO}_2/\text{mL}) = \frac{(A - B)(N_T)(32,000)}{25} \times 0.02 \quad (4)$$

where:

A = volume of thiosulfate titrant required for the blank, mL;

B = volume of thiosulfate titrant required for the sample, mL;

N_T = normality of the thiosulfate titrant, from equation (3);

32,000 = milliequivalent weight of 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. (16) If not kept at 5 °C, prepare fresh daily.

8.2.12 *Purified pararosaniline (PRA) stock solution* (0.2% nominal):

8.2.12.1 *Dye specifications*—

- The dye must have a maximum absorbance at a wavelength of 540 nm when assayed in a buffered solution of 0.1 M sodium acetate-acetic acid;
- The absorbance of the reagent blank, which is temperature sensitive (0.015 absorbance unit/°C), must not exceed 0.170 at 22 °C with a 1-cm optical path length when the blank is prepared according to the specified procedure;
- The calibration curve (Section 10.0) must have a slope equal to 0.030 ± 0.002 absorbance unit/ $\mu\text{g SO}_2$ with a 1-cm optical path length when the dye is pure and the sulfite solution is properly standardized.

8.2.12.2 *Preparation of stock PRA solution*—A specially purified (99 to 100 percent pure) solution of pararosaniline, which meets the above specifications, is commercially available in the required 0.20 percent concentration (Harleco Co.). Alternatively, the dye may be purified, a stock solution prepared, and then assayed according to the procedure as described below.(10)

8.2.12.3 *Purification procedure for PRA*—

1. Place 100 mL each of 1-butanol and 1 N HCl in a large separatory funnel (250-mL) and allow to equilibrate. Note: Certain batches of 1-butanol contain oxidants that create an SO_2 demand. Before using, check by placing 20 mL of 1-butanol and 5 mL of 20

percent potassium iodide (KI) solution in a 50-mL separatory funnel and shake thoroughly. If a yellow color appears in the alcohol phase, redistill the 1-butanol from silver oxide and collect the middle fraction or purchase a new supply of 1-butanol.

2. Weigh 100 mg of pararosaniline hydrochloride dye (PRA) in a small beaker. Add 50 mL of the equilibrated acid (drain in acid from the bottom of the separatory funnel in 1.) to the beaker and let stand for several minutes. Discard the remaining acid phase in the separatory funnel.

3. To a 125-mL separatory funnel, add 50 mL of the equilibrated 1-butanol (draw the 1-butanol from the top of the separatory funnel in 1.). Transfer the acid solution (from 2.) containing the dye to the funnel and shake carefully to extract. The violet impurity will transfer to the organic phase.

4. Transfer the lower aqueous phase into another separatory funnel, add 20 mL of equilibrated 1-butanol, and extract again.

5. Repeat the extraction procedure with three more 10-mL portions of equilibrated 1-butanol.

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

7. To check the purity of the PRA, perform the assay and adjustment of concentration (Section 8.2.12.4) and prepare a reagent blank (Section 11.2); the absorbance of this reagent blank at 540 nm should be less than 0.170 at 22 °C. If the absorbance is greater than 0.170 under these conditions, further extractions should be performed.

8.2.12.4 *PRA assay procedure*—The concentration of pararosaniline hydrochloride (PRA) need be assayed only once after purification. It is also recommended that commercial solutions of pararosaniline be assayed when first purchased. The assay procedure is as follows:(10)

1. Prepare 1 M acetate-acetic acid buffer stock solution with a pH of 4.79 by dissolving

13.61 g of sodium acetate trihydrate in distilled water in a 100-mL volumetric flask. Add 5.70 mL of glacial acetic acid and dilute to volume with distilled water.

2. Pipet 1 mL of the stock PRA solution obtained from the purification process or from a commercial source into a 100-mL volumetric flask and dilute to volume with distilled water.

3. Transfer a 5-mL aliquot of the diluted PRA solution from 2. into a 50-mL volumetric flask. Add 5 mL of 1 M acetate-acetic acid buffer solution from 1. and dilute the mixture to volume with distilled water. Let the mixture stand for 1 hour.

4. Measure the absorbance of the above solution at 540 nm with a spectrophotometer against a distilled water reference. Compute the percentage of nominal concentration of PRA by

$$\%PRA = \frac{A \times K}{W} \quad (5)$$

where:

A = measured absorbance of the final mixture (absorbance units);

W = weight in grams of the PRA dye used in the assay to prepare 50 mL of stock solution (for example, 0.100 g of dye was used to prepare 50 mL of solution in the purification procedure; when obtained from commercial sources, use the stated concentration to compute W; for 98% PRA, W=.098 g.); and

K = 21.3 for spectrophotometers having a spectral bandwidth of less than 15 nm and a path length of 1 cm.

