



Designation: E223 – 23

## Standard Test Methods for Analysis of Sulfuric Acid<sup>1</sup>

This standard is issued under the fixed designation E223; 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 reappraisal. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reappraisal.

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

### 1. Scope\*

1.1 These test methods cover the analysis of sulfuric acid.

1.2 The following applies for the purposes of determining the conformance of the test results using this test method to applicable specifications, results shall be rounded off in accordance with the rounding-off method of Practice E29.

1.3 The values stated in SI units are to be regarded as standard. The values given in parentheses are for information only.

1.4 The analytical procedures appear in the following order:

	Sections
Total Acidity	8 to 16
Baumé Gravity	17 to 26
Nonvolatile Matter	27 to 33
Iron	34 to 43
Sulfur Dioxide	44 to 51
Arsenic	52 to 61

1.5 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use. Consult current OSHA regulations, suppliers' Safety Data Sheets, and local regulations for all materials used in this specification. Specific hazards statements are given in Section 5.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee D16 on Aromatic, Industrial, Specialty and Related Chemicals and are the direct responsibility of Subcommittee D16.10 on Acids.

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### 2. Referenced Documents

2.1 *ASTM Standards:*<sup>2</sup>

D1193 Specification for Reagent Water

D6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials

E1 Specification for ASTM Liquid-in-Glass Thermometers

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry

E100 Specification for ASTM Hydrometers

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)<sup>3</sup>

E200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis

E300 Practice for Sampling Industrial Chemicals

### 3. Significance and Use

3.1 These test methods provide for the classification of various grades of sulfuric acid and for the determination of various impurities. Acid strength and impurity levels are important factors in many uses of sulfuric acid.

### 4. Purity of Reagents

4.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society,

<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>3</sup> The last approved version of this historical standard is referenced on [www.astm.org](http://www.astm.org).

\*A Summary of Changes section appears at the end of this standard

where such specifications are available.<sup>4</sup> 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.

4.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type I or Type II reagent water conforming to Specification D1193.

**5. Hazards**

5.1 Consult current OSHA regulations, suppliers’ Safety Data Sheets, and local regulations for all materials used in this test method. Use of safety goggles and gloves highly recommended.

5.2 Sulfuric acid is a strong corrosive acid and is dangerous if improperly handled. Avoid any skin or eye contact.

5.3 Clean up all spills immediately by covering the spill with vermiculite or some other inert absorbent material and sweeping into a pan. Dispose of the absorbent by flooding with water and discarding in a suitable container. Flush the area with water.

**6. Photometers and Photometric Practice**

6.1 Photometers and the photometric practice used in these test methods shall conform to Practice E60.

**7. Sampling**

7.1 Sample sulfuric acid in accordance with the appropriate sections of Practice E300 for simple liquids.

7.2 The sample to be analyzed shall be considered to be that sample in a single bottle submitted to the analytical laboratory.

7.3 The size of the sample shall be sufficient to perform all analyses without the reuse of any portion of the sample.

**TOTAL ACIDITY**

**8. Scope**

8.1 This test method covers the determination of the total acidity of 75 % to 99 % mass (m/m) sulfuric acid. Two test methods are given for weighing the sample, namely, the Dely tube and the snake tube test methods.

<sup>4</sup> ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, 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.

**TABLE 1 Sample Size for Total Acidity**

H <sub>2</sub> SO <sub>4</sub> , % mass (m/m)	Sample Size, g
98	1.9 to 2.2
94	2.0 to 2.3
90	2.1 to 2.4
85	2.2 to 2.6
80	2.3 to 2.7
77	2.4 to 2.8
75	2.5 to 2.9

