Designation: E 224 – 96 (Reapproved 2002)

Standard Test Methods for Analysis of Hydrochloric Acid[1]

This standard is issued under the fixed designation E 224; 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 analysis of hydrochloric acid.

1.2 The analytical procedures appear in the following order:

	Sections
Total Acidity	8 to 16
Baumé Gravity	17 to 26
Sulfated Ash	27 to 34
Iron	35 to 44
Color	45 to 52
Total Sulfur	53 to 59

1.3 *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.* Specific hazards statements are given in Section 5 and 30.1, 39.7, and 48.4.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

D 1209 Test Method for Color of Clear Liquids (Platinum-Cobalt Scale)[3]

E 1 Specification for ASTM Thermometers[4]

E 60 Practice for Analysis of Metals, Ores, and Related Materials by Molecular Absorption Spectrometry[5]

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals[6]

E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis[6]

3. Significance and Use

3.1 These test methods provide for the classification of various grades of hydrochloric acid and for the determination of various impurities. Acid strength and impurity levels are important factors in many uses of hydrochloric 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, where such specifications are available.[7] 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 II or Type III reagent water conforming to Specification D 1193.

5. Hazards

5.1 Hydrochloric acid is a corrosive acid and is dangerous if improperly handled. Avoid any skin contact.

5.2 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 prescribed in these test methods shall conform to Practice E 60.

7. Sampling

7.1 Sampling of hydrochloric acid is not within the scope of these test methods.

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.

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[1] These test methods are under the jurisdiction of ASTM Committee E15 on Industrial and Specialty Chemicals and are the direct responsibility of Subcommittee E15.02 on Product Standards.

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[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 06.04.

[4] *Annual Book of ASTM Standards*, Vol 14.03.

[5] *Annual Book of ASTM Standards*, Vol 03.05.

[6] *Annual Book of ASTM Standards*, Vol 15.05.

[7] *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.

TOTAL ACIDITY

8. Scope

8.1 This test method covers the determination of the total acidity of 27 to 37 % hydrochloric acid.

9. Summary of Test Method

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

10. Interferences

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

11. Apparatus

11.1 *Buret*, 50-mL, Class A.

11.2 *Weighing Bottle*, glass-stoppered, 50-mL.

12. Reagents

12.1 *Phenolphthalein Indicator, Solution* (10 g/L)—Dissolve 1 g of phenolphthalein in 100 mL of ethanol (95 %), methanol, or isopropanol.[8]

12.2 *Sodium Hydroxide, Standard Solution* (0.5 *N*)—See Practice E 200. Correct for differences in temperature in accordance with the following formula:

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

where:

N = normality of NaOH solution at temperature t,
N_s = normality of NaOH solution at temperature s during standardization,
s = temperature of NaOH solution during standardization, and
t = temperature of NaOH solution during analysis,° C.

13. Procedure

13.1 Transfer approximately 30 mL of water to a 50-mL glass-stoppered weighing bottle, stopper, and weigh to the nearest 0.1 mg. Rapidly add a convenient size sample, depending upon the acid strength as given in Table 1, stopper immediately, and reweigh. Transfer the sample to a 400-mL beaker containing approximately 50 mL of water and add 3 to 5 drops of phenolphthalein indicator solution. Record the temperature of the 0.5 *N* NaOH solution, and then titrate the sample to a pink end point. Record the titration to the nearest 0.02 mL.

TABLE 1 Sample Size For Total Acidity

HCl, %	Sample Size, g
37	1.9 to 2.3
35	2.0 to 2.4
33	2.2 to 2.6
31	2.3 to 2.8
29	2.5 to 3.0
27	2.7 to 3.2

14. Calculation

14.1 Correct the buret reading for calibration errors, and record as *V* the corrected delivered volume at the recorded temperature.

14.2 Calculate the total acidity as percentage of hydrochloric acid as follows:

$$\text{Hydrochloric acid, \%} = \left(\frac{VN \times 0.03646}{W}\right) \times 100 \quad (2)$$

where:

V = corrected mL of NaOH solution required for titration of the sample,
N = normality of the NaOH solution, and
W = sample used, g.