8.2.13 *Pararosaniline reagent*: To a 250-mL volumetric flask, add 20 mL of stock PRA solution. Add an additional 0.2 mL of stock solution for each percentage that the stock assays below 100 percent. Then add 25 mL of 3 M phosphoric acid and dilute to volume with distilled water. The reagent is stable for at least 9 months. Store away from heat and light.

9.0 Sampling Procedure.

9.1 *General Considerations*. Procedures are described for short-term sampling (30-minute and 1-hour) and for long-term sampling (24-hour). Different combinations of absorbing reagent volume, sampling rate, and sampling time can be selected to meet special needs. For combinations other than those specifically described, the conditions must be ad-

justed so that linearity is maintained between absorbance and concentration over the dynamic range. Absorbing reagent volumes less than 10 mL are not recommended. The collection efficiency is above 98 percent for the conditions described; however, the efficiency may be substantially lower when sampling concentrations below 25 $\mu\text{gSO}_2/\text{m}^3$.(8,9)

9.2 *30-Minute and 1-Hour 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 in Figure 1, making sure that all connections between the various components are leak tight. Greaseless ball joint fittings, heat shrinkable Teflon® tubing, or Teflon® 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 Section 9.4.2. Collect the sample at 1 \pm 0.10 L/min for 30-minute sampling or 0.500 \pm 0.05 L/min for 1-hour sampling. Record the exact sampling time in minutes, as the sample volume will later be determined using the sampling flow rate and the sampling time. Record the atmospheric pressure and temperature.

9.3 *24-Hour Sampling*. Place 50 mL of TCM absorbing solution in a large absorber, close the cap, and, if needed, apply the heat shrink material as shown in Figure 3. Verify that the reagent level is at the 50 mL mark on the absorber. Insert the sealed absorber into the sampling train as shown in Figure 2. At this time verify that the absorber temperature is controlled to 15 \pm 10 °C. During sampling, the absorber temperature must be controlled to prevent decomposition of the collected complex. From the onset of sampling until analysis, the absorbing solution must be protected from direct sunlight. Determine the flow rate according to Section 9.4.2. Collect the sample for 24 hours from midnight to midnight at a flow rate of 0.200 \pm 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.

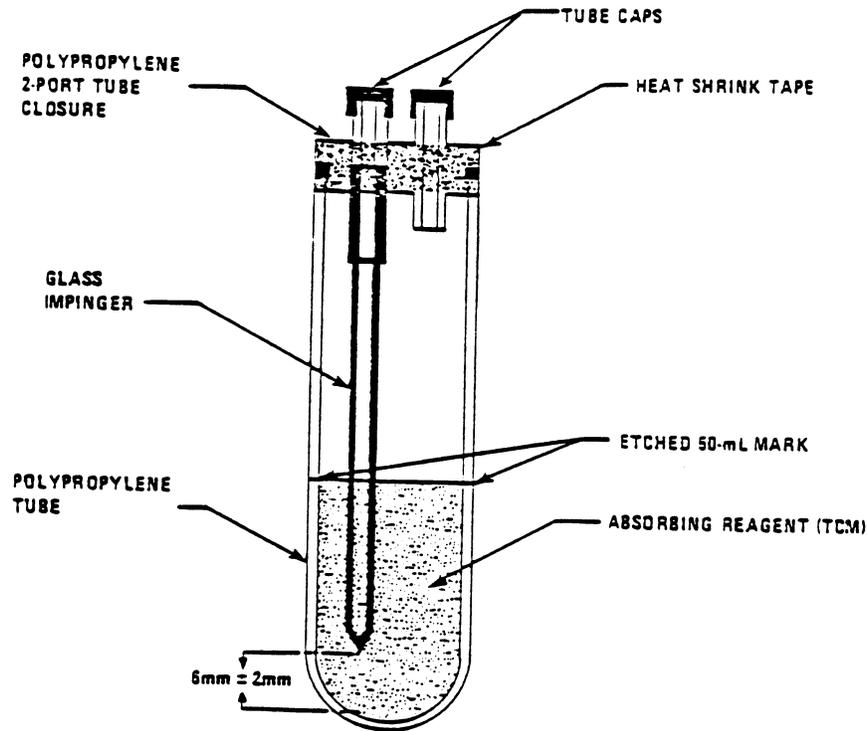


Figure 3. An absorber (24-hour sample) filled and assembled for shipment.