**9. Summary of Test Method**

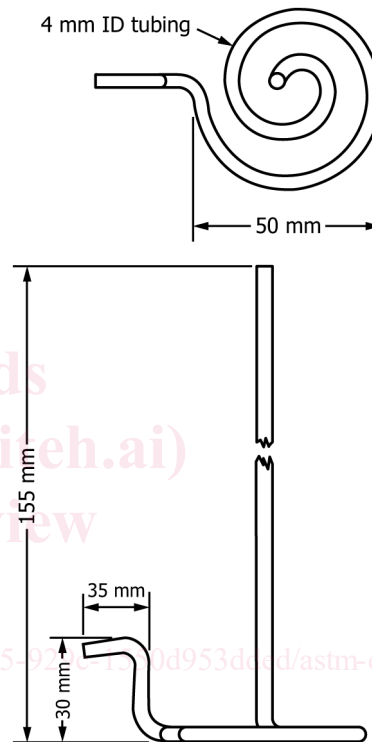
9.1 A weighed sample of acid is diluted in water and titrated with standardized 0.5 meq/mL(N) sodium hydroxide solution, using phenolphthalein as the indicator.

**10. Interferences**

10.1 Acids other than sulfuric and compounds that consume sodium hydroxide will affect the accuracy of this test method.

**11. Apparatus**

11.1 *Dely Tube* (Fig. 1) or *Snake Tube* (Fig. 2).<sup>5</sup>



**FIG. 1 Dely Tube**

11.2 *Buret*, 100 mL, Class A, bulb-type.

**12. Reagents**

12.1 *Phenolphthalein Indicator Solution* (10 g/L)—Dissolve 1 g of phenolphthalein in 100 mL of ethanol (95 %), methanol, or isopropanol.<sup>6</sup>

12.2 *Sodium Hydroxide, Standard Solution* (0.5 meq/mL(N))—See Practice E200.

**13. Procedure**

13.1 *Dely Tube Test Method*—Invert the sample bottle several times. (Hold the stopper in tight.) Insert the long arm of

<sup>5</sup> The sole source of supply of the Suitable Dely and snake tubes known to the committee at this time is Corning Glass Works, Corning, NY. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,<sup>1</sup> which you may attend.

<sup>6</sup> This reagent is also described in Practice E200.

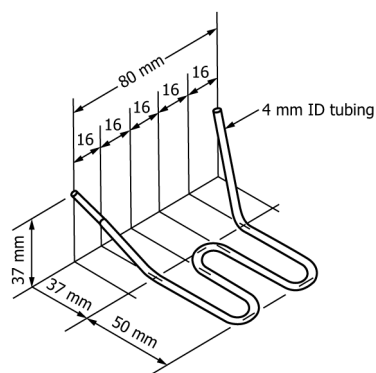


FIG. 2 Snake Tube

a dry, weighed Dely tube and withdraw by suction a convenient size sample depending upon the acid strength as given in Table 1 (Note 1). Invert the Dely tube and wipe the acid from the long arm with disposable tissue several layers thick. Discard the tissue immediately to avoid burning the fingers. Reweigh to the nearest 0.0001 g and record the weight of the sample. Incline the tube so that the acid runs back nearly to the bend of the short arm. Attach the short arm to an elevated water reservoir by means of a rubber tube closed near the lower end with a pinch clamp. Insert the long arm of the Dely tube into 400 mL glass beaker containing approximately 100 mL of water. Open the pinch clamp and flush the sample into the beaker. Continue the flow of water until all acid is washed from the Dely Tube (Note 2 and Note 3). Wash the long end of the Dely tube, collecting the washings in the beaker. Add 3 to 5 drops of phenolphthalein indicator solution. Record the temperature of the 0.5 meq/mL(N) NaOH solution, and then titrate the sample to a pink end point. Record the titration to the nearest 0.02 mL.

NOTE 1—The Dely tube can be marked at points equivalent to weights given in Table 1.

NOTE 2—The presence of acid in the Dely tube may be detected by coloring the water in the reservoir with phenolphthalein indicator and the minimum amount of dilute NaOH solution that will produce a slight pink. The water flowing through the tube is discolored as long as acid is present, and the appearance of a pink color indicates the absence of acid.

