



Designation: D 2914 – 01

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

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

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

1. Scope

1.1 These test methods cover the bubbler collection and colorimetric determination of sulfur dioxide (SO₂) in the ambient or workplace atmosphere.

1.2 These test methods are applicable for determining SO₂ over the range from approximately 25 µg/m³ (0.01 ppm(v)) to 1000 µg/m³ (0.4 ppm(v)), corresponding to a solution concentration of 0.03 µg SO₂/mL to 1.3 µg SO₂/mL. Beer's law is followed through the working analytical range from 0.02 µg SO₂/mL to 1.4 µg SO₂/mL.

1.3 The lower limit of detection is 0.075 µg SO₂/mL (**1**)², representing an air concentration of 25 µg SO₂/m³ (0.01 ppm(v)) in a 30-min sample, or 13 µg SO₂/m³ (0.005 ppm(v)) in a 24-h sample.

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

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

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

NOTE 1—These test methods are applicable at concentrations below 25 µg/m³ 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/m³ 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 These test methods are under the jurisdiction of ASTM Committee D22 on Air Quality and are the direct responsibility of Subcommittee D22.03 on Ambient Atmospheres and Source Emissions.

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² The boldface numbers in parentheses refer to a list of references at the end of this standard.

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

2. Referenced Documents

2.1 ASTM Standards:³

D 1071 Test Methods for Volumetric Measurement of Gaseous Fuel Samples

D 1193 Specification for Reagent Water

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres

D 1357 Practice for Planning the Sampling of the Ambient Atmosphere

D 1605 Practices for Sampling Atmospheres for Analysis of Gases and Vapors

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

D 3195 Practice for Rotameter Calibration

D 3609 Practice for Calibration Techniques Using Permeation Tubes

D 3631 Test Methods for Measuring Surface Atmospheric Pressure

E 1 Specification for ASTM Thermometers

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

2.2 Other Standards:

40 CFR Part 58 Probe and Monitoring Path Siting Criteria

³ For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.



from Ambient Air Quality Monitoring, Appendix E⁴

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 (SO₂) is absorbed by aspirating a measured air sample through a tetrachloromercurate (TCM) solution, resulting in the formation of a dichlorosulfonatomercurate complex (**2,3**).⁵ Ethylenediaminetetraacetic acid disodium salt (EDTA) is added to this solution to complex heavy metals that interfere with this method (**4**). Dichlorosulfonatomercurate, once formed, is stable to strong oxidants (for example, ozone and oxides of nitrogen) (**2**). After the absorption is completed, any ozone in the solution is allowed to decay (**5**). The liquid is treated first with a solution of sulfamic acid to destroy the nitrite anion formed from the absorption of oxides of nitrogen present in the atmosphere (**6**). It is treated next with solutions of formaldehyde and specially purified acid-bleached pararosaniline containing phosphoric acid (H₃PO₄) to control pH. Pararosaniline, formaldehyde, and the bisulfite anion react to form the intensely colored pararosaniline methyl sulfonic acid which behaves as a two-color pH indicator (**2**). The pH of the final solution is adjusted to the desired value by the addition of prescribed amounts of 3 N H₃PO₄ to the pararosaniline reagent (**5**).

5. Significance and Use

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

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

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

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

6. Interferences

6.1 The interferences of oxides of nitrogen are eliminated by sulfamic acid (**5,6**), of ozone by time delay (**5**), and of heavy metals by EDTA and phosphoric acid (**4,5**). At least 60 µg of Fe(III), 10 µg of Mn(II), and 10 µg of Cr(III), 10 µg of Cu(II) and 22 µg of V(V) in 10 mL of absorbing reagent can be tolerated in the procedure. No significant interference was found with 2.3 µg of NH₃(**9**).

7. Apparatus

7.1 For Sampling:

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

7.1.2 *Absorber, 24-h Sampling*—A glass or polypropylene tube 32 mm in diameter and 164 mm long with a polypropylene two-port cap (rubber stoppers are unacceptable because the absorbing reagent can react with the stopper to yield erroneously high SO₂ concentrations, and cause high and variable blank values). Insert a glass impinger stem, 6 mm inside diameter and 158 mm long, into one port of the absorber cap. Taper the tip of the stem to a small diameter orifice (0.4 ± 0.1 mm) such that a No. 79 jeweler's drill bit will pass through the opening but a No. 78 drill bit will not. Clearance from the bottom of the absorber to the tip of the stem shall be 6 ± 2 mm. Perform the orifice test before use to verify the orifice size. Permanently mark the 50 mL volume level on the absorber. See **Fig. 1**.