9.4 Flow Measurement.

9.4.1 *Calibration:* Flow measuring devices used for the on-site flow measurements required in 9.4.2 must be calibrated against a reliable flow or volume standard such as an NBS traceable bubble flowmeter or calibrated wet test meter. Rotameters or critical orifices used in the sampling train may be calibrated, if desired, as a quality control check, but such calibration shall not replace the on-site flow measurements required by 9.4.2. In-line rotameters, if they are to be calibrated, should be calibrated in situ, with the appropriate volume of solution in the absorber.

9.4.2 *Determination of flow rate at sampling site:* For short-term samples, the standard flow rate is determined 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-hour samples, the standard flow rate is determined 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. The flow rate determination must be made with all components of the sampling system in operation (e.g., the absorber temperature controller and any sample box heaters must also be operating). Equation 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.

$$Q_{\text{std}} = Q_{\text{act}} \times \frac{P_b - (1 - \text{RH})P_{\text{H}_2\text{O}}}{P_{\text{std}}} \times \frac{298.16}{(T_{\text{meter}} + 273.16)} \quad (6)$$

where:

Q_{std} = flow rate at standard conditions, std L/min (25 °C and 760 mm Hg);

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

P_b = barometric pressure at monitoring site conditions, mm Hg or kPa;

RH = fractional relative humidity of the air being measured;

$P_{\text{H}_2\text{O}}$ = 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, i.e., bubble flowmeter or wet test meter; for dry standards, i.e., dry test meter, $P_{\text{H}_2\text{O}}=0$);

P_{std} = standard barometric pressure, in the same units as P_b (760 mm Hg or 101 kPa); and

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

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

$$P_b = 760 - .076(H) \text{ mm Hg, or } P_b = 101 - .01(H) \text{ kPa} \quad (7)$$

where:

H = sampling site elevation above sea level in meters.

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 equation (8), check for leaks and redetermine Q_c .

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

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 equation (9):

$$\% \text{ Diff} = \frac{Q_i - Q_f}{Q_f} \times 100 \quad (9)$$

9.5 Sample Storage and Shipment. 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 (e.g., grease pencil) mark. If the sample will not be analyzed within 12 hours of sampling, it must be stored at 5° ±5 °C until analysis. Analysis must occur within 30 days. If the sample is transported or shipped for a period exceeding 12 hours, it is recommended that thermal coolers using eutectic ice packs, refrigerated shipping containers, etc., be used for periods up to 48 hours. (17) Measure the temperature of the absorber solution when the shipment is received. Invalidate the sample if the tempera-

ture is above 10 °C. Store the sample at 5° ±5 °C until it is analyzed.

10.0 Analytical Calibration.

10.1 Spectrophotometer Cell Matching. If unmatched spectrophotometer cells are used, an absorbance correction factor must be determined as follows:

1. Fill all cells with distilled water and designate the one that has the lowest absorbance at 548 nm as the reference. (This reference cell should be marked as such and continually used for this purpose throughout all future analyses.)

2. Zero the spectrophotometer with the reference cell.

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.

The corrected absorbance during future analyses using each cell is determined as follows:

$$A = A_{\text{obs}} - A_c \quad (10)$$

where:

A = corrected absorbance,

A_{obs} = uncorrected absorbance, and

A_c = cell correction.

10.2 Static Calibration Procedure (Option 1). Prepare a dilute working sulfite-TCM solution by diluting 10 mL of the working sulfite-TCM solution (Section 8.2.11) to 100 mL with TCM absorbing reagent. Following the table below, accurately pipet the indicated volumes of the 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.

Sulfite-TCM solution	Volume of sulfite-TCM solution	Volume of TCM, mL	Total $\mu\text{g SO}_2$ (approx.*
Working	4.0	6.0	28.8
Working	3.0	7.0	21.6
Working	2.0	8.0	14.4
Dilute working	10.0	0.0	7.2
Dilute working	5.0	5.0	3.6
	0.0	10.0	0.0

*Based on working sulfite-TCM solution concentration of 7.2 $\mu\text{g SO}_2/\text{mL}$; the actual total $\mu\text{g SO}_2$ must be calculated using equation 11 below.

