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100 Barr Harbor Dr., West Conshohocken, PA 19428
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Standard Test Methods for Analysis of Aqueous Hydrofluoric Acid[1]

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1. Scope

1.1 These test methods cover the analysis of aqueous hydrofluoric acid.

1.2 The analytical procedures appear in the following order:

	Range, %	Sections
Sulfur dioxide	0.001 to 0.2	9-16
Total acidity	to 70	17-25
Iron	0.0001 to 0.5	26-35
Sulfuric acid	0.001 to 1.0	36-44
Nonvolatile acidity	0.01 to 2	45-53
Fluosilicic acid	0.0005 to 0.2	54-63
Arsenic	0.0001 to 0.1	64-66

1.3 The values stated in SI units are to be regarded as the standard.

1.4 *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 7.

1.5 Review the current material safety data sheet (MSDS) for detailed information concerning toxicity, first-aid procedures, handling, and safety precautions.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals[3]

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals[4]

E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis[4]

E 223 Test Methods for Analysis of Sulfuric Acid[4]

E 1615 Test Method for Iron in Trace Quantities Using the "Ferrozine" Method[4]

3. Significance and Use

3.1 These measurements provide for the determination of acid strength and for the determination of various impurities in aqueous hydrofluoric acid. Acid strength and impurity levels are important factors in many uses of hydrofluoric acid.

4. Apparatus

4.1 All apparatus or equipment used in direct contact with hydrofluoric acid must be hydrofluoric-acid resistant. In cases where the hydrofluoric acid must be heated, the apparatus must be both hydrofluoric acid and heat-resistant.

5. Reagents

5.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[5] 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.

5.2 *Purity of Water*— Unless otherwise indicated, references to water shall be understood to mean Type II or Type III water conforming to Specification D 1193.

6. Photometers and Photometric Practice

6.1 Photometers and photometric practices used in these test methods shall conform to Practice E 60.

7. Hazards

7.1 Hydrofluoric acid is an extremely hazardous chemical capable of inflicting serious and painful burns. Anyone working with hydrofluoric acid should be thoroughly familiar with the associated hazards and appropriate first-aid procedures.[6]

7.2 Every precaution should be taken in the handling of hydrofluoric acid to avoid contact with any part of the body.

7.3 Inhalation of acid fumes should be avoided, as they are extremely irritating to all parts of the respiratory system.

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[1] These test methods are under the jurisdiction of ASTM Committee E-15 on Industrial Chemicals and are the direct responsibility of Subcommittee E15.51 on Acids.

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

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

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

[5] *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.

[6] Producers and distributors of hydrofluoric acid can provide product data sheets recommending appropriate safety procedures. See 1.5.

Exposure cases should receive prompt medical care.

7.4 Clean up all spills immediately by washing the spill area with water followed by sodium carbonate solution or lime slurry to neutralize the acid.

7.5 It is imperative in the following analytical procedures that all weighings and evaporations of the concentrated acid in open vessels are performed in a well ventilated hood.

7.6 In all operations where transfers of acid by pipet are required, a rubber bulb, preferably one equipped with check valves, should be used.

8. Sampling

8.1 Sampling of hydrofluoric acid is not within the scope of this test method.

8.2 The sample to be analyzed shall be considered to be the sample in a single container submitted to the analytical laboratory.

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

NOTE 1—**Caution:** To prevent loss of volatile components, samples should be chilled to about 10°C before opening. Sulfur dioxide should be determined first, followed by total acidity.

SULFUR DIOXIDE

9. Scope

NOTE 2—This constituent should be determined first, since during the opening and closing of the sample bottle a loss of sulfur dioxide may result.

9.1 This test method is applicable to the determination of sulfur dioxide in hydrofluoric acid in the range from 0.001 to 0.2 %.

10. Summary of Test Method

10.1 A weighed sample of acid is diluted with water and titrated with standardized iodine solution to the starch end point.

11. Interferences

11.1 Substances capable of being oxidized by iodine will cause interference.

12. Reagents

12.1 *Iodine, Standard Solution* (0.1 *N*) (for acids with SO_2 values greater than 0.02 %)—Prepare and standardize in accordance with Practice E 200.

12.2 *Iodine, Standard Solution* (0.01 *N*) (for acids with SO_2 values less than 0.02 %)—Pipet 100 mL of 0.1 *N* standard iodine solution into a 1 L volumetric flask and dilute to volume with water. Determine the normality of the prepared solution by dividing the normality of the 0.1 *N* iodine by 10.

12.3 *Starch Indicator* (10 g/L)—See Practice E 200.