15. Report

15.1 Report the percentage of hydrochloric acid to the nearest 0.01 %.

16. Precision and Bias

16.1 The following criteria should be used for judging the acceptibility of results (see Note 1):

16.1.1 *Repeatability (Single Analyst)*—The coefficient of variation for a single determination has been estimated to be 0.133 % relative at 50 df. The 95 % limit for the difference between two such runs is 0.37 % relative.

16.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability), Formerly Called Repeatability*—The coefficient of variation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.170 % relative at 25 df. The 95 % limit for the difference between two such averages is 0.48 % relative.

16.1.3 *Reproducibility (Multilaboratory)*—The coefficient of variation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.285 % relative at 7 df. The 95 % limit for the difference between two such averages is 0.80 % relative.

NOTE 1—These precision estimates are based on an interlaboratory study of analyses performed in 1963 on three samples containing approximately 28, 31, and 38 % hydrochloric acid. One analyst in each of ten laboratories performed duplicate determinations and repeated one day later, for a total of 120 determinations.[9] Practice E 180 was used in developing these precision estimates.

16.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

BAUMÉ GRAVITY

17. Scope

17.1 This test method covers the determination of the Baumé gravity of hydrochloric acid by means of a glass

[8] This reagent is also described in Practice E 200.

[9] Details of the interlaboratory study are available from ASTM International Headquarters. Request RR: E15 - 1046.

hydrometer in the range from 17.5 to 23° Baumé. The Baumé gravity is determined at 15.5°C (60°F).

18. Terminology

18.1 *Definition:*

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

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

19. Summary of Test Method

19.1 A sample of hydrochloric 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 hydrochloric acid.

21. Apparatus

21.1 *Hydrometer,*[10] streamline or torpedo design, precision grade, for liquids heavier than water in ranges from 17.5 to 23°Bé. The total length shall be approximately 12 in. (305 mm) divided to 0.1°Bé over a 6-in. (152-mm) (approximate) scale and standardized at 15.5/15.5°C (60/60°F) with a tolerance of 0.1°Bé throughout. The modulus is as follows:

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

Each of the hydrometers shall show on the scale the modulus (or formula).

21.2 *Thermometer*, having a range from − 2 to + 80°C (30 to 180°F) and conforming to the requirements for Thermometer 15C (15F) in accordance with Specification E 1.

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

22. Temperature of Test

22.1 Baumé gravity shall be determined at 15.5± 0.3°C (60 ± 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 ± 0.3°C (60 ± 0.5°F). Place the cylinder in a vertical position in a location free of air currents. Insert 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 of 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.

24. Calculation

24.1 Calculate the specific gravity for use in the determination of iron using the following equation:

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

25. Report

25.1 Report the Baumé gravity to the nearest 0.1 unit.

26. Precision and Bias

26.1 The following criteria should be used for judging the acceptibility of results (see Note 2):

26.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.048 unit absolute at 48 df. The 95 % limit for the difference between two such runs is 0.1 unit absolute.

26.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability), Formerly Called Repeatability*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.046 unit absolute at 24 df. The 95 % limit for the difference between two such averages is 0.1 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 0.084 unit absolute at 7 df. The 95 % limit for the difference between two such averages is 0.2 unit absolute.

NOTE 2—These precision estimates are based on an interlaboratory study of analyses performed in 1963 on three samples having Baumé gravities of approximately 18, 20, and 23 units. One analyst in each of nine laboratories performed duplicate determinations and repeated one day later, for a total of 108 determinations.[9] Practice E 180 was used in developing these precision estimates.

26.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

SULFATED ASH

27. Scope

27.1 This test method covers the gravimetric determination of material not volatile after treatment with sulfuric acid. The lower limit of determination of sulfated ash is 0.001 %.

28. Summary of Test Method

28.1 A weighed sample of acid, to which sulfuric acid has been added, 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 ± 25°C (1472 ± 45°F).

29.3 *Crucible Tongs*.

30. Reagent

30.1 *Sulfuric Acid* (1 + 1)—Add slowly with stirring 1 volume of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) to 1 volume of water. (**Warning**—Use goggles when preparing this solution.)

[10] Suitable hydrometers are available from Walter H. Kessler, Inc., 160 Hicks St., Westbury, L.I., NY 11590.

31. Procedure

31.1 Clean a platinum or a high-silica glass dish (see warning above and Note 3) and ignite in a muffle furnace at 800 ± 25°C (1472 ± 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 5).