To each volumetric flask, add 1 mL 0.6% sulfamic acid (Section 8.2.1), accurately pipet 2 mL 0.2% formaldehyde solution (Section 8.2.2), then add 5 mL pararosaniline solution (Section 8.2.13). Start a laboratory

timer that has been set for 30 minutes. Bring all flasks to volume with recently boiled and cooled distilled water and mix thoroughly. The color must be developed (during the 30-minute 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 minutes, determine the corrected absorbance of each standard at 548 nm against a distilled water reference (Section 10.1). 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 micrograms SO_2 in each solution:

$$\mu\text{g SO}_2 = V_{\text{TCM/SO}_2} \times C_{\text{TCM/SO}_2} \times D \quad (11)$$

where:

$V_{\text{TCM/SO}_2}$ = volume of sulfite-TCM solution used, mL;

$C_{\text{TCM/SO}_2}$ = concentration of sulfur dioxide in the working sulfite-TCM, $\mu\text{g SO}_2/\text{mL}$ (from equation 4); and

D = dilution factor (D = 1 for the working sulfite-TCM solution; D = 0.1 for the diluted working sulfite-TCM solution).

A calibration equation is determined using the method of linear least squares (Section 12.1). The total micrograms 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, the slope must be in the range of 0.030 ± 0.002 absorbance unit/ $\mu\text{g SO}_2$, 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. A calibration factor (B_c) is determined by calculating the reciprocal of the slope and is subsequently used for calculating the sample concentration (Section 12.3).

10.3 *Dynamic Calibration Procedures* (Option 2). 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 Figure 4 and this system and other similar systems have been described in detail by O'Keefe and Ortman; (19) Scaringelli, Frey, and Saltzman, (20) and Scaringelli, O'Keefe, Rosenberg, and Bell. (21) Permeation devices may be prepared or purchased and in both cases must be traceable either to a National Bureau of Standards (NBS) Standard Reference Material (SRM 1625, SRM 1626, SRM 1627) or to an NBS/EPA-approved commercially available Certified Reference Material (CRM). CRM's are described in Reference 22, and a list of CRM sources is available from the address shown for Reference 22. A recommended protocol for certifying a permeation device to an NBS SRM or CRM is given in Section 2.0.7 of Reference 2. Device permeation rates of 0.2 to 0.4 $\mu\text{g}/\text{min}$, 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 $\mu\text{g SO}_2/\text{m}^3$ (0.010 to 0.230 ppm).

10.3.1 *Calibration Option 2A* (30-minute and 1-hour samples): Generate a series of six standard atmospheres of SO_2 (e.g., 0, 50, 100, 200, 350, 500, 750 $\mu\text{g}/\text{m}^3$) by adjusting the dilution flow rates appropriately. The concentration of SO_2 in each atmosphere is calculated as follows:

$$C_a = \frac{P_r \times 10^3}{Q_d + Q_p} \quad (12)$$

where:

C_a = concentration of SO_2 at standard conditions, $\mu g/m^3$;
 P_r = permeation rate, $\mu g/min$;

Q_d = flow rate of dilution air, std L/min; and
 Q_p = flow rate of carrier gas across permeation device, std L/min.