NOTE 3—The acid and water are separated by a bubble of air.

13.2 Snake Tube Test Method—Invert the sample bottle several times. (Hold the stopper in tight). Insert the capillary end of a dry, weighed snake tube and withdraw by suction a convenient size sample depending upon the acid strength as given in Table 1. Invert the tube so that the double bend is in a horizontal position. Wipe the acid from the capillary with disposable tissue several layers thick. Discard the tissue immediately to avoid burning the fingers. Reweigh to the nearest 0.0001 g and record the weight of the sample. Submerge the capillary of the tube in approximately 100 mL of water contained in the 400 mL beaker. Force the weighed sample from the tube by a stream of water from a wash bottle by placing the delivery tip in the exposed end of the snake tube (Note 4). Wash the tube with 50 mL to 70 mL of water. Remove the tube and wash the outside free of acid. Swirl the contents of the beaker gently while washing. Accumulate all washings in the beaker and add 3 to 5 drops of phenolphthalein

indicator solution. Record the temperature of the 0.5 meq/mL(N) NaOH solution, and then titrate the sample to a pink end point. Record the titration to the nearest 0.02 mL.

NOTE 4—Do not introduce the water into the snake tube too rapidly, as this will cause spattering.

#### 14. Calculation

14.1 If necessary, correct the buret reading for calibration errors and record the volume of titrant as  $V$  and the temperature as  $t$ .

14.2 Correct the normality of the sodium hydroxide standard solution for any difference in temperature between time of standardization and time of use according to the following equation:

$$N = N_s + 0.00014 (s - t) \quad (1)$$

where:

$N$  = normality meq/mL(N) of NaOH solution at temperature  $t$  during use,

$N_s$  = normality meq/mL(N) of NaOH solution at temperature  $s$  during standardization,

$s$  = temperature of NaOH solution during standardization, and

$t$  = temperature of NaOH solution during analysis.

14.3 Calculate the total acidity as % mass (m/m) of sulfuric acid as follows:

$$\text{Sulfuric acid, \% mass (m/m)} = \frac{(VN \times 0.04904)}{W} \times 100 \quad (2)$$

where:

$V$  = corrected millilitre of NaOH solution required for titration of the sample,

$N$  = meq/mL(N) normality of the NaOH solution, and

$W$  = grams of sample used.

#### 15. Report

15.1 Report the % mass (m/m) of sulfuric acid to the nearest 0.01 % mass(m/m).

#### 16. Precision and Bias

16.1 The following criteria should be used for judging the acceptability of results (see Note 5):

16.1.1 Repeatability (Single Analyst)—The standard deviation for a single determination has been estimated to be 0.069 % mass (m/m) absolute at 56 df. The 95 % limit for the difference between two such runs is 0.19 % mass (m/m) absolute.

16.1.2 Laboratory Precision (Within-Laboratory, Between-Days Variability)—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.104 % mass (m/m) absolute at 28 df. The 95 % limit for the difference between two such averages is 0.29 % mass (m/m) absolute.

16.1.3 Reproducibility (Multilaboratory)—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be

0.124 % mass (m/m) absolute at 7 df. The 95 % limit for the difference between two such averages is 0.35 % mass (m/m) absolute.

NOTE 5—These precision estimates are based on an interlaboratory study of analyses performed in 1963 on three samples containing approximately 80 %, 90 %, and 95 % mass (m/m) sulfuric acid. One analyst in each of ten laboratories performed duplicate determinations and repeated one day later, for a total of 120 determinations.<sup>7</sup> Practice E180 was used in developing these precision estimates.

16.2 Since there is no accepted reference material for determining the bias for measuring the total acidity of sulfuric acid, the bias of this test method has not been determined.