13. Procedure

13.1 Half fill a 250-mL dish with crushed distilled water ice cubes and weigh to the nearest 0.1 g.

13.2 Carefully add about 50 g of the chilled sample and reweigh to obtain the exact sample weight.

13.3 Add 50 mL of water, 5 mL of starch indicator, and titrate with the appropriate standard iodine solution to the first permanent blue color of the indicator.

13.4 Prepare a blank consisting of the same quantities of ice and reagents, acidify with five to ten drops of reagent grade hydrofluoric acid and titrate to the same end point as for the sample.

14. Calculation

14.1 Calculate the percentage of reducing substances expressed as sulfur dioxide, as follows:

$$\text{Reducing substances as } SO_2, \% = \frac{(A - B) \times N \times 0.032}{W} \times 100 \quad (1)$$

where:

A = iodine solution required for titration of the sample, mL,
B = iodine solution required for titration of the blank, mL,
N = normality of the iodine solution, and
W = sample used, g.

15. Report

15.1 Report the percentage of sulfur dioxide to two significant figures.

16. Precision and Bias

16.1 The following criteria should be used in judging the acceptability of results (Note 3).

16.1.1 *Repeatability (Single Analyst)*—The coefficient of variation for a single determination has been estimated to be 1.77 % relative at 54 df. The 95 % limit for the difference between two such runs is 5 % 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 5.05 % relative at 28 df. The 95 % limit for the difference between two such averages is 14 % 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 8.13 % relative at 8 df. The 95 % limit for the difference between two such averages is 23 % relative.

NOTE 3—The preceding precision statements are based on an interlaboratory study performed around 1965 on three samples containing less than 0.2 % sulfur dioxide. Two analysts in each of six laboratories performed duplicate determinations and repeated them on a second day, for a total of 144 determinations.[7] 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.

TOTAL ACIDITY

17. Scope

17.1 This test method covers the determination of the

[7] Details of the interlaboratory study are available as Research Report E15-1008 from ASTM Headquarters.

acidity of up to 70 % hydrofluoric acid.

18. Summary of Test Method

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

19. Interferences

19.1 The presence of acids, other than hydrofluoric acid will affect the accuracy of this test method.

20. Apparatus

20.1 *Pipet*, HF-resistant, 1-mL serological, graduated in 0.1 mL.

21. Reagents

21.1 *Phenolphthalein Indicator, Alcoholic Solution* (10 g/L)—See Practice E 200.

21.2 *Sodium Hydroxide, Standard Solution* (0.5 *N*)—Prepare and standardize a 0.5 *N* solution of sodium hydroxide (NaOH) in accordance with Practice E 200. For calculation of total acidity, the normality shall be corrected to the temperature at which the determination is performed by the following equation:

$$N_{t2} = N_{t1} + (t_1 - t_2) \times F \quad (2)$$

where:

N_{t1} = normality when standardized,
N_{t2} = normality during analysis of samples,
t_1 = temperature of solution (Celsius) during standardization,
t_2 = temperature of solution (Celsius) during analysis of samples, and
F = 0.00014, the factor to correct for thermal expansion of the solution.

22. Procedure (See Note 4)

22.1 From a zeroed buret, transfer about 40 mL of 0.5 *N* sodium hydroxide solution into an HF-resistant vessel and add 50 mL of water.

22.2 Pipet a portion of the chilled sample containing 0.4 to 0.5 g of HF into a tared HF-resistant weighing bottle containing 10 mL of water (see Note 5). Cover and reweigh to the nearest 0.1 mg.

22.3 Invert the weighing bottle and immerse the top in the diluted NaOH solution. By means of a stirring rod, remove the weighing bottle lid, keeping the mouth of the bottle under the solution. Leave the bottle and lid in the solution (see Note 6).

22.4 Add 1 mL of phenolphthalein indicator solution and titrate to the pink end point (see Note 7). Heat the solution to boiling and, if the color fades, titrate again to a pink end point permanent in the hot solution. Record the titration and the temperature of the titrant (see Note 8).

NOTE 4—The following alternative sample dispensing technique may be used in place of 22.2 and 22.3. The precision and bias data given in Section 25, however, are based on the sample dispensing technique described in 22.2 and 22.3.

Weigh a 2-mL disposable plastic syringe equipped with a 1.5-in., 18-gage stainless steel needle to the nearest 0.0001 g. Draw 0.4 to 0.5 g of sample into the syringe and again weigh to the nearest 0.0001 to determine the exact sample weight. Dispense the sample below the surface of the dilute NaOH solution. Rinse the syringe three times by removing the plunger, filling the chamber with water, replacing the plunger, and injecting the rinsings into the NaOH solution.

NOTE 5—In using a pipet for this purpose a rubber bulb equipped with check valves, and *not* the analyst's finger, should be used to control the flow.

NOTE 6—If significant amounts of iron and heavy metals are present, their interference in this test can be eliminated by appropriate additions of neutralized potassium fluoride and sodium potassium tartrate solutions.