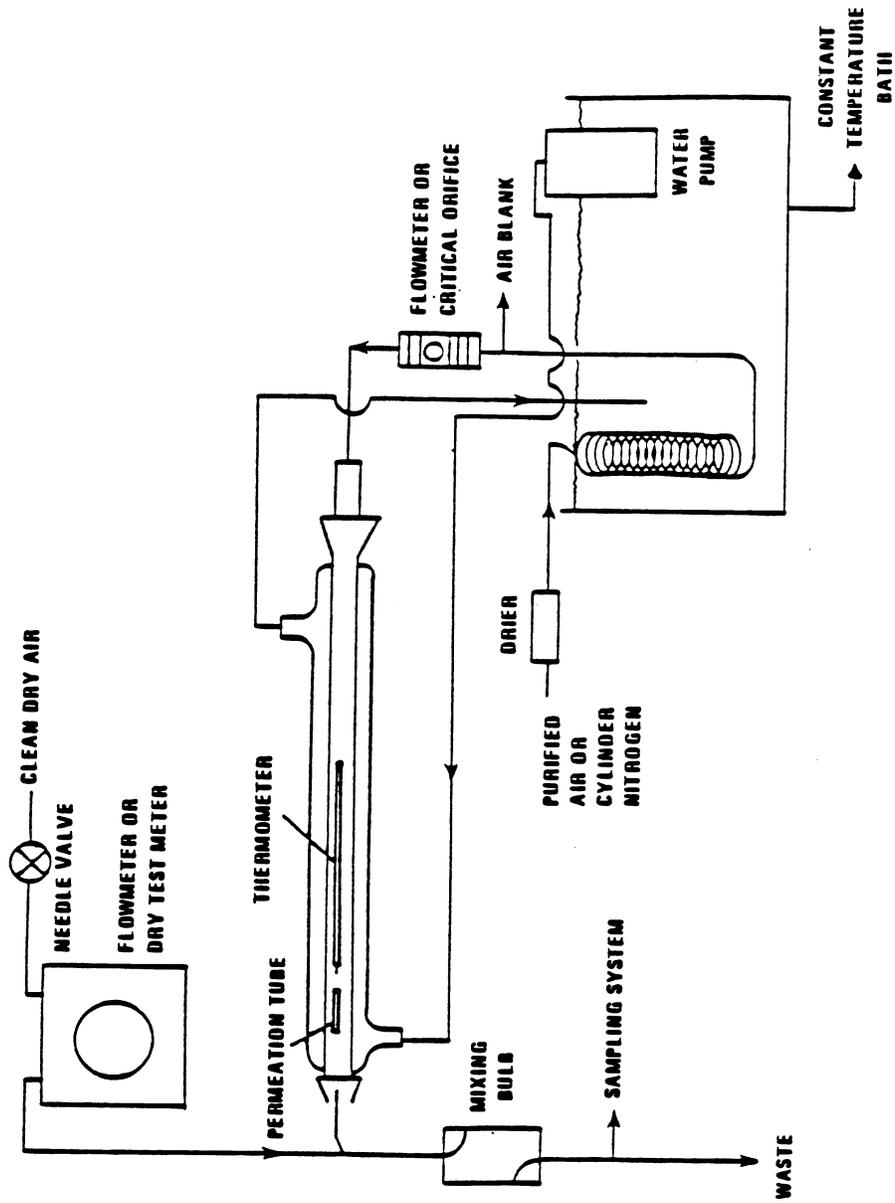


Figure 4. Permeation tube schematic for laboratory use.

Be sure 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 apparatus as shown in Figure 1 and under the same conditions as field sampling (*i.e.*, use same absorbing reagent volume and sample 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-hour 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 H₂O 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 hours of sampling, store the solutions at 5° ±5 °C. Calculate the total micrograms SO₂ in each solution as follows:

$$\mu\text{gSO}_2 = \frac{C_a \times Q_s \times t \times V_a \times 10^{-3}}{V_b} \quad (13)$$

where:

C_a = concentration of SO₂ in the standard atmosphere, µg/m³;

Q_s = sampling flow rate, std 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 Section 10.2 for static solutions. Calculate a calibration equation and a calibration factor (B₂) according to Section 10.2, adhering to all the specified criteria.

10.3.2 Calibration Option 2B (24-hour samples): Generate a standard atmosphere containing approximately 1,050 µg SO₂/m³ and calculate the exact concentration according to equation 12. Set up a series of six absorbers according to Figure 2 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. The absorbers are then allowed to sample the atmosphere for varying time periods to yield solutions containing 0, 0.2, 0.6, 1.0, 1.4, 1.8, and 2.2 µg SO₂/mL solution. The sampling times required to attain these solution concentrations are calculated as follows:

$$t = \frac{V_b \times C_s}{C_a \times Q_s \times 10^{-3}} \quad (14)$$

where:

t = sampling time, min;

V_b = volume of absorbing solution used for sampling (50 mL);

C_s = desired concentration of SO₂ in the absorbing solution, µg/mL;

C_a = concentration of the standard atmosphere calculated according to equation 12, µg/m³; and

Q_s = sampling flow rate, std 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 hours of sampling, store the solutions at 5° ±5 °C. Add the remaining reagents for color development in the same manner as in Section 10.2 for static solutions. Calculate the total µg SO₂ in each standard as follows:

$$\mu\text{gSO}_2 = \frac{C_a \times Q_s \times t \times V_a \times 10^{-3}}{V_b} \quad (15)$$

where:

V_a = volume of absorbing solution used for color development (10 mL).

All other parameters are defined in equation 14.

Calculate a calibration equation and a calibration factor (B₂) according to Section 10.2 adhering to all the specified criteria.

