



Designation: E224 – 23

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

This standard is issued under the fixed designation E224; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

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

## 1. Scope\*

1.1 These test methods cover the analysis of hydrochloric acid.

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

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

1.4 The analytical procedures appear in the following order:

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

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use. Consult current OSHA regulations, suppliers' Safety Data Sheets, and local regulations for all materials used in this specification. Specific hazards statements are given in Section 5, 30.1, 39.7, and 48.4.*

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

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

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## 2. Referenced Documents

- 2.1 *ASTM Standards*:<sup>2</sup>
  - D1193 Specification for Reagent Water
  - D1209 Test Method for Color of Clear Liquids (Platinum-Cobalt Scale)
  - D6809 Guide for Quality Control and Quality Assurance Procedures for Aromatic Hydrocarbons and Related Materials
  - E1 Specification for ASTM Liquid-in-Glass Thermometers
  - E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
  - E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry
  - E100 Specification for ASTM Hydrometers
  - E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)<sup>3</sup>
  - E200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis
  - E300 Practice for Sampling Industrial Chemicals

## 3. Significance and Use

3.1 These test methods provide for the classification of various grades of 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,

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

<sup>3</sup> The last approved version of this historical standard is referenced on www.astm.org.

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

where such specifications are available.<sup>4</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

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

## 5. Hazards

5.1 Consult current OSHA regulations, suppliers' Safety Data Sheets, and local regulations for all materials used in this test method.

5.2 Hydrochloric acid is a corrosive acid and is dangerous if improperly handled. Avoid any skin contact. Use of safety goggles and gloves highly recommended.

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

## 6. Photometers and Photometric Practice

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

## 7. Sampling

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

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

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

## TOTAL ACIDITY

## 8. Scope

8.1 This test method covers the determination of the total acidity of 27 % to 37 % mass (m/m) hydrochloric acid.

## 9. Summary of Test Method

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

## 10. Interferences

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

<sup>4</sup> *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

## 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.<sup>5</sup>

12.2 *Sodium Hydroxide, Standard Solution* (0.5 meq/mL (*N*))—See Practice **E200**. Correct for differences in temperature in accordance with the following formula:

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

where:

*N* = normality meq/mL (*N*) of NaOH solution at temperature *t*,

*N<sub>s</sub>* = normality meq/mL (*N*) of NaOH solution at temperature *s* during standardization,

*s* = temperature of NaOH solution during standardization, °C, 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 meq/mL (*N*) NaOH solution, and then titrate the sample to a pink end point. Record the titration to the nearest 0.02 mL.

## 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 % mass (m/m) of hydrochloric acid as follows:

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

<sