



Designation: E 271 – 98

AMERICAN SOCIETY FOR TESTING AND MATERIALS
100 Barr Harbor Dr., West Conshohocken, PA 19428
Reprinted from the Annual Book of ASTM Standards. Copyright ASTM

Standard Test Methods for Analysis of Aqueous Hydrofluoric Acid¹

This standard is issued under the fixed designation E 271; 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.

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 Water²

E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals³

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals⁴

E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis⁴

E 223 Test Methods for Analysis of Sulfuric Acid⁴

E 1615 Test Method for Iron in Trace Quantities Using the “Ferrozine” Method⁴

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.

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.

Current edition approved Sept. 10, 1998. Published February 1999. Originally published as E 271 – 65 T. Last previous edition E 271 – 91.

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.

 E 271

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 SO₂ 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 SO₂ 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.

ASTM E 271

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:

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

where:

N_{t_1} = normality when standardized,

N_{t_2} = 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.



Documents

Document Sharing Hub