11.0 Sample Preparation and Analysis.

11.1 *Sample Preparation.* Remove the samples from the shipping container. If the shipment period exceeded 12 hours 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:

1. For 30-minute or 1-hour 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.

2. For 24-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, the volume must be measured using a graduated cylinder. To analyze, pipet 10 mL

of the solution into a 25-mL volumetric flask.

11.2 *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 prepared according to Section 10.2 or 10.3. The analysis is carried out as follows:

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

2. To each 25-mL volumetric flask containing reagent blank, sample, or control standard, add 1 mL of 0.6% sulfamic acid (Section 8.2.1) and allow to react for 10 min.

3. Accurately pipet 2 mL of 0.2% formaldehyde solution (Section 8.2.2) and then 5 mL of pararosaniline solution (Section 8.2.13) into each flask. Start a laboratory timer set at 30 minutes.

4. Bring each flask to volume with recently boiled and cooled distilled water and mix thoroughly.

5. During the 30 minutes, the solutions must be in a temperature controlled environment in the range of 20° to 30 °C maintained to ± 1 °C. This temperature must also be within 1 °C of that used during calibration.

6. After 30 minutes and before 60 minutes, determine the corrected absorbances (equation 10) of each solution at 548 nm using 1-cm optical path length cells against a distilled water reference (Section 10.1). (*Distilled water is used as a reference instead of the reagent blank because of the sensitivity of the reagent blank to temperature.*)

7. 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.

8. The reagent blank must be within 0.03 absorbance units of the intercept of the calibration equation determined in Section 10.

11.3 *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 minutes. 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 than 1:1.

11.4 *Reagent disposal.* All reagents containing mercury compounds must be stored and disposed of using one of the procedures contained in Section 13. Until disposal, the discarded solutions can be stored in closed glass containers and should be left in a fume hood.

12.0 Calculations.

12.1 *Calibration Slope, Intercept, and Correlation Coefficient.* The method of least squares

is used to calculate a calibration equation in the form of:

$$y = mx + b \quad (16)$$

where:

y = corrected absorbance,

m = slope, absorbance unit/ μg SO_2 ,

x = micrograms of SO_2 ,

b = y intercept (absorbance units).

The slope (m), intercept (b), and correlation coefficient (r) are calculated as follows:

$$m = \frac{n \sum xy - (\sum x)(\sum y)}{n \sum x^2 - (\sum x)^2} \quad (17)$$

$$b = \frac{\sum y - m \sum x}{n} \quad (18)$$

$$r = \frac{m(\sum xy - \sum x \sum y / n)}{\sqrt{\sum y^2 - (\sum y)^2 / n}} \quad (19)$$

where n is the number of calibration points.

A data form (Figure 5) is supplied for easily organizing calibration data when the slope, intercept, and correlation coefficient are calculated by hand.

12.2 *Total Sample Volume.* Determine the sampling volume at standard conditions as follows:

$$V_{\text{std}} = \frac{Q_i + Q_f}{2} \times t \quad (20)$$

where:

V_{std} = sampling volume in std L,

Q_i = standard flow rate determined at the initiation of sampling in std L/min,

Q_f = standard flow rate determined at the completion of sampling in std L/min, and

t = total sampling time, min.

12.3 *Sulfur Dioxide Concentration.* Calculate and report the concentration of each sample as follows:

$$\mu\text{g SO}_2/\text{m}^3 = \frac{(A - A_o)(B_x)(10^3)}{V_{\text{std}}} \times \frac{V_b}{V_a} \quad (21)$$

where:

A = corrected absorbance of the sample solution, from equation (10);

A_o = corrected absorbance of the reagent blank, using equation (10);

B_x = calibration factor equal to B_s , B_g , or B_l 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 (see 11.1-2), mL; and

V_{std} = standard air volume sampled, std L (from Section 12.2).

DATA FORM
[For hand calculations]

Calibration point no.	Micrograms SO ₂	Absorbance units			
	(x)	(y)	x ²	xy	y ²
1
2
3
4
5
6

$\Sigma x =$ _____ $\Sigma y =$ _____ $\Sigma x^2 =$ _____ $\Sigma xy =$ _____
 $\Sigma y^2 =$ _____
 $n =$ _____ (number of pairs of coordinates.)

FIGURE 5. Data form for hand calculations.

12.4 Control Standards. Calculate the analyzed micrograms of SO₂ in each control standard as follows:

$$C_q = (A - A_o) \times B_x \quad (22)$$

where:

C_q = analyzed µg SO₂ in each control standard,

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, the source of the discrepancy must be identified and corrected.