## BAUMÉ GRAVITY

### 17. Scope

17.1 This test method covers the determination of the Baumé gravity of concentrated sulfuric acid by means of a glass hydrometer in the range from 57° Baumé to 66.2° Baumé. The Baumé gravity is determined at 15.5 °C (60 °F). This test method is not applicable to readings above 66.2 Baumé gravity units.

### 18. Definition

18.1 *Baumé Gravity*—a unit of density based on specific gravity and defined by the following equation:

$$\text{Baumé gravity} = 145 - [145/\text{sp gr}] \text{ at } 15.5/15.5^\circ\text{C (60/60}^\circ\text{F)} \quad (3)$$

### 19. Summary of Test Method

19.1 A sample of sulfuric acid is placed in a hydrometer cylinder and when the temperature is constant, the Baumé gravity is read from the glass hydrometer.

### 20. Significance and Use

20.1 The Baumé gravity is used to classify various grades of sulfuric acid. This test method is not applicable for accurate determinations of the concentration of sulfuric acid.

### 21. Apparatus

21.1 *Hydrometer*,<sup>8</sup> streamline or torpedo design, precision grade for liquids heavier than water in ranges from 57° Bé to 62° Bé and 63° Bé to 67° Bé. The total length shall be approximately 305 mm (12 in.) divided to 0.05° Bé over a 152 mm (6 in.) (approximate) scale and standardized at 15.5 °C/15.5 °C (60 °F/60 °F) with a tolerance of 0.05° Bé throughout. The modulus is as follows:

$$\text{Bé} = 145 - [145/\text{sp gr}] \text{ at } 15.5/15.5^\circ\text{C (60/60}^\circ\text{F)} \quad (4)$$

Each of the hydrometers shall show on the scale the modulus.

21.2 *Thermometer*, having a range from – 2 °C to + 80 °C (30 °F to 180 °F) and conforming to the requirements for Thermometer 15C (15F) as prescribed in Specification E1.

21.3 *Cylinder, Hydrometer*, glass, with or without lip, diameter 38 mm to 40 mm, height 325 mm to 375 mm.

### 22. Temperature of Test

22.1 Baumé gravity shall be determined at 15.5 °C ± 0.3 °C (60 °F ± 0.5 °F).

### 23. Procedure

23.1 Rinse a clean hydrometer cylinder with the sample to be tested, add the sample, and adjust the temperature to 15.5 °C ± 0.3 °C (60 °F ± 0.5 °F). Place the cylinder in a vertical position in a location free of air currents. Insert the hydrometer in the sample. Push it down about 3 mm below the level at which it will float and release it. Read the hydrometer when it has come to rest, floating freely, and the temperature is 15.5 °C (60 °F). The correct reading is that point on the hydrometer scale at which the surface of the liquid cuts the scale. Determine this point by placing the eye slightly below the level of the liquid and slowly raising it until the surface, first seen as a distorted ellipse, appears to become a straight line cutting the hydrometer scale. Record as Baumé gravity.

### 24. Calculation

24.1 Calculate the specific gravity for later calculations in accordance with the following equation:

$$\text{sp gr} = \frac{145}{145 - \text{Bé}} \quad (5)$$

### 25. Report

25.1 Report the Baumé gravity to the nearest 0.01 unit.

### 26. Precision and Bias

26.1 The following criteria should be used for judging the acceptability of results (see Note 6):

26.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.018 unit absolute at 48 df. The 95 % limit for the difference between two such runs is 0.05 unit absolute.

26.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.016 unit absolute at 24 df. The 95 % limit for the difference between two such averages is 0.045 unit absolute.

26.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.063 unit absolute at 7 df. The 95 % limit for the difference between two such averages is 0.18 unit absolute.

NOTE 6—These precision estimates are based on an interlaboratory study of analyses performed in 1963 on three samples having Baumé gravities of approximately 61, 65, and 66 units. One analyst in each of nine laboratories performed duplicate determinations and repeated one day later, for a total of 104 determinations.<sup>7</sup> Practice E180 was used in developing these precision estimates.