NOTE 7—The solution may be transferred to a glass beaker at this point.

NOTE 8—The titration should be concluded in hot solution even if the sample does not contain significant quantities of fluosilicic acid because the NaOH solution may contain sufficient silica to cause erroneous results in the cold solution.

23. Calculation

23.1 Correct the normality for temperature and calibration errors and record the corrected delivered volume at the existing temperature as *V*.

23.2 Calculate the total acidity as the percentage of hydrofluoric acid as follows:

$$\text{total acidity as hydrofluoric acid, \%} = \frac{V \times N \times 0.02001}{W} \times 100 \quad (3)$$

where:

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

24. Report

24.1 Report the percentage of hydrofluoric acid to the nearest 0.01 %.

25. Precision and Bias

25.1 The following criteria should be used in judging the acceptability of results (see Note 9):

25.1.1 *Repeatability (Single Analyst)*—The coefficient of variation for a single determination has been estimated to be 0.14 % relative at 60 df. The 95 % limit for the difference between two such runs is 0.4 % relative.

25.1.2 *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 0.27 % relative at 30 df. The 95 % limit for the difference between two such averages is 0.8 % relative.

25.1.3 *Reproducibility (Multilaboratory)*—The coefficient of variation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.52 % relative at 9 df. The 95 % limit for the difference between two such averages is 1.5 % relative.

NOTE 9—The preceding precision statements are based on an interlaboratory study performed around 1965 on three samples containing approximately 50, 60, and 70 % HF. Two analysts in each of six laboratories performed duplicate determinations and repeated them on a second day, for a total of 144 determinations.[7] Practice E 180 was used in developing these precision estimates.

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

IRON

26. Scope

26.1 This test method covers the determination of iron in hydrofluoric acid in the range from 0.0001 to 0.5 %.

27. Summary of Test Method

27.1 The hydrofluoric acid in the sample is removed by evaporation, and the iron is reduced and reacted with 1,10-phenanthroline that forms an orange-red complex. The intensity of the color produced is measured in a photometer which has been calibrated using standard iron solutions.

27.2 An alternative procedure for this determination is described in Test Method E 1615. After the hydrofluoric acid in the sample is removed by evaporation, the sample residue is dissolved in a suitable solvent and is reacted with ferrozine reagent solution which will convert the dissolved iron compounds to form a magenta color iron (II) complex. The iron content of the sample solution is determined by measurement of the magenta color at 560 nm using a suitable photometer.

28. Interferences

28.1 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 ions to have an 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 1,10-phenanthroline reagent. Metals capable of complexing iron in the presence of fluoride, for example, potassium, aluminum, beryllium, zinc, etc., can cause significant errors on the low side.

29. Apparatus

29.1 *Photometer*—Any photoelectric spectrophotometer or filter photometer capable of measuring the absorbance of the solutions in the range from 500 to 525 nm.

29.2 *Absorption Cells*, having a 2-cm light path. Cells with other dimensions may be used provided suitable adjustments can be made in the quantities of sample and reagents used.

30. Reagents

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

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

30.3 *Congo Red Paper*.

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

30.5 *Iron Standard Solution* (1 mL = 0.010 mg Fe)[9]—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 100 mL of this solution to 1 L.

30.6 *1,10-Phenanthroline Solution* (3 g/L)[9]—Dissolve 3 g of 1,10-phenanthroline in 500 mL of water, add 1 mL of hydrochloric acid (HCl), mix, filter, and dilute to 1 L. Prepare a fresh solution every two weeks.

30.7 *Sulfuric Acid* (H_2SO_4).

31. Calibration

31.1 To a series of 100-mL volumetric flasks, or glass-stoppered graduated cylinders, add 0, 2, 4, 6, 8, 10, and 15 mL of standard iron solution using a 25-mL buret.

31.2 Dilute the contents of each flask to 50 mL with water and add the following reagents in the order indicated, mixing after each addition: 1 mL of H_2SO_4, 1 mL of $NH_2OH·HCl$ solution, and 5 mL of 1,10-phenanthroline solution.

31.3 Adjust the pH of the solution to 3.5 to 4.0 by adding NH_4OH solution (1 + 1) dropwise until an alkaline condition is just indicated when a drop is tested with congo red paper (a color change from blue to red).

31.4 Add 5 mL of ammonium acetate-acetic acid solution, mix, and dilute to 100 mL with water. Mix thoroughly and allow to stand for 15 min.

31.5 Determine the absorbance of the solution using a photometer with a wavelength setting of 510 nm or a filter photometer equipped with a filter in the range from 500 to 525 nm, adjusting the photometer to read zero absorbance with the reagent blank.