12.5 Conversion of µg/m³ to ppm (v/v). If desired, the concentration of sulfur dioxide at reference conditions can be converted to ppm SO₂ (v/v) as follows:

$$\text{ppm SO}_2 = \frac{\mu\text{g SO}_2}{\text{m}^3} \times 3.82 \times 10^{-4} \quad (23)$$

13.0 The TCM absorbing solution and any reagents containing mercury compounds must be treated and disposed of by one of the methods discussed below. Both methods remove greater than 99.99 percent of the mercury.

13.1 *Disposal of Mercury-Containing Solutions.*

13.2 *Method for Forming an Amalgam.*

1. Place the waste solution in an uncapped vessel in a hood.

2. For each liter of waste solution, add approximately 10 g of sodium carbonate until neutralization has occurred (NaOH may have to be used).

3. Following neutralization, add 10 g of granular zinc or magnesium.

4. Stir the solution in a hood for 24 hours. Caution must be exercised as hydrogen gas is evolved by this treatment process.

5. After 24 hours, allow the solution to stand without stirring to allow the mercury amalgam (solid black material) to settle to the bottom of the waste receptacle.

6. Upon settling, decant and discard the supernatant liquid.

7. Quantitatively transfer the solid material to a container and allow to dry.

8. The solid material can be sent to a mercury reclaiming plant. It must not be discarded.

13.3 *Method Using Aluminum Foil Strips.*

1. Place the waste solution in an uncapped vessel in a hood.

2. For each liter of waste solution, add approximately 10 g of aluminum foil strips. If all the aluminum is consumed and no gas is evolved, add an additional 10 g of foil. Repeat until the foil is no longer consumed and allow the gas to evolve for 24 hours.

3. Decant the supernatant liquid and discard.

4. Transfer the elemental mercury that has settled to the bottom of the vessel to a storage container.

5. The mercury can be sent to a mercury reclaiming plant. It must not be discarded.

14.0 *References for SO₂ Method.*

1. Quality Assurance Handbook for Air Pollution Measurement Systems, Volume I, Principles. EPA-600/9-76-005, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, 1976.

2. Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II, Ambient Air Specific Methods. EPA-600/4-77-027a, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, 1977.

3. Dasgupta, P. K., and K. B. DeCesare. Stability of Sulfur Dioxide in Formaldehyde and Its Anomalous Behavior in Tetrachloromercurate (II). Submitted for publication in *Atmospheric Environment*, 1982.

4. West, P. W., and G. C. Gaeke. Fixation of Sulfur Dioxide as Disulfitomercurate (II) and Subsequent Colorimetric Estimation. *Anal. Chem.*, 28:1816, 1956.

5. Ephraim, F. *Inorganic Chemistry*. P. C. L. Thorne and E. R. Roberts, Eds., 5th Edition, Interscience, 1948, p. 562.

6. Lyles, G. R., F. B. Dowling, and V. J. Blanchard. Quantitative Determination of Formaldehyde in the Parts Per Hundred Million Concentration Level. *J. Air. Poll. Cont. Assoc.*, Vol. 15(106), 1965.

7. McKee, H. C., R. E. Childers, and O. Saenz, Jr. Collaborative Study of Reference Method for Determination of Sulfur Dioxide in the Atmosphere (Pararosaniline Method). EPA-APTD-0903, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, September 1971.

8. Urone, P., J. B. Evans, and C. M. Noyes. Tracer Techniques in Sulfur-Air Pollution Studies Apparatus and Studies of Sulfur Dioxide Colorimetric and Conductometric Methods. *Anal. Chem.*, 37: 1104, 1965.

9. Bostrom, C. E. The Absorption of Sulfur Dioxide at Low Concentrations (pphm) Studied by an Isotopic Tracer Method. *Intern. J. Air Water Poll.*, 9:333, 1965.

10. Scaringelli, F. P., B. E. Saltzman, and S. A. Frey. Spectrophotometric Determination of Atmospheric Sulfur Dioxide. *Anal. Chem.*, 39: 1709, 1967.

11. Pate, J. B., B. E. Ammons, G. A. Swanson, and J. P. Lodge, Jr. Nitrite Interference in Spectrophotometric Determination of Atmospheric Sulfur Dioxide. *Anal. Chem.*, 37:942, 1965.