26.2 Since there is no accepted reference material for determining the bias for measuring the Baumé gravity of sulfuric acid, the bias of this test method has not been determined.

<sup>7</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E15-1047. Contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org).

<sup>8</sup> See Specification E100.

## NONVOLATILE MATTER

### 27. Scope

27.1 This test method covers the gravimetric determination of nonvolatile matter in sulfuric acid. The lower limit of determination of nonvolatile matter is 0.001 % mass (m/m).

### 28. Summary of Test Method

28.1 A weighed sample of acid is evaporated, ignited, and the residue weighed.

### 29. Apparatus

29.1 *Evaporating Dish*, platinum or high-silica glass, 150 mL.

29.2 *Muffle Furnace*, maintained at 800 °C ± 25 °C (1472 °F ± 45 °F).

29.3 *Crucible Tongs*.

### 30. Procedure

30.1 Clean a platinum or a high-silica glass dish (Note 7 and Note 8) and ignite in a muffle furnace at 800 °C ± 25 °C (1472 °F ± 45 °F) for at least 10 min. Cool in a desiccator to room temperature and weigh the dish to the nearest 0.1 mg (Note 9).

NOTE 7—New platinum or high-silica glass dishes should be boiled in HCl (1 + 1) for 10 min, washed, and ignited in the muffle furnace for at least 1 h before their first use.

NOTE 8—High-silica glass dishes should be used only for low nonvolatile material. The residue remaining from samples containing large amounts of nonvolatile matter may fuse into the dish.

NOTE 9—High-silica glass dishes should be allowed to cool at least 45 min and platinum dishes at least 20 min before weighing.

30.2 Mix the sample by inverting the sample bottle repeatedly until all solids are in suspension.

NOTE 10—It is important that the sample be well mixed and that all solids are in homogeneous suspension so that a representative sample can be obtained.

30.3 Transfer a weighed sample containing a minimum of 50 g, weighed to the nearest 0.1 g, or a weighed sample of sufficient size to yield not less than 1 mg of residue, to the evaporating dish and evaporate to dryness over a burner or hot plate in a hood. After evaporation, ignite the sample in the muffle furnace for 10 min. Use crucible tongs in handling the evaporating dish at all times.

30.4 Allow the dish to cool to room temperature in a desiccator and rapidly weigh the sample dish to the nearest 0.1 mg.

### 31. Calculation

31.1 Calculate the % mass (m/m) of nonvolatile matter as follows (Note 11):

$$\text{Nonvolatile matter, \% mass (m/m)} = \frac{(RxD)}{W} \times 100 \quad (6)$$

where:

*R* = weight of evaporating dish and residue, g,

*D* = weight of evaporating dish, g, and

*W* = sample used, g.

NOTE 11—If this value is less than 0.0010 % mass (m/m), report as less than 0.0010 % mass (m/m).

### 32. Report

32.1 Report the percentage of nonvolatile matter to the nearest 0.0001 % mass (m/m).

### 33. Precision and Bias

33.1 The following criteria should be used for judging the acceptability of results (see Note 12):

33.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be the value in Table 2 at the indicated degrees of freedom. The 95 % limit for the difference between two such runs is given in Table 2.

33.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be the value in Table 2 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is given in Table 2.

33.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be the value given in Table 2 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is given in Table 2.

NOTE 12—These precision estimates are based on an interlaboratory study of analyses performed in 1963 to 1964 on five samples containing approximately 0.003 %, 0.005 %, 0.010 %, 0.014 %, 0.024 %, and 0.048 % mass (m/m) nonvolatile matter. One analyst in each of eight to ten laboratories performed duplicate determinations and repeated one day later.<sup>7</sup> Practice E180 was used in developing these precision estimates.

33.2 Since there is no accepted reference material for determining the bias for measuring the nonvolatile matter of sulfuric acid, the bias of this test method has not been determined.

