



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) to 1000 µg/m³ (0.4 ppm), 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 limit of detection, corresponding to twice the standard deviation, is 0.02 µg SO₂/mL, representing an air concentration of 4 µg SO₂/m³ (0.0015 ppm) in a 24-h sample, or 7 µg SO₂/m³ (0.003 ppm) in a 1-h sample.

1.4 These test methods incorporate sampling for 1 h and for 24 h.

1.5 These test methods describe manual and automated determinations of the collected (impinged) samples. Each method of determination has two submethods designated as Manual Methods 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 Method A is preferred over Manual Method B, as it gives the higher sensitivity, but it has a higher blank. 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/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.

1.8 *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, Section 9, and A3.1.1.

2. Referenced Documents

2.1 ASTM Standards:

D 1071 Test Methods for Volumetric Measurement of Gaseous Fuel Samples²

D 1193 Specification for Reagent Water³

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres⁴

D 1357 Practice for Planning the Sampling of the Ambient Atmosphere⁴

D 1605 Practices for Sampling Atmospheres for Analysis of Gases and Vapors⁵

D 1914 Practice for Conversion Units and Factors Relating to Sampling and Analysis of Atmospheres⁴

D 3195 Practice for Rotameter Calibration⁴

D 3609 Practice for Calibration Techniques Using Permeation Tubes⁴

D 3631 Test Methods for Measuring Surface Atmospheric Pressure⁴

E 1 Specification for ASTM Thermometers⁶

E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near-Infrared Spectrophotometers⁷

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

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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² Annual Book of ASTM Standards, Vol 05.05.

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.

complex **(1, 2)**.⁸ Ethylenediaminetetraacetic acid disodium salt (EDTA) is added to this solution to complex heavy metals that interfere with this method **(3)**. Dichlorosulfonatomercurate, once formed, is stable to strong oxidants (for example, ozone and oxides of nitrogen) **(1)**. 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)**. It is treated next with solutions of formaldehyde and specially purified acid-bleached pararosaniline containing phosphoric acid (H_3PO_4) to control pH. Pararosaniline, formaldehyde, and the bisulfite anion react to form the intensely colored pararosaniline methyl sulfonic acid which behaves as a two-color pH indicator **(1)**. 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 **(4)**.

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)** 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 **(7)**.

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 A has been designed to correspond to the EPA-Designated Reference Method **(6)** 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)**.

6. Interferences

6.1 The interferences of oxides of nitrogen are eliminated by sulfamic acid **(4, 5)** of ozone by time delay **(4)** and of heavy metals by EDTA and phosphoric acid **(3, 4)**. At least 60 μg of Fe(III), 10 μg of Mn(II), and 10 μg of Cr(III) in 10 mL of absorbing reagent can be tolerated in the procedure. No significant interference was found with 10 μg of Cu(II) and 22 μg of V(V).

7. Apparatus

7.1 For Sampling:

7.1.1 *Absorber, 1-h Sampling*—An all-glass midget impinger having a 25-mm outside diameter, a total capacity of 30 mL, and a 1-mm diameter orifice having a clearance from the bottom of the impinger of 4 ± 1 mm. An impinger meeting these specifications is commercially available from a number of manufacturers.

7.1.2 *Absorber, 24-h Sampling*—A glass or polypropylene absorption tube approximately 30 mm in diameter and 160 mm

long, with a polypropylene two-port closure (rubber stoppers are unacceptable because they cause high and variable blank values). The closure shall be fitted with a 8-mm outside diameter, 6-mm inside diameter glass orifice tube approximately 150 mm long, having the end drawn out to form an orifice of 0.4 ± 0.1 mm and positioned to allow a clearance of 6 mm from the orifice to the bottom of the tube.

7.1.3 *Air Sample Probe*—TFE-fluorocarbon, polypropylene, or glass tube with a polypropylene or glass funnel at the end.

7.1.4 *Moisture Trap*—Glass or polypropylene tube equipped with a two-port closure. The entrance port of the closure is fitted with tubing that extends to the bottom of the trap. The unit is loosely packed with 16-mesh activated coconut charcoal and glass wool to prevent moisture entrainment. The charcoal should be changed weekly.