NOTE 3—New platinum or high-silica glass dishes should be boiled in hydrochloric acid (HCl, 1 + 1) for 10 min, washed, and ignited in the muffle furnace for at least 1 h before their first use.

NOTE 4—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 5—High-silica glass dishes should be allowed to cool at least 45 min and platinum dishes at least 20 min before weighing.

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

31.3 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, add 4 drops of H_2SO_4, evaporate almost to dryness on a steam bath, and then to dryness over a burner or hotplate 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.

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

32. Calculation

32.1 Calculate the percentage of sulfated ash as follows (Note 6):

$$\text{Sulfated ash, \%} = \frac{[R - D]}{W} \times 100 \qquad (6)$$

where:

R = weight of evaporating dish and residue, g,
D = weight of evaporating dish, g, and
W = sample used, g.

NOTE 6—When this value is less than 0.0010 %, report as less than 0.0010 %.

33. Report

33.1 Report the percentage of sulfated ash to the nearest 0.0001 %.

34. Precision and Bias

34.1 The following criteria should be used for judging the acceptibility of results (see Note 7):

34.1.1 *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.

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

34.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be the amount 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 7—The precision estimates in 34.1.1, 34.1.2, and 34.1.3 are based on an interlaboratory study of analyses performed in 1963–1964 on five samples containing approximately 0.004, 0.014, 0.018, 0.035, and 0.054 % sulfated ash. One analyst in each of eight to thirteen laboratories performed duplicate determinations and repeated one day later, for a total of 216 determinations.[9] Practice E 180 was used in developing these precision estimates.

34.2 *Bias*—The bias of this test method has not been determined because of the lack of acceptable reference material.

IRON

35. Scope

35.1 This test method is a colorimetric estimation of iron in hydrochloric acid. The lower limit of determination of iron is 0.0001 %.

36. Summary of Test Method

36.1 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 is measured in a photometer calibrated against standard iron solutions.

37. Interferences

37.1 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 or chromate ion to have a masking effect. Copper, antimony, cobalt, mercury (I), and tin (II, IV) interfere in concentrations of 10 to 50 ppm. Cadmium, mercury (II), zinc, and nickel complexes may interfere, but can be overcome by the use of excess of the 1,10-phenanthroline reagent.

TABLE 2 Sulfated Ash Precision Values

Level,%	Repeatability			Laboratory Precision			Reproducibility		
	Standard Deviation	Degrees of Freedom	95 % Limit	Standard Deviation	Degrees of Freedom	95 % Limit	Standard Deviation	Degrees of Freedom	95 % Limit
0.005	0.0007	24	0.0020	0.0008	12	0.0022	0.0011	11	0.0031
0.015	0.0009	38	0.0024	0.0011	19	0.0032	0.0011	6	0.0032
0.050	0.0028	42	0.0080	0.0028	21	0.0078	0.0028	8	0.0078

38. Apparatus

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

38.2 *Absorption Cells*, 2-cm light path.

NOTE 8—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.

39. Reagents

39.1 *Ammonium Acetate—Acetic Acid Solution*—Dissolve 100 g ammonium acetate (CH_3COONH_4) in about 600 mL of water, filter, add 200 mL of glacial acetic acid to the filtrate, and dilute to 1 L.[8]

39.2 *Ammonium Hydroxide Solution* (1 + 1)—Dilute 500 mL of ammonium hydroxide (NH_4OH) with 500 mL of water, and mix.[8]

39.3 *Congo Red Paper*.

39.4 *Hydroxylamine Hydrochloride Solution* (100 g/L)—Dissolve 100 g of hydroxylamine hydrochloride ($NH_2OH·HCl$) in about 600 mL of water, filter, and dilute to 1 L.[8]

39.5 *Iron, Standard Solution* (1 mL = 0.01 mg Fe)—Dissolve 0.1000 g of iron in 10 mL of hydrochloric acid (HCl, 1 + 1) and 1 mL of bromine water. Boil until the excess bromine is removed. Add 200 mL of HCl, cool, and dilute to 1 L in a volumetric flask. Dilute 10 mL of this solution to 1 L.[8,11]

39.6 *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.[8]

39.7 *Sulfuric Acid* (1 + 1)—Add slowly with stirring one volume of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) with one volume of water. (**Warning**—Use goggles when preparing this solution.)