**TABLE 2 Nonvolatile Matter Precision Values**

NVM, % mass (m/m)	Repeatability			Laboratory Precision			Reproducibility		
	Standard Deviation	Degrees of Freedom	95 % Range	Standard Deviation	Degrees of Freedom	95 % Range	Standard Deviation	Degrees of Freedom	95 % Range
0.003	0.0004	22	0.0010	0.0004	11	0.0010	0.0015	10	0.0040
0.004	0.0008	16	0.0023	0.0007	8	0.0019	0.0013	7	0.0036
0.01 to 0.024	0.0015	54	0.0042	0.0009	27	0.0024	0.0013	7	0.0036
0.048	0.0009	20	0.0025	0.0013	10	0.0036	0.0046	9	0.0130

## IRON

### 34. Scope

34.1 This test method describes the determination of iron in sulfuric acid. The lower limit of determination of iron is 0.0001 % mass (m/m).

### 35. Summary of Test Method

35.1 The iron is reduced and determined colorimetrically with 1,10-phenanthroline (*ortho*-phenanthroline), which forms an orange-red complex with ferrous iron. The intensity of the color so formed is measured in a photometer calibrated with standard iron solutions.

### 36. Interferences

36.1 It is beyond the scope of this test method to describe procedures for overcoming all possible interferences that may be encountered. Chromium interferes if it is present in sufficient quantity for the color of chromic ion to have a masking effect. Copper, antimony, cobalt, mercury (I), and tin (II, IV) interfere in concentrations of 10 µg/g to 50 µg/g (ppm). Cadmium, mercury (II), zinc, and nickel may interfere, but can be overcome by the use of excess 1,10-phenanthroline reagent.

### 37. Apparatus

37.1 *Photometer*—Any photoelectric spectrophotometer or filter photometer that will measure the absorbance of the solutions in the wavelength range from 500 nm to 525 nm.

37.2 *Absorption Cells*, 2 cm light path.

NOTE 13—This procedure has been written for a cell having a 2 cm light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagents used.

### 38. Reagents

38.1 *Ammonium Acetate–Acetic Acid Solution*—Dissolve 100 g of ammonium acetate (CH<sub>3</sub>COONH<sub>4</sub>) in about 600 mL of water, filter, add 200 mL of glacial acetic acid to the filtrate, and dilute to 1 L.

38.2 *Ammonium Hydroxide Solution (1 + 1)*—Dilute to 500 mL of ammonium hydroxide (NH<sub>4</sub>OH) with 500 mL of water, and mix.<sup>6</sup>

38.3 *Congo Red Paper*.

38.4 *Hydroxylamine Hydrochloride Solution (100 g/L)*—Dissolve 100 g of hydroxylamine hydrochloride (NH<sub>2</sub>OH·HCl) in about 600 mL of water, filter, and dilute to 1 L.<sup>6</sup>

38.5 *Iron, Standard Solution (1 mL = 0.01 mg Fe)<sup>9</sup>*—See Practice E200.

38.6 *1,10-Phenanthroline (o-Phenanthroline) Solution (3 g/L)*—Dissolve 3 g of *ortho*-phenanthroline monohydrate in 500 mL of water, add 1 mL of hydrochloric acid (HCl), mix, filter, and dilute to 1 L.<sup>6</sup>

### 39. Calibration

39.1 To a series of 100 mL volumetric flasks, pipet 0 mL, 2 mL, 4 mL, 8 mL, and 10 mL of standard iron solution. To

each flask add the following reagents in order, mixing after addition of each: 20 mL of water, 1 mL of hydroxylamine hydrochloride solution, 5 mL of 1,10-phenanthroline solution, and NH<sub>4</sub>OH (1 + 1) as required to bring the pH to 3.5 to 4.0 (just alkaline to Congo red paper). Add 5 mL of ammonium acetate solution, dilute to the mark with water, mix thoroughly, and allow to stand approximately 15 min.