31.6 Plot absorbance values against milligrams of iron present per 100 mL of solution using square coordinate paper.

32. Procedure

32.1 Transfer approximately 25 g of sample to a clean, tared platinum dish and reweigh to the nearest 0.1 g to obtain the exact sample weight. Let the dish stand at room temperature under a hood until any white fumes are not longer observed. Evaporate to apparent dryness on a steam bath.

32.2 Add 1.0 mL of H_2SO_4, transfer the dish to a hot plate, and heat to fumes of H_2SO_4. Cool and wash down the sides of the dish with 10 mL of water and re-evaporate to fumes of H_2SO_4. Do not evaporate to dryness.

32.3 Cool and transfer quantitatively to a 100-mL volumetric flask, or 100-mL graduated cylinder, and dilute to volume. Aliquots of this dilution are to be used if the iron content of the acid being tested is less than 0.003 %. If the iron value is greater than 0.003 % use aliquots from a solution prepared by pipetting an appropriate volume of the first dilution to a second volumetric flask and diluting to volume.

32.4 Transfer an aliquot which will give a final absorbance of 0.10 to 0.4 to 100-mL volumetric flask or graduated cylinder.

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

[9] This reagent is used for calibration purposes only.

32.5 Dilute the contents of the flask, or graduate, to 50 mL with water and add the following reagents in the order indicated, mixing after each addition: 1 mL of $NH_2OH·HCl$ solution and 5 mL of 1,10-phenanthroline solution.

32.6 Adjust the pH of the solution to 3.5 to 4.0 by adding NH_4OH solution (1 + 1) dropwise until an alkaline condition is just produced when a drop is tested with congo red paper.

32.7 Add 5 mL of ammonium acetate-acetic acid solution, mix, and dilute to 100 mL with water. Mix thoroughly and allow to stand for 15 min.

32.8 Prepare a blank using all reagents but omitting the sample and allow to stand for 15 min.

32.9 Determine the absorbance of the sample at the same wavelength used for the calibration curve, adjusting the instrument to read zero absorbance with the reagent blank.

32.10 Determine from the calibration curve the milligrams of iron corresponding to the absorbance measured. If the absorbance obtained is out of the range of the calibration curve, repeat the test using an appropriate sample size.

33. Calculation

33.1 Calculate the percentage of iron, expressed as Fe, as follows:

$$\text{Iron as Fe, \%} = \frac{M}{W \times 1000} \times 100 \quad (4)$$

where:
M = iron found from calibration curve, mg, and
W = sample in aliquot, g.

34. Report

34.1 Report the percentage of iron to the number of digits indicated in the following table:

Level, %	Report to, %
<0.01	0.0001
0.010 to 0.10	0.001
0.10 to 0.50	0.01

35. Precision and Bias

35.1 The following criteria should be used in judging the acceptability of results (see Note 10).

35.1.1 *Repeatability (Single Analyst)*—The coefficient of variation for a single determination has been estimated to be 2.1 % relative at 54 df. The 95 % limit for the difference between two such runs is 6 % relative.

35.1.2 *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 values given in Table 1 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is also given in Table 1.

35.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be the values given in Table 1 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is also given in Table 1.

NOTE 10—The preceding precision statements are based on an interlaboratory study performed around 1965 on three samples containing approximately 0.0015, 0.06, and 0.5 % iron. Two analysts in each of six laboratories performed duplicate determinations and repeated them on a second day, for a total of 144 determinations.[7] Practice E 180 was used in developing these precision estimates.

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

SULFURIC ACID GRAVIMETRIC METHOD

36. Scope

36.1 This test method covers the determination of sulfuric acid (H_2SO_4) in hydrofluoric acid (HF) in the range from 0.001 to 1.0 %.

37. Summary of Test Method

37.1 HF is evaporated to leave nonvolatile material. Sulfate is precipitated and weighed as barium sulfate.

38. Interferences

38.1 Normal amounts of impurities present in commercial, aqueous HF do not interfere with the gravimetic determination of H_2SO_4. Tests in a single laboratory show results to be within the precision statements for samples containing 0.1 % Fe. Results for samples containing 0.5 % Fe are both high and erratic.

39. Apparatus

39.1 *Dish*, platinum or polytetrafluoroethylene, 100-mL capacity.

39.2 *Filtering Crucible*, porcelain, fine porosity.

40. Reagents

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

40.2 *Silver Nitrate Solution* (17 g/L, approximately 0.1 *N*)[8]—Dissolve 17 g of silver nitrate ($AgNO_3$) in water, mix, dilute to 1 L, and store in a light-resistant glass container.