40. Calibration

40.1 To a series of 100-mL volumetric flasks, pipet 0, 2, 4, 8, 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_4OH (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.

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

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

41. Procedure

41.1 Mix the sample by inverting the sample bottle.

41.2 Pipet 25 mL of the sample into a 150-mL beaker, add 1 mL of H_2SO_4 (1 + 1), and evaporate to almost dryness on the steam bath in a hood. Cool, add about 25 mL of water, and transfer to a 100-mL volumetric flask.

41.3 Add to the flask the following reagents in order, mixing after addition of each: 1 mL of hydroxylamine hydrochloride solution, 5 mL of 1,10-phenanthroline solution, and NH_4OH (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.

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

41.5 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 (Note 9).

NOTE 9—If the color obtained is too intense to fall within the range of the calibration curve, repeat with a smaller volume of sample and make appropriate calculations based on this smaller volume.

42. Calculation

42.1 Calculate the percentage of iron as follows (Note 10):

$$\text{Iron, \%} = \left[\frac{M}{25 \times \text{sp gr} \times 1000}\right] \times 100 \qquad (7)$$

where:

M = iron found from calibration curve, mg.

NOTE 10—When this value is less than 0.0001 %, report as less than 0.0001 %.

43. Report

43.1 Report the percentage of iron to the nearest 0.0001 %.

44. Precision and Bias

44.1 The following criteria should be used for judging the acceptibility of results (see Note 11):

44.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be 0.000115 % absolute at 56 df. The 95 % limit for the difference between two such runs is 0.0003 % absolute.

44.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability), Formerly Called Repeatability*—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.000178 % absolute at 28 df. The 95 % limit for the difference between two such averages is 0.0005 % absolute.

44.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.000590 % absolute at 6 df. The 95 % limit for the difference between two such averages is 0.0016 % absolute.

NOTE 11—These precision estimates cover only the range from 0.001 to 0.007 % iron and are based on an interlaboratory study of analyses performed in 1963–1964 on three samples containing approximately 0.002, 0.004, and 0.006 % iron. One analyst in each of seven to eleven laboratories performed duplicate determinations and repeated one day

[11] This reagent is used for calibrating purposes only.

later, for a total of 112 determinations.[9] Practice E 180 was used in developing these precision estimates.

One sample, containing approximately 0.0002 % iron and analyzed by one analyst in each of nine laboratories for a total of 36 determinations, gave the following precision data:

Repeatability (Single Analyst)—The standard deviation for a single determination has been estimated to be 0.0000088 % absolute at 18 df. The 95 % limit for the difference between two such runs is 0.00002 % absolute.

Laboratory Precision (Within-Laboratory, Between-Days Variability), Formerly Called Repeatability—The standard deviation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 0.000015 % absolute at 9 df. The 95 % limit for the difference between two such averages is 0.00004 % absolute.

Reproducibility (Multilaboratory)—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.000015 % absolute at 8 df. The 95 % limit for the difference between two such averages is 0.00004 % absolute.

44.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

COLOR

45. Scope

45.1 This test method covers the determination of the color of hydrochloric acid. The lower limit of determination of equivalent color is 0.05 mg of ferric iron per 100 mL.

46. Summary of Test Method

46.1 An arbitrary color scale is used that is based on the color produced by adding known amounts of ferric iron to hydrochloric acid.

47. Apparatus

47.1 *Photometer*—Any photoelectric spectrophotometer or filter photometer that will measure the absorbance of the solutions in the range from 400 to 450 nm.

47.2 *Absorption Cells*, 2-cm light path (Note 8).

48. Reagents

48.1 *Ferric Iron, Standard Solution* (1 mL = 0.050 mg Fe)—Dissolve 0.5 g of pure iron wire (99 % Fe min) in 10 mL of H_2SO_4 and 3 mL of HNO_3. Dilute to 1 L with water in a volumetric flask. Pipet 10 mL of this solution into a 100-mL volumetric flask and dilute with HCl to the mark.[8]

48.2 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

48.3 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO_3).

48.4 *Sulfuric Acid* (1 + 9)—Add slowly with stirring 1 volume of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) to 9 volumes of water. (**Warning**—Use goggles when preparing this solution.)