12. Zurlo, N., and A. M. Griffini. Measurement of the Sulfur Dioxide Content of the Air in the Presence of Oxides of Nitrogen and Heavy Metals. *Medicina Lavoro*, 53:330, 1962.

13. Rehme, K. A., and F. P. Scaringelli. Effect of Ammonia on the Spectrophotometric Determination of Atmospheric Concentrations of Sulfur Dioxide. *Anal. Chem.*, 47:2474, 1975.

14. McCoy, R. A., D. E. Camann, and H. C. McKee. Collaborative Study of Reference Method for Determination of Sulfur Dioxide in the Atmosphere (Pararosaniline Method) (24-Hour Sampling). EPA-650/4-74-027, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, December 1973.

15. Fuerst, R. G. Improved Temperature Stability of Sulfur Dioxide Samples Collected by the Federal Reference Method. EPA-600/4-78-018, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, April 1978.

16. Scaringelli, F. P., L. Elfers, D. Norris, and S. Hochheiser. Enhanced Stability of Sulfur Dioxide in Solution. *Anal. Chem.*, 42:1818, 1970.

17. Martin, B. E. Sulfur Dioxide Bubbler Temperature Study. EPA-600/4-77-040, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, August 1977.

18. American Society for Testing and Materials. ASTM Standards, Water; Atmospheric Analysis. Part 23. Philadelphia, PA, October 1968, p. 226.

19. O'Keeffe, A. E., and G. C. Ortman. Primary Standards for Trace Gas Analysis. *Anal. Chem.*, 38:760, 1966.

20. Scaringelli, F. P., S. A. Frey, and B. E. Saltzman. Evaluation of Teflon Permeation Tubes for Use with Sulfur Dioxide. *Amer. Ind. Hygiene Assoc. J.*, 28:260, 1967.

21. Scaringelli, F. P., A. E. O'Keeffe, E. Rosenberg, and J. P. Bell. Preparation of Known Concentrations of Gases and Vapors With Permeation Devices Calibrated Gravimetrically. *Anal. Chem.*, 42:871, 1970.

22. A Procedure for Establishing Traceability of Gas Mixtures to Certain National Bureau of Standards Standard Reference Materials. EPA-600/7-81-010, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory

(MD-77), Research Triangle Park, NC 27711, January 1981.

[47 FR 54899, Dec. 6, 1982; 48 FR 17355, Apr. 22, 1983. Redesignated at 75 FR 35595, June 22, 2010]

APPENDIX B TO PART 50—REFERENCE METHOD FOR THE DETERMINATION OF SUSPENDED PARTICULATE MATTER IN THE ATMOSPHERE (HIGH-VOLUME METHOD)

1.0 *Applicability.*

1.1 This method provides a measurement of the mass concentration of total suspended particulate matter (TSP) in ambient air for determining compliance with the primary and secondary national ambient air quality standards for particulate matter as specified in §50.6 and §50.7 of this chapter. The measurement process is nondestructive, and the size of the sample collected is usually adequate for subsequent chemical analysis. Quality assurance procedures and guidance are provided in part 58, appendixes A and B, of this chapter and in References 1 and 2.

2.0 *Principle.*

2.1 An air sampler, properly located at the measurement site, draws a measured quantity of ambient air into a covered housing and through a filter during a 24-hr (nominal) sampling period. The sampler flow rate and the geometry of the shelter favor the collection of particles up to 25–50 μm (aerodynamic diameter), depending on wind speed and direction.⁽³⁾ The filters used are specified to have a minimum collection efficiency of 99 percent for 0.3 μm (DOP) particles (see Section 7.1.4).

2.2 The filter is weighed (after moisture equilibration) before and after use to determine the net weight (mass) gain. The total volume of air sampled, corrected to EPA standard conditions (25 °C, 760 mm Hg [101 kPa]), is determined from the measured flow rate and the sampling time. The concentration of total suspended particulate matter in the ambient air is computed as the mass of collected particles divided by the volume of air sampled, corrected to standard conditions, and is expressed in micrograms per standard cubic meter ($\mu\text{g}/\text{std m}^3$). For samples collected at temperatures and pressures significantly different than standard conditions, these corrected concentrations may differ substantially from actual concentrations (micrograms per actual cubic meter), particularly at high elevations. The actual particulate matter concentration can be calculated from the corrected concentration using the actual temperature and pressure during the sampling period.

3.0 *Range.*

3.1 The approximate concentration range of the method is 2 to 750 $\mu\text{g}/\text{std m}^3$. The upper limit is determined by the point at which the