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

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

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

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

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

7.1.8 Flow Control and Measurement Devices:

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

⁴ Available from U.S. Government Printing Office, Superintendent of Documents, 732 North Capitol Street, NW, Mail Stop: SDE, Washington, DC 20401.

⁵ The boldface numbers in parentheses refer to the list of references at the end of this standard.

TFE-fluorocarbon OR GLASS

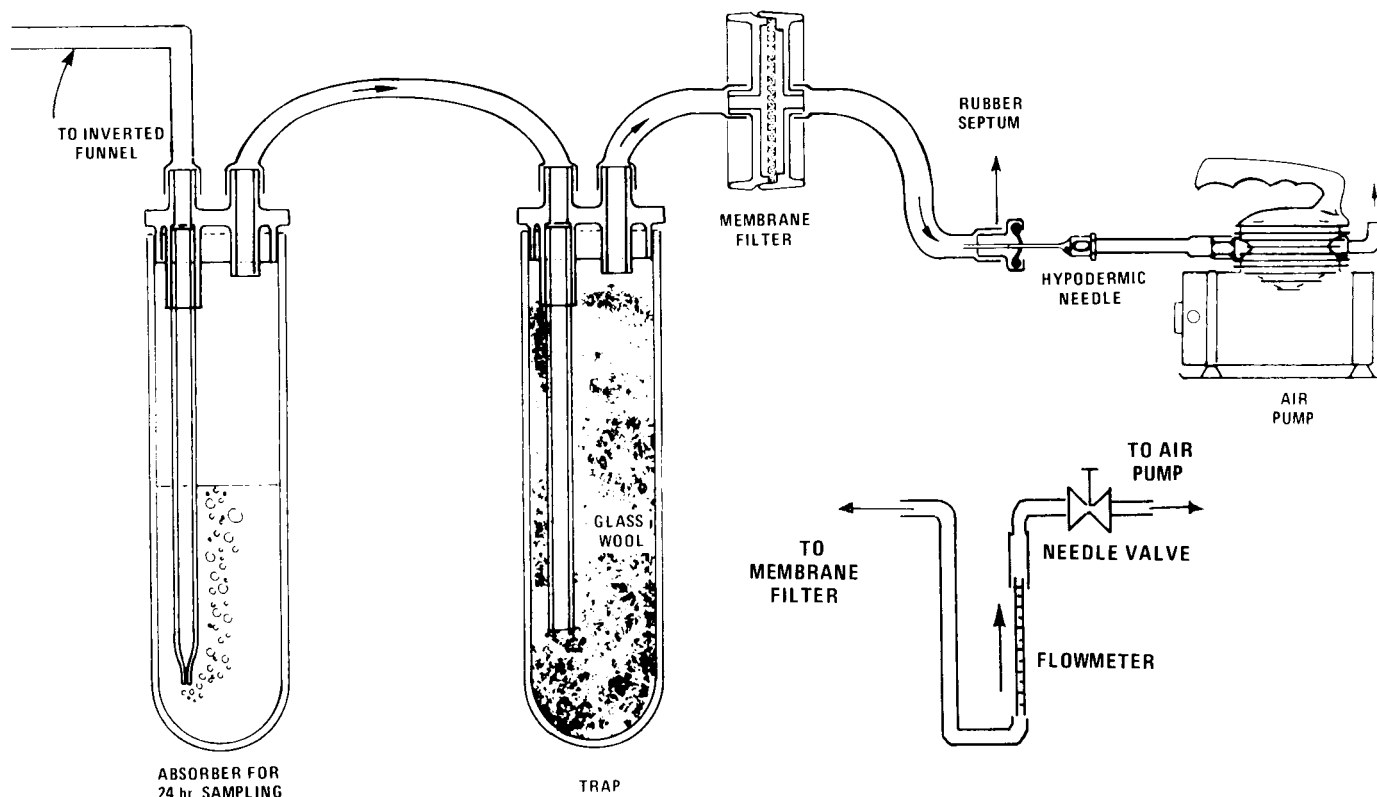


FIG. 1A Alternative Flow Control

FIG. 1 Sampling System

hypodermic needle critical orifice that is 9.5 mm in length so that the flow rate is in the range of 0.18 to 0.22 L/min.