39.2 Measure the absorbances of the solutions using a photometer with a wavelength setting of 510 nm or a filter photometer equipped with a filter in the range from 500 nm to 525 nm, adjusting the photometer to read zero absorbance for the reagent blank.

39.3 Plot on coordinate paper the absorbances of the calibration solutions against milligrams of iron present per 100 mL of solution.

### 40. Procedure

40.1 Mix the sample by inverting the sample bottle until all solids are in suspension (Note 10).

40.2 Insert a 70 mm stem funnel in a 100 mL volumetric flask and add 50 mL of water (Note 14). Remove the funnel and slowly add, with continual swirling of the contents of the flask, 1 g of sample weighed by difference to the nearest 0.001 g. Wash down the neck of the flask with approximately 5 mL of water.

NOTE 14—This is done to keep the neck of the flask dry and prevent spitting or spattering on introducing the sample.

40.3 Add to the flask the following reagents in order, mixing after the addition of each: 1 mL of hydroxylamine hydrochloride solution, 5 mL of 1,10-phenanthroline solution, and NH<sub>4</sub>OH (1 + 1) as required to bring the pH of the solution to 3.5 to 4.0 (just alkaline to Congo red paper). Add 5 mL of ammonium acetate solution, dilute to the mark with water, mix thoroughly, and allow to stand approximately 15 min.

40.4 Prepare a blank solution using all reagents but omitting the sample. Allow to stand about 15 min.

40.5 Determine the absorbance of the sample at the same wavelength used for the calibration curve, blanking the instrument at zero absorbance with the blank solution. Determine from the calibration curve the milligrams of iron that correspond to the observed absorbance of the sample.

NOTE 15—If the color obtained is too intense to fall within the range of the calibration curve, repeat with a smaller sample.

NOTE 16—If the color obtained is less than that obtained with 0.01 mg of iron, repeat as follows: Transfer 10 g of sample, weighed by difference to the nearest 0.01 g, to a 50 mL beaker and evaporate almost to dryness over a burner or hotplate in a hood. Cool. Add 10 mL of water and 2 mL of HCl (sp gr 1.19) and heat to dissolve any solids. Transfer the solution to a 100 mL volumetric flask with a minimum amount of water and proceed in accordance with 40.3 starting with the addition of 1 mL of hydroxylamine hydrochloride solution.

### 41. Calculation

41.1 Calculate the % mass (m/m) of iron as follows (Note 17):

$$\text{Iron, mass \% (m/m)} = \frac{M}{W \times 1000} \times 100 \quad (7)$$

<sup>9</sup> This reagent is used for calibrating purposes only.

where:

$M$  = iron, found from calibration curve, mg, and

$W$  = sample used, g.

NOTE 17—If this value is less than 0.0001 % mass (m/m), report as less than 0.0001 % mass (m/m).

## 42. Report

42.1 Report the % mass (m/m) of iron to the nearest 0.0001 % mass (m/m).

## 43. Precision and Bias

43.1 The following criteria should be used for judging the acceptability of results (see Note 18):

43.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.00018 % mass (m/m) absolute at 52 df. The 95 % limit for the difference between two such runs is 0.0005 % mass (m/m) absolute.

43.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.00021 % mass (m/m) absolute at 26 df. The 95 % limit for the difference between two such averages is 0.0006 % mass (m/m) absolute.

43.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.00034 % mass (m/m) absolute at 6 df. The 95 % limit for the difference between two such averages is 0.0009 % mass (m/m) absolute.

NOTE 18—These precision estimates are based on an interlaboratory study of analyses performed in 1963 to 1964 on three samples containing approximately 0.004 %, 0.005 %, and 0.008 % mass (m/m) iron. One analyst in each of nine laboratories performed duplicate determinations and repeated one day later, for a total of 108 determinations.<sup>7</sup> Practice E180 was used in developing these precision estimates.