41. Procedure

41.1 Transfer approximately 50 g of the sample, chilled to about 10°C to the tared dish and weigh to the nearest 0.1 g.

TABLE 1 Precision for Iron Method

	Laboratory Precision			Reproducibility		
Level, % Iron	Standard Deviation, % absolute	Degrees of Freedom	95 % Limit, % absolute	Standard Deviation, % absolute	Degrees of Freedom	95 % Limit, % absolute
0.0015	0.00005	9	0.0001	0.00008	8	0.0002
0.06	0.0024	10	0.007	0.0125	9	0.035
0.47	0.0035	8	0.01	0.0522	7	0.15

Evaporate to dryness or to residual H_2SO_4 on a steam bath. Weighing and evaporation should be carried out under a fume hood. Add 5 mL of water and again evaporate. If acid is detected in the vapor by moist litmus or other test paper as dryness is approached in the second evaporation, add an additional 5 mL of water and again evaporate. Repeat until no acid is detected in the vapor.

41.2 Add 3 mL of 1 + 1 HCl and swirl to wet the entire bottom of the container. Add 50 mL of water and transfer to a 400-mL beaker, washing the evaporating dish with additional water. Heat to near boiling and inspect the solution for any insoluble matter. If any is present, filter the solution through fine filter paper into another 400-mL beaker and wash with two portions of hot water.

41.3 Dilute to about 300 mL and heat to boiling. Add 10 mL of $BaCl_2$ solution dropwise while stirring. Continue boiling for 5 min. Remove from the hot plate and permit the precipitate to settle. Add 1 mL of $BaCl_2$ solution to test for complete precipitation. Continue the addition of $BaCl_2$ until an excess of 1 mL is added. If additional $BaCl_2$ is required, heat to boiling and continue boiling for 5 min. Cover the beaker and digest on the steam bath for at least 3 h.

41.4 Filter the solution through a low-ash, fine filter paper or a tared, fine-porosity porcelain filtering crucible and transfer the precipitate quantitatively to the filter. 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. Dry the paper, then char without inflaming and ignite to constant weight at 800°C 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 to the nearest 0.1 mg.

42. Calculation

42.1 Calculate the sulfate as percent H_2SO_4 as follows:

$$H_2SO_4, \% = \frac{A \times 0.4202}{W} \times 100 \quad (5)$$

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

43. Report

43.1 Report the percentage of sulfuric acid to the percent given as follows:

Level, %	Report to, %
<0.01	0.0001
0.01 to 0.50	0.001
>0.50	0.01

44. Precision and Bias

44.1 The following criteria should be used in judging the acceptability of results (see Note 11).

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

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 the absolute value given in Table 2 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the absolute value given in Table 2.

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 the absolute value given in Table 2 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the absolute value given in Table 2.

NOTE 11—The preceding precision statements are based on an interlaboratory study performed around 1964 on three samples containing the indicated levels of sulfuric acid. Two analysts in each of five laboratories performed duplicate determinations and repeated them on a second day.[7] Practice E 180 was used in developing these precision estimates.

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

NONVOLATILE ACIDITY

45. Scope

45.1 This test method covers the determination of nonvolatile acidity in hydrofluoric acid in the range from 0.01 to 2 %, calculated as H_2SO_4.

46. Summary of Test Method

46.1 A weighed sample of the acid is evaporated at steam-bath temperature, water is added to hydrolyze complex fluorides, and the residue titrated with standard sodium hydroxide solution after adding neutral potassium fluoride to prevent hydrolysis of metallic salts.

47. Significance and Use

47.1 Nonvolatile acidity is the amount of nonvolatile acid calculated as H_2SO_4 minus H_2SO_4 equivalent to metallic salts present in the sample. When metallic impurities are absent, the titration is a measure of nonvolatile acids calculated as H_2SO_4.

48. Apparatus

48.1 *Dish*, platinum or polytetrafluoroethylene, 250-mL capacity.

TABLE 2 Precision for Sulfuric Acid Method

	Repeatability			Laboratory Precision			Reproducibility		
H_2SO_4 Level, %	Standard Deviation, %	Degrees of Freedom	95 % Limit, %	Standard Deviation, %	Degrees of Freedom	95 % Limit, %	Standard Deviation, %	Degrees of Freedom	95 % Limit, %
0.001	0.00034	20	0.0010	0.000437	10	0.0012	0.000472	9	0.0013
0.06	0.0017	20	0.005	0.00174	10	0.005	0.00230	9	0.006
1.0	0.020	20	0.06	0.0313	10	0.09	0.0327	9	0.09

48.2 *Stirring Rod*, platinum or polytetrafluoroethylene.

48.3 *Steam Bath*, or hot plate capable of being controlled at 100 to 110°C.

48.4 *Balance*, torsion or platform, capable of weighing accurately to 0.1 g.

48.5 *Buret*, Class A, 50-mL capacity.