49. Calibration

49.1 To a series of 100-mL volumetric flasks pipet 0, 2, 4, 8, and 10 mL of standard ferric iron solution. Dilute to volume with HCl. Mix well.

49.2 Measure the absorbances of the solutions using a photometer with a wavelength setting of 425 nm or a filter photometer equipped with a filter in the range from 400 to 450 µm, adjusting the photometer to read zero absorbance for the blank.

49.3 Plot on coordinate paper the absorbances of the calibration solution against milligrams of ferric iron per 100 mL of solution.

50. Procedure

50.1 Transfer the sample to an absorption cell and measure the absorbance at the same wavelength used for the calibration curve, blanking the instrument at zero absorbance with HCl from the same lot used for the calibration curve.

50.2 Read from the calibration curve the milligrams of ferric iron that correspond to the observed absorbance.

NOTE 12—If the color is too intense to fall within the range of the calibration curve, dilute the sample with HCl from the same lot used for the calibration curve and make the appropriate calculation based on the dilution factor.

51. Report

51.1 Report the color, to the nearest 0.1 mg, as the number of milligrams of ferric iron per 100 mL equivalent to the color of the sample (see Note 13 and Note 14).

NOTE 13—The platinum-cobalt color scale (Test Method D 1209)[9] has wide-spread use to determine color in HCl. By the use of the ferric iron scale a more exact color match can be made. An accurate correlation of the two scales cannot be made because of the difference in color between the two scales. A fairly accurate correlation based on visual observation is as follows:

Milligrams of Ferric Iron per 100 mL	Platinum-Cobalt Color
0.05	5
0.10	20
0.20	35
0.30	60
0.40	75
0.50	110

NOTE 14—If the color is less than that of 0.05 mg of ferric iron per 100 mL, report as less than 0.05.

52. Precision and Bias

52.1 The following criteria should be used for judging the acceptability of results (see Note 15):

52.1.1 *Repeatability (Single Analyst)*—The coefficient of variation for a single determination has been estimated to be 1.75 % relative at 70 df. The 95 % limit for the difference between two such runs is 4.9 % relative.

52.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability), Formerly Called Repeatability*—The coefficient of variation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 3.09 % relative at 35 df. The 95 % limit for the difference between two such averages is 8.6 % relative.

52.1.3 *Reproducibility (Multilaboratory)*—The coefficient of variation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 12.81 % relative at 10 df. The 95 % limit for the difference between two such averages is 35.9 % relative.

NOTE 15—These precision estimates cover only the range from 2 to 10 mg and are based on an interlaboratory study of analyses performed in 1963–1964 on three samples containing approximately 3, 5, 7, and 10 mg of ferric iron per 100 mL. One analyst in each of five to twelve laboratories performed duplicate determinations and repeated one day later, for a total of 136 determinations.[9] Practice E 180 was used in developing these precision estimates.

One sample, containing color equivalent to approximately 0.3 mg of ferric iron per 100 mL, and analyzed by one analyst in each of twelve laboratories for a total of 48 determinations, gave the following precision data:

Repeatability (Single Analyst)—The coefficient of variation for a single determination has been estimated to be 3.84 % relative at 24 df. The 95 % limit for the difference between two such runs is 10.7 % relative.

Laboratory Precision (Within-Laboratory, Between-Days Variability), Formerly Called Repeatability—The coefficient of variation of results (each the average of duplicates), obtained by the same analyst on different days, has been estimated to be 8.50 % relative at 12 df. The 95 % limit for the difference between two such averages is 23.8 % relative.

Reproducibility (Multilaboratory)—The coefficient of variation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 19.5 % relative at 11 df. The 95 % limit for the difference between two such averages is 54.7 % relative.

52.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

TOTAL SULFUR

53. Scope

53.1 This test method covers the determination of total sulfur, exclusive of certain organo sulfur compounds, in hydrochloric acid. The lower limit of determination of total sulfur as sulfuric acid is 0.0002 %.

54. Summary of Test Method

54.1 A sample of acid is treated with bromine to oxidize any oxidizable sulfur compounds to sulfate. The sulfate is precipitated and weighed as barium sulfate.