7.1.5 *Filter*, membrane, of 0.8 to 2.0- μm porosity, with filter holder.⁹

7.1.6 *Pump*, capable of maintaining a vacuum greater than 70 kPa (0.7 atm) at the specified flow rate.

7.1.7 Flow Control and Measurement Devices:

7.1.7.1 *Flow Control Device*—Any device capable of maintaining a constant flow rate ($\pm 2\%$) can be used. For 1-h sampling (0.5 L/min), a 23-gage hypodermic needle 16 mm long **(10)** or a needle valve is suggested. For 24-h sampling (0.2 L/min), a 27-gage hypodermic needle 10 mm long is suggested. In either case, protect the needle valve or critical orifice from particulate matter and moisture entrainment.

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

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

7.1.10 The arrangement of the component parts for sampling is shown in Fig. 1. See Practice D 1605 for discussion of this apparatus.

7.2 For Manual Methods A and B:

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 having a spectral bandwidth greater than 10 nm. The wavelength calibration of the spectrophotometer shall be verified in accordance with Practice E 275. The optical cell shall have a minimum path length of 10 mm.

7.2.2 *Constant-Temperature Bath*, capable of controlling temperature to $\pm 2^\circ\text{C}$.

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

⁸ The boldface numbers in parentheses refer to the list of references at the end of this standard.

⁹ Gelman 37-mm in-line filters have been found satisfactory for this purpose.