49. Reagents

49.1 *Phenolphthalein Indicator Solution* (10 g/L)[8]—Dissolve 1 g of phenolphthalein, in ethanol (95 %) or isopropanol and dilute to 100 mL with the alcohol. Neutralize to a faint pink color.

49.2 *Potassium Fluoride Solution* (300 g/L)—Dissolve 300 g of potassium fluoride ($KF \cdot 2H_2O$) in about 750 mL of water, add 1.0 mL of phenolphthalein indicator solution, and titrate to a faint pink with 0.1 *N* NaOH solution. Dilute to 1 L with water, and store in a polyolefin container.

49.3 *Sodium Hydroxide, Standard Solution* (0.1 *N*) (*for Concentrations 0.01 to 0.5 % Nonvolatile Acidity*)—Prepare and standardize in accordance with Practice E 200.

49.4 *Sodium Hydroxide, Standard Solution* (0.5 *N*) (*for Concentrations 0.5 to 2.0 % Nonvolatile Acidity*)—Prepare and standardize in accordance with Practice E 200.

50. Procedure

50.1 Transfer approximately 50 g of the sample chilled to about 10°C to the tared 250-mL dish and weigh to the nearest 0.1 g.

50.2 Allow the dish to stand at room temperature in the hood until any white fumes are no longer observed.

50.3 Place the dish on a hot plate or steam bath in a hood. Evaporate to apparent dryness or to a residue of nonvolatile material at steam-bath temperatures. Wash the sides of the dish with 5 to 10 mL of water and again evaporate.

50.4 Repeat the water addition and evaporation. On this evaporation, check vapor with moist blue litmus paper to determine if any acid fumes are present. If any acid fumes are present, repeat water addition until no acid vapor is detected during evaporation.

50.5 Add 25 mL of KF solution to the dish and titrate with the appropriate standard NaOH solution using phenolphthalein as the indicator.

51. Calculation

51.1 Calculate the percent nonvolatile acidity expressed as sulfuric acid as follows:

$$\text{nonvolatile acidity as } H_2SO_4, \% = \frac{A \times N \times 0.04904}{W} \times 100 \qquad (6)$$

where:

A = standard NaOH solution required, mL,

N = normality of standard sodium hydroxide solution, and

W = sample used, g.

52. Report

52.1 Report the percent nonvolatile acidity to the nearest percentage given as follows:

Level, %	Report to, %
1.6	0.01
0.3	0.001
0.02	0.001

53. Precision and Bias

53.1 The following criteria should be used for judging the acceptability of results (Note 12).

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

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

53.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be the percent absolute value given in Table 3 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the percent absolute value given in Table 3.

NOTE 12—The preceding precision statements are based on an interlaboratory study performed around 1965 on three samples containing the indicated levels of nonvolatile acidity. Independent analysts in each of six laboratories performed duplicate determinations and repeated them on another day.[10] Practice E 180 was used in developing these precision estimates.

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

FLUOSILICIC ACID

54. Scope

54.1 This test method covers the colorimetric determination of fluosilicic acid in hydrofluoric acid in the range from 0.0005 to 0.2 % H_2SiF_6.

[10] Details of the interlaboratory study are available as Research Report E15-1008 from ASTM Headquarters.

TABLE 3 Precision for Nonvolative Acidity Method

	Repeatability			Laboratory Precision			Reproducibility		
Level, %	Standard Deviation, %	Degrees of Freedom	95 % Limit, %	Standard Deviation, %	Degrees of Freedom	95 % Limit, %	Standard Deviation, %	Degrees of Freedom	95 % Limit, %
1.6	0.024	24	0.07	0.0159	12	0.04	0.0160	11	0.04
0.3	0.0024	24	0.007	0.00403	12	0.011	0.00552	11	0.015
0.02	0.0014	24	0.004	0.00156	12	0.004	0.00241	11	0.006

55. Summary of Test Method

55.1 Sodium chloride is added to the sample, and hydrofluoric acid is removed by low-temperature evaporation, leaving a residue containing sodium fluosilicate and sodium hydrogen fluoride. The fluoride is complexed by the addition of boric acid permitting liberated silicic acid to form silicomolybdic acid on the addition of ammonium molybdate. The silicomolybdic acid is reduced to heteropoly blue permitting photometric determination of the corresponding H_2SiF_6.

56. Interferences

56.1 The addition of tartaric acid before the development of the complex heteropoly blue eliminates the interferences from all elements normally present in hydrofluoric acid. Sulfuric acid consumes equivalent amounts of sodium chloride added to fix H_2SiF_6 as Na_2SiF_6.

57. Apparatus

57.1 *Dish*, platinum or polytetrafluoroethylene 100-mL capacity (see Note 13).

NOTE 13—A platinum dish is preferred for observation of undissolved Na_2SiF_6 in the boric acid solution.