55. Reagents

55.1 *Barium Chloride Solution* (120 g/L)—Dissolve 120 g of barium chloride ($BaCl_2 \cdot 2H_2O$) in about 750 mL of water, filter, and dilute to 1 L.[8]

55.2 *Bromine Water (Saturated)*—To 1 L of water in a glass-stoppered bottle add bromine and shake until no more bromine is dissolved by the solution. Keep a few drops of bromine on the bottom of the bottle, and use only the clear water solution.[8]

55.3 *Silver Nitrate Solution* (17 g/L)—Dissolve 17 g of silver nitrate ($AgNO_3$) in water, mix, dilute to 1 L, and store in a light-resistant glass container.[8]

56. Procedure

56.1 Weigh to the nearest 0.1 g approximately 50 g of sample and transfer to a 400-mL beaker. Add sufficient bromine water to the sample to yield a definite yellow-red color. Evaporate the sample to a volume of approximately 3 mL on the steam bath in a hood.

56.2 Dilute the solution to 300 mL with water and inspect the solution for any turbidity or insoluble matter. If such is present, filter the solution through a fine filter paper and collect the filtrate in a 400-mL beaker. Wash the filter paper and any insoluble material twice with small portions of hot water.

56.3 Heat the solution to boiling and add 10 mL of $BaCl_2$ solution dropwise to the boiling solution. Continue gentle boiling for 5 min. Cover the beaker and digest on the steam bath at least 3 h. Overnight digestion is preferable, especially in cases of low sulfur concentration.

56.4 Filter the solution through a low-ash, fine filter or a tared, medium-porosity filtering crucible, and transfer the precipitate quantitatively to the paper or crucible. Wash with hot water until free of chloride as determined by testing a portion of the washings with a few drops of $AgNO_3$ solution. If filter paper is used, transfer the filter paper containing the precipitate to a tared platinum or porcelain crucible, heat and char without inflaming, and ignite to constant weight at 800°C (1472°F) in a muffle furnace. If a filtering crucible is used, heat and ignite to constant weight at 800°C in a muffle furnace. Determine the weight of the barium sulfate residue to the nearest 0.1 mg.

57. Calculation

57.1 Calculate the total sulfur expressed as percentage of H_2SO_4 as follows (Note 16):

$$\text{Total S as } H_2SO_4, \% = \left[\frac{A \times 0.4202}{W}\right] \times 100 \quad (8)$$

where:
A = $BaSO_4$ precipitate, g, and
W = sample used, g.

NOTE 16—When this value is less than 0.0002 %, report as less than 0.0002 %.

58. Report

58.1 Report the total sulfur expressed as percentage of sulfuric acid to the nearest 0.0001 %.

59. Precision and Bias

59.1 The following criteria should be used for judging the acceptibility of results (see Note 17):

59.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be the value given in Table 3 at the indicated degrees of freedom. The 95 % limit for the difference between two such runs is given in Table 3.

59.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability), Formerly Called Repeatability*—The standard deviation of results (each the average of duplicates),

TABLE 3 Total Sulfur Precision Values

% H_2SO_4	Between Runs			Between Days			Between Laboratories		
	Standard Deviation	Degrees of Freedom	95 % Limit	Standard Deviation	Degrees of Freedom	95 % Limit	Standard Deviation	Degrees of Freedom	95 % Limit
0.002 to 0.009	0.00033	40	0.0009	0.00039	20	0.0011	0.0012	8	0.0033
0.038	0.00111	20	0.0031	0.000997	10	0.0028	0.00173	9	0.0048

obtained by the same analyst on different days, has been estimated to be the value given in Table 3 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is given in Table 3.

59.1.3 *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 3 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is given in Table 3.

NOTE 17—These precision estimates are based on an interlaboratory study of analyses performed in 1964 on three samples containing approximately 0.002, 0.009, and 0.038 % total sulfur expressed as sulfuric acid. One analyst in each of nine to eleven laboratories performed duplicate determinations and repeated one day later, for a total of 120 determinations.[9] Practice E 180 was used in developing these precision estimates.

59.2 *Bias*—The bias of this test method has not been determined due to the unavailability of suitable reference materials.

60. Keywords

60.1 analysis; Baumé gravity; color; hydrochloric acid; iron; sulfated ash; sulfur; total acidity