TFE-fluorocarbon OR GLASS

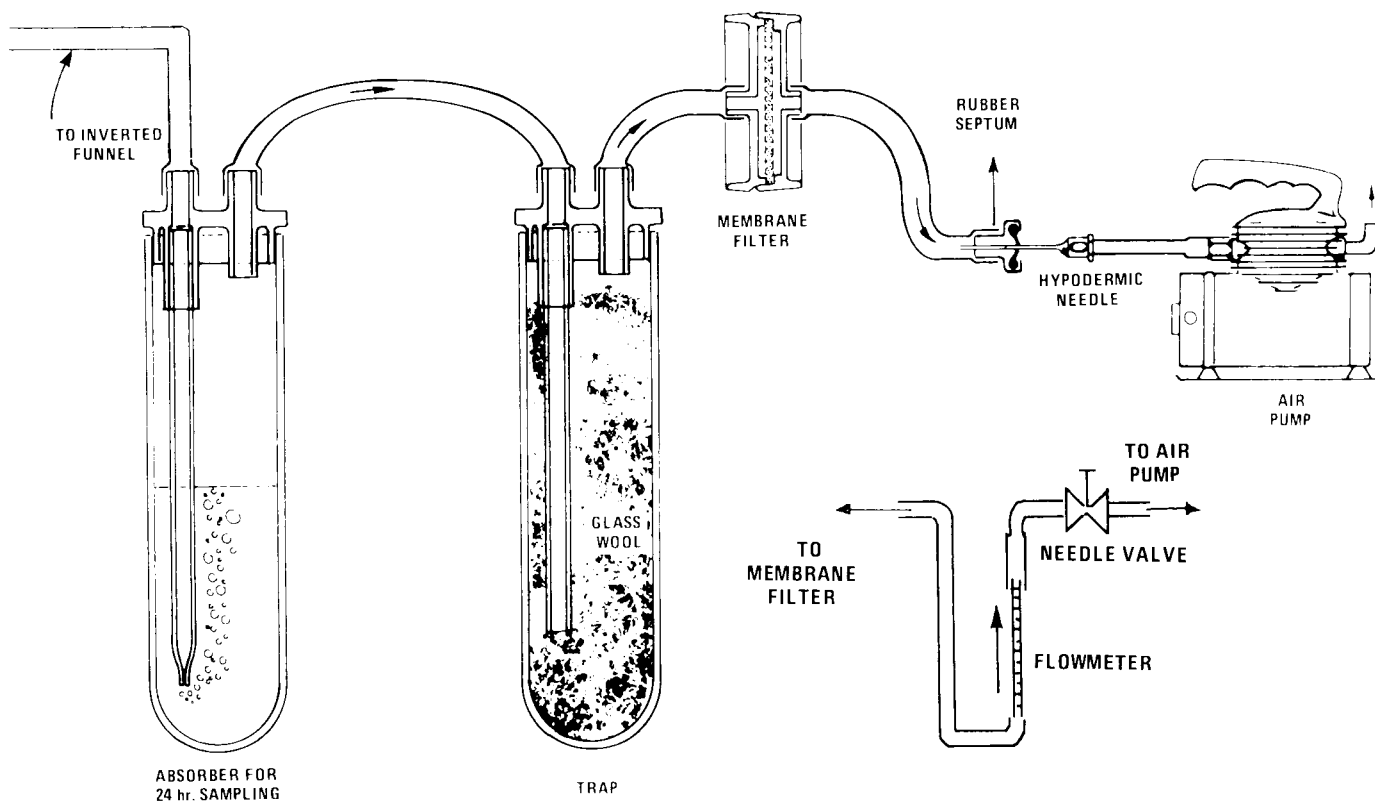


FIG. 1A Alternative Flow Control

FIG. 1 Sampling System

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

7.3.1 *Automated System for Method I* (see Fig. 2) consists of the following:

7.3.1.1 *Turntable*,¹² set 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*,¹³ capable of maintaining the flow rates in Table 1. Pump tubing shall be poly(vinyl chloride), or other inert tubing for sample and reagent.

7.3.1.4 *Sampler Probe*, made of polychlorotrifluoroethylene or glass. Because of the corrosive properties 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 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 to the extent that a proper calibration curve 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 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*,¹⁴ 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, 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*.

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

7.3.2.1 *Sampler Turntable*, 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

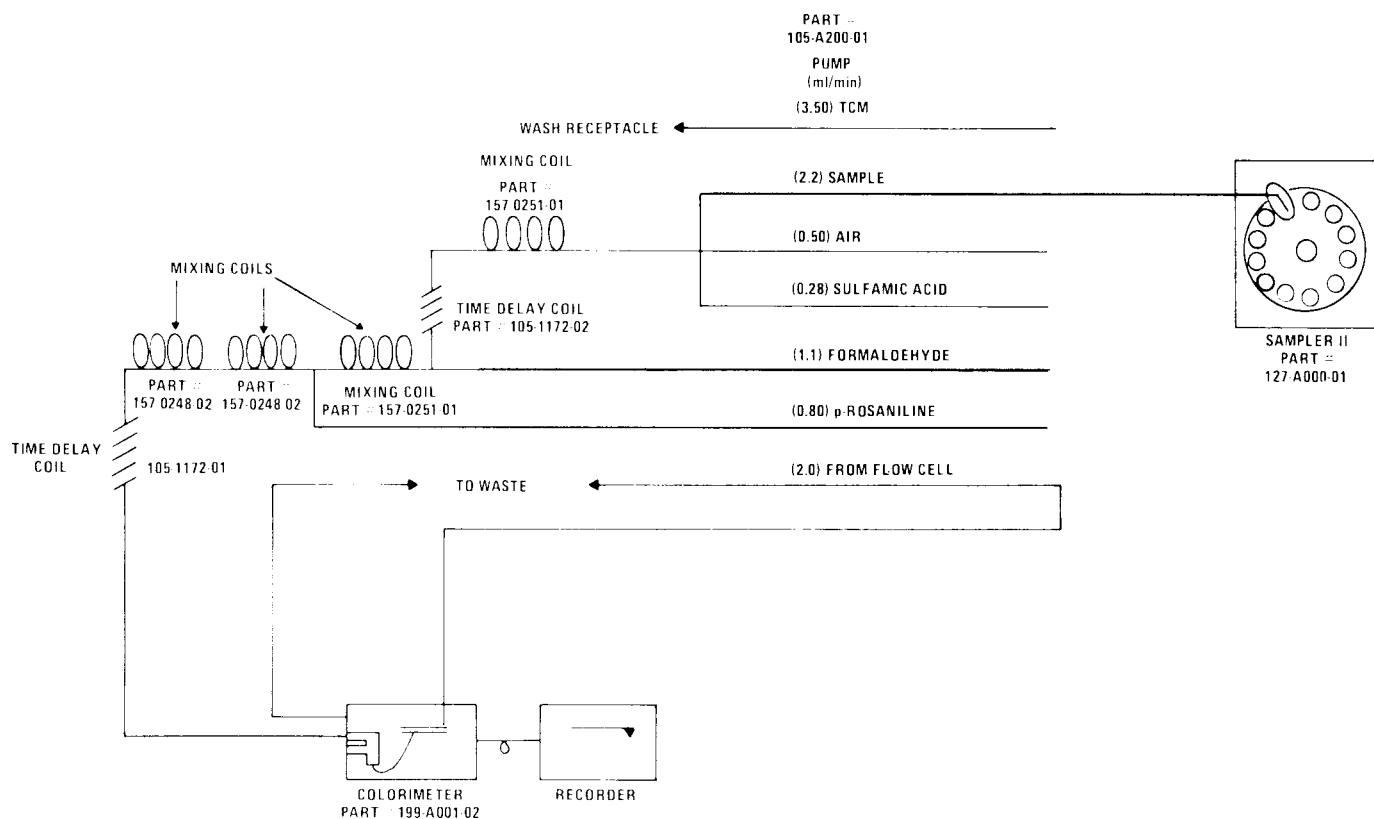
¹⁰ Technicon I Automated Analyzer System has been found satisfactory for Method I.