57.2 *Stirring Rod*, platinum or polytetrafluoroethylene.

57.3 *Steam Bath*, or hot plate capable of being controlled at 100 to 110°C.

57.4 *Volumetric Flasks*, 100-mL capacity.

57.5 *Volumetric Flasks*, 50-mL capacity.

57.6 *Pipets*, transfer.

57.7 *Photometer*—Any spectrophotometer or filter photometer capable of measuring the absorbance of the solutions in the range from 625 to 675 nm.

57.8 *Absorption Cells*, 1.0 to 2.5-cm light path.

58. Reagents

58.1 *General*—All the reagents prepared as outlined in this section are to be stored in polyolefin bottles. The water used to prepare reagents should be equivalent to triple distilled water. Distilled water passed through a mixed bed ion exchange will give water satisfactory for use in this test.

58.2 *1-Amino-2-Naphthol-4-Sulfonic Acid Solution* (2.5 g/L)—Dissolve 30 g of sodium hydrogen sulfite in 100 mL of water. Dissolve 1 g of sodium sulfite in 25 mL of water and add 0.5 g of 1-amino-2-naphthol-4-sulfonic acid. Mix solutions and dilute to 200 mL. Filter before using. Prepare weekly.

58.3 *Ammonium Molybdate* (50 g/L)—Dissolve 25 g of ammonium molybdate $[(NH_4)_6MO_7O_{24}\cdot 4H_2O]$ in water and dilute to 500 mL. Prepare fresh daily.

58.4 *Boric Acid Solution (Saturated)*—Dissolve 70 g of boric acid (H_3BO_3) in 800 mL of hot water and dilute to 1 L.

58.5 *Sodium Chloride Solution* (10 g/L)—Dissolve 10 g of sodium chloride (NaCl) in water and dilute to 1 L.

58.6 *Sodium Fluosilicate, Standard Solution* (1 mL = 0.1 mg H_2SiF_6)—Dry sodium fluosilicate (Na_2SiF_6) for 1 h at 110°C. Weigh 0.1305 g into a 250-mL beaker and add 200 mL of hot water. Stir until dissolved. Cool to room temperature, transfer to a 1-L volumetric flask, and dilute to the mark. Transfer to a polyolefin container for storage.

58.7 *Sulfuric Acid* (5 *N*)—Carefully pour 35 mL of sulfuric acid (H_2SO_4) into about 150 mL of water. Cool and dilute to 250 mL.

58.8 *Tartaric Acid Solution* (500 g/L)—Dissolve 100 g of tartaric acid in 140 mL water and dilute to 200 mL. Prepare fresh weekly.

59. Calibration

59.1 To a series of 100-mL volumetric flasks, accurately measure 0, 1, 2, 3, 4, 6, 8, and 10 mL of standard sodium fluosilicate solution (1 mL = 0.1 mg H_2SiF_6).

59.2 Pipet 10 mL of NaCl solution and 20 mL of boric acid solution to each flask. Dilute to 60 mL and mix. Add 10 mL of ammonium molybdate solution and mix.

59.3 Add 3.0 mL of 5 *N* H_2SO_4, mix, and allow to stand for 10 min.

59.4 Add 10 mL of tartaric acid solution, mix, and add 1.0 mL of 1-amino-2-naphthol-4-sulfonic acid solution. Dilute to 100 mL, mix, and allow to stand for 30 min.

59.5 Determine the absorbance values of the solutions using a spectrophotometer at a wavelength setting of 650 nm or a filter photometer equipped with a filter in the range from 625 to 675 nm, adjusting the photometer to read zero absorbance with the reagent blank (0 mL of Na_2SiF_6 solution added).

59.6 Plot the absorbance values against milligrams of H_2SiF_6 present per 100 mL of solution using square coordinate paper.

60. Procedure

60.1 Transfer 10 mL of NaCl solution to an HF- and heat-resistant dish.

60.2 Weigh the dish and solution to the nearest 0.1 g and carefully add about 20 g (Note 14) of the sample. Reweigh to obtain the exact sample weight (see Note 14).

NOTE 14—Absorbance values may be lower than desired for amounts of H_2SiF_6 near the low range of the scope (0.0005 % H_2SiF_6) particularly if 1.0-cm optical cells are used. A larger sample may be taken if it is known that the total H_2SiF_6 does not exceed 0.04 g, an amount which can be held by 0.1 g NaCl during the evaporation.

60.3 Evaporate to dryness at steam bath temperature. Remove the dish from the steam bath and wash down the inside of the rim with about 10 mL of water. Add 25 mL of H_3BO_3 solution. If insoluble material remains after a few minutes, add 5 *N* H_2SO_4 dropwise with continued stirring. Add no more than 2.0 mL of the acid solution (see Note 15).