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

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

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

7.1.11 *Temperature Control Device*—To maintain the temperature of the absorbing solution during sampling at $15 \pm 10^\circ\text{C}$. Maintain the temperature of the collected sample at $5 \pm 5^\circ\text{C}$, 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 $15 \pm 10^\circ\text{C}$ 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 ($<7^\circ\text{C}$) to prevent the absorbing solution from freezing (11).

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

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

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

7.2 Shipping:

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

7.3 Analysis:

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

using a standard wavelength filter traceable to the National Institute of Standards and Technology.

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

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

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

8. Reagents and Materials

8.1 Purity of Reagents—Reagent grade chemicals shall be used in all tests. All reagents shall conform to the specification of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁶ 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:

⁶ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

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

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

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

8.3 Sampling Reagents:

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

8.3.1.1 Ethylenediaminetetraacetic acid disodium salt (EDTA).

8.3.1.2 Mercuric chloride, HgCl_2 .

8.3.1.3 Potassium chloride, KCl.

8.3.2 Acetate Buffer (1 M)—Dissolve in a 100 mL volumetric flask, 13.61 g of sodium acetate trihydrate ($\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$) in 50 mL of water. Add 5.7 mL of glacial acetic acid (CH_3COOH) and dilute to 100 mL. The pH should be 4.74.



8.3.3 *1-Butanol*—Certain batches of 1-butanol contain oxidants that create a sulfur dioxide (SO₂) demand. Check by shaking 20 mL of 1-butanol with 5 mL of 15 % potassium iodide (KI) solution. If a yellow color appears in the alcohol phase, redistill the 1-butanol from silver oxide.

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

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

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

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

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

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

8.3.6.3 The calibration curve ([Annex A2](#)) shall have a slope of 0.030 ± 0.002 absorbance units/ $\mu\text{g SO}_2$, at the same optical path length, when the sulfite solution is properly standardized.

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

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

8.3.6.5 Alternatively, the dye may be purified as indicated in [Annex A1](#).

8.3.7 *Pararosaniline Reagent*

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

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

where:

M = % PRA in sample,

A = absorbance of solutions,

W = the mass in g of the PRA dye used in the assay to prepare 50 mL of stock solution (that is, 0.1 g of dye was used to prepare 50 mL of the solution in the purification procedure described in [Annex A1](#)) (see [Note 5](#)), and

21.3 = constant to convert absorbance to mass.

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

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

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

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

8.3.8 *Phosphoric Acid (3.0 M)*—Dilute 205 mL of concentrated phosphoric acid (H₃PO₄, sp gr 1.69) to 1 L by pouring the acid into 700 mL of water while stirring, then dilute to volume. This is stable for one year.

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

8.3.10 *Potassium Iodate Solution*—Accurately weigh to the nearest 0.1 mg, 1.5 g (record weight) of primary standard grade potassium iodate, KIO₃, that has been previously dried at 180°C for at least 3 h and cooled in a desiccator. Dissolve, then dilute to volume in a 500 mL volumetric flask with distilled water.

8.3.11 *Sulfamic Acid (0.6 %)*—Dissolve 0.6 g of sulfamic acid (NH₂SO₃H) in 100 mL of water. Prepare fresh daily.

8.4 *Calibration Reagents:*

8.4.1 *Iodine Solution, Stock (0.1 N)*—Dissolve 12.7 g of resublimed iodine (I₂) and 40 g of potassium iodide (KI) in 25 mL of water, and dilute to 1 L in a volumetric flask.

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

8.4.3 *Potassium Iodate Solution*—Accurately weigh to the nearest 0.1 mg, 1.5 g (record weight) of primary standard grade potassium iodate (KIO₃) that has been previously dried at 180°C for at least 3 h and cooled in a desiccator. 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 (HgI₂) (preservative) with a little water and add the paste slowly to 200 mL of boiling water. Boil until clear; cool and transfer to a glass-stoppered bottle.

8.4.5 *Sodium Thiosulfate, Stock Solution (0.1 N)*—Dissolve 24.82 g of sodium thiosulfate (Na₂S₂O₃·5 H₂O) in freshly boiled, cooled water, add 0.1 g of sodium carbonate (Na₂CO₃), and dilute to 1 L. Allow the solution to stand for a day before standardizing.

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

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

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

where:

N_s = normality of the sodium thiosulfate solution