¹¹ Technicon II Automated Analyzer System has been found satisfactory for Method II.

¹² The Technicon Sampler II Turntable has been found to be satisfactory for this purpose.

¹³ The Technicon Proportioning Pump I has been found satisfactory for this purpose.

¹⁴ Technicon Part No. 199-A001-02 has been found satisfactory for this purpose.



NOTE 1—The part numbers refer to Technicon parts that have been found satisfactory for this purpose.

FIG. 2 Method I Automated Sulfur Dioxide Analysis System

TABLE 1 Pump Tubes Flow Rates

Pump Tube Reagent	Automated Method I Flow Rate, mL/min	Automated Method II Flow Rate, mL/min
TCM	3.5	1.8
Sample	2.2	0.32
Air	0.50	0.56
Sulfamic acid	0.28	0.32
Formaldehyde	1.1	0.10
p-Rosaniline	0.80	0.16
Waste	2.0	0.60

TABLE 2 Coil Sizes

Part Number ^A	Description	Number of Turns or Length	Internal Diameter or Volume
157-0251-01	Mixing Coil	10 turns	2 mm
157-0248-01	Mixing Coil	20 turns	2 mm
157-B089	Mixing Coil	20 turns	2 mm
157-B095	Mixing Coil	20 turns	2 mm
105-1172-01	Time Delay Coil	12.2 m	2.4 mm
105-1172-02	Time Delay Coil	6.1 m	2 mm
157-B273-06	Heating Bath	40 turns	5.4 mm

^A The part numbers refer to Technicon coils.

flow rates indicated in Table 1. Pump tubing for 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 the corrosive properties of the TCM absorbing reagent, no metal shall contact the sample solution.

7.3.2.5 Pump Tubes—The pump tubes are such that sample and reagent flow rates are as specified 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 to the extent that a proper calibration curve and acceptable quality 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,¹⁵ with proper filters for measurement of absorbance at 560 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, 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.