NOTE 15—Na_2SiF_6 is poorly soluble. Larger amounts may dissolve slowly, but the pure material does not require the addition of acid for complete solution. Acid is required when metallic impurities as calcium, aluminum, or iron are present.

60.4 Transfer the contents of the dish to a 50-mL volumetric flask and dilute to volume. Complete the analysis from this point without delay (see Note 16).

NOTE 16—The solution may be held in the 50 mL volumetric flask for the time required to select the proper aliquot. If it is necessary to hold over 1 h, transfer to a polyolefin container.

60.5 Transfer an aliquot (1.00 to 40.0 mL) that will give a final absorbance value between 0.1 and 0.8 to a 100-mL volumetric flask. Add a volume of H_3BO_3 solution that will bring the total to that in the standards (see Note 17). Add 10 mL

of ammonium molybdate solution and mix. Add 3.0 mL of 5 *N* sulfuric acid solution, mix, and allow to stand for 10 min. Add 10 mL of tartaric acid solution, mix, and add 1 mL 1-amino-2-naphthol-4-sulfonic acid solution. Dilute to 100 mL and mix. Allow to stand for 30 min.

NOTE 17—If an aliquot of less than 40 mL is taken, the amount of H_3BO_3 will be less than that in the standards and blank. Make up this deficiency by adding 1 mL of H_3BO_3 solution for each 2 mL of aliquot less than 40 mL (5 mL for a 30-mL aliquot, 10 mL for a 20-mL aliquot, etc.).

60.6 Prepare a blank using all reagents but omitting the sample, following steps outlined in 59.2 to 59.4.

60.7 Determine the absorbance of the ample at the same wavelength used for the calibration curve, adjusting the instrument to read zero absorbance with the reagent blank.

60.8 Determine from the calibration curve the milligrams of fluosilicic acid corresponding to the absorbance measured. If the absorbance obtained is out of the range of the calibration curve, repeat the test using an appropriate aliquot.

61. Calculation

61.1 Calculate the percentage of fluosilicic acid expressed as H_2SiF_6 as follows:

$$\text{fluosilicic acid as } H_2SiF_6, \% = \frac{M}{W \times 1000} \times 100 \quad (7)$$

where:

M = fluosilicic acid found from the calibration curve, mg, and

W = sample in aliquot, g.

62. Report

62.1 Report the percentage of fluosilicic acid the nearest percent given as follows:

Level, %	Report to, %
0.2	0.001
0.01	0.0001
0.001	0.0001

63. Precision and Bias

63.1 The following criteria should be used for judging the acceptability of results (Note 18).

63.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be percent absolute values given in Table 4 at the indicated degrees of freedom. The 95 % limit for the difference between two such runs is the percent absolute values given in Table 4.

63.1.2 *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 percent absolute values given in Table 4 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the percent absolute values given in Table 4.

63.1.3 *Reproducibility (Multilaboratory)*—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be the percent absolute values given in Table 4 at the indicated degrees of freedom. The 95 % limit for the difference between two such averages is the percent absolute values given in Table 4.

NOTE 18—The preceding precision statements are based on an interlaboratory study performed around 1965 on three samples containing the indicated levels of fluosilicic acid. One analyst in each of seven laboratories performed duplicate determinations and repeated them on a second day.[10] Practice E 180 was used in developing these precision estimates.

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

ARSENIC

64. Scope

64.1 Arsenic may be determined in the range from 0.01 to 100 ppm using the procedure for the colorimetric determination of arsenic in sulfuric acid described in Test Method E 223.

65. Summary of Test Method

65.1 The arsenic is reduced to arsine gas, which is absorbed in a pyridine solution of silver diethyldithiocarbamate, forming a red-colored complex, the intensity of which is measured on a photometer.

66. Precision and Bias

66.1 No studies of precision and bias have been made for the determination of arsenic in hydrofluoric acid, but the results are estimated to be similar as for those reported for the determination of arsenic in sulfuric acid.

67. Keywords

67.1 arsenic; ferrozine; fluosilicic acid; hydrofluoric acid; iron; nonvolatile acidity; sulfur dioxide; sulfuric acid; total acidity

TABLE 4 Precision for Fluosilicic Acid Method

	Repeatability			Laboratory Precision			Reproducibility		
Level, %	Standard Deviation, %	Degrees of Freedom	95 % Limit, %	Standard Deviation, %	Degrees of Freedom	95 % Limit, %	Standard Deviation, %	Degrees of Freedom	95 % Limit, %
0.2	0.0063	10	0.02	0.020	5	0.06	0.020	4	0.06
0.01	0.00066	14	0.002	0.0008	6	0.002	0.0010	6	0.003
0.001	0.00032	12	0.0009	0.00024	7	0.0007	0.00056	5	0.002