One sample, containing approximately 0.0003 % mass (m/m) iron and analyzed by one analyst in each of eight laboratories for a total of 32 determinations, gave the following precision data:

*Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.000041 % mass (m/m) absolute at 16 df. The 95 % limit for the difference between two such runs is 0.0001 % mass (m/m) absolute.

*Laboratory Precision (Within-Laboratory, Between-Days Variability)*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.000051 % mass (m/m) absolute at 8 df. The 95 % limit for the difference between two such averages is 0.0001 % mass (m/m) absolute.

*Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.00014 % mass (m/m) absolute at 7 df. The 95 % limit for the difference between two such averages is 0.0004 % mass (m/m) absolute.

43.1.4 Above 0.01 % mass (m/m) iron, the precision is poor because of difficulty in sampling.

43.2 Since there is no accepted reference material for determining the bias for measuring the iron content of sulfuric acid, the bias of this test method has not been determined.

## 44. Scope

44.1 This test method covers the determination of free sulfur dioxide dissolved in sulfuric acid. The lower limit of determination of sulfur dioxide is 0.002 % mass (m/m).

## 45. Summary of Test Method

45.1 The sulfur dioxide is swept out of the sample of sulfuric acid by means of a current of nitrogen gas. The evolved sulfur dioxide is absorbed in an alkaline solution, treated with an excess of iodate-iodide solution and the excess is titrated with sodium thiosulfate.

## 46. Apparatus

46.1 *Evolution and Absorption Train*, consisting of:

46.1.1 *Source of Pure Nitrogen Gas*, connected to

46.1.2 *Gas-Washing Bottle*, 125 mL, connected as a safety trap to prevent acid suck-back, connected to

46.1.3 *Gas-Washing Bottle*, 125 mL, with fritted glass disk on the inlet tube, connected to

46.1.4 *Gas-Washing Bottle*, 250 mL, with fritted glass disk on the inlet tube.

## 47. Reagents

47.1 *Potassium Iodate-Potassium Iodide Solution* (approximately 0.1 meq/mL (N))—Dissolve 4 g of potassium iodate ( $KIO_3$ ) and 100 g of potassium iodide (KI) in water and dilute to 1 L with water.

47.2 *Sodium Hydroxide Solution* (4 g/L)—Dissolve 4 g of sodium hydroxide (NaOH) in water and dilute to 1 L.<sup>6</sup>

47.3 *Sodium Thiosulfate, Standard Solution* (0.1 meq/mL (N))—See Practice E200.

47.4 *Sodium Thiosulfate, Standard Solution* (0.01 meq/mL (N))—Pipet 100 mL of 0.1 meq/mL (N) sodium thiosulfate ( $Na_2S_2O_3$ ) solution into a 1 L volumetric flask, dilute to volume with water, and mix. The normality is exactly one tenth that of the 0.1 N solution.

47.5 *Starch Indicator Solution* (10 g/L)—Mix 1 g of soluble starch with 5 mg of red mercuric iodide ( $HgI_2$ ) and enough cold water to make a thin paste, and pour slowly, with constant stirring, into 100 mL of boiling water. Boil the mixture while stirring until a thin, translucent fluid is obtained. Cool before use.<sup>6</sup>

47.6 *Sulfuric Acid* (1 + 5) —Mix carefully while stirring, 1 volume of concentrated sulfuric acid ( $H_2SO_4$ , sp gr 1.84) with 5 volumes of water.

## 48. Procedure

48.1 Flush out the safety bottle with nitrogen.

48.2 From a graduated cylinder, transfer about 50 mL of the sample into the 125 mL gas-washing bottle and connect to the safety bottle. Note the millilitres of sample used,  $W$ .

48.3 Place about 100 mL of the NaOH solution in 250 mL gas-washing bottle and connect to the 125 mL gas-washing bottle.