8. Reagents and Materials

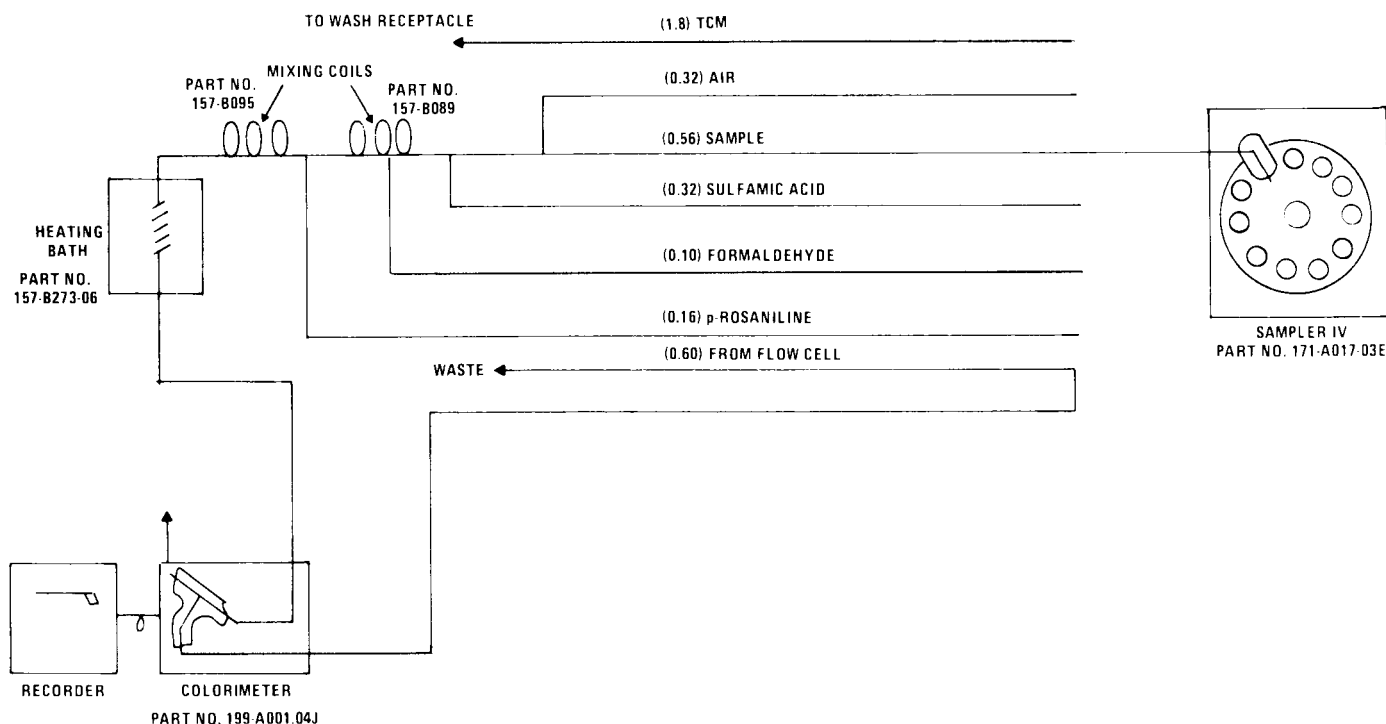
8.1 Purity of Reagents—Reagent grade chemicals shall be used in all tests. All reagents shall conform to the specification of the Committee on Analytical Reagents of the American

¹⁵ Technicon Parts Nos. 199-A001.04J and 161-A007-01, respectively, have been found satisfactory for this purpose.

ASTM D 2914

PART NO.
133-A000-05L

PUMP
(ml/min)



NOTE 1—The part numbers refer to Technicon parts that have been found satisfactory for this purpose.

FIG. 3 Method II Automated Sulfur Dioxide Analysis System

Chemical Society, where such specifications are available.¹⁶ 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.

8.3 Reagents Common to Manual Methods A and B and Automated Methods I and II:

8.3.1 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.

¹⁶ 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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

8.3.2 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.

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

8.3.4 Hydrochloric Acid (1 N)—Dilute 86 mL of concentrated hydrochloric acid (HCl , sp gr 1.19) to 1 L by pouring the acid into 800 mL of water while stirring, then dilute to volume. This is stable for one year.

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

8.3.5.1 The solutions shall have a wavelength of maximum absorbance at 540 μm in a solution of the acetate buffer.

8.3.5.2 The absorbance of the reagent blank, which is temperature-sensitive (0.015 absorbance units/ $^\circ\text{C}$) shall not exceed 0.170 absorbance units at 22 $^\circ\text{C}$ 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.

8.3.5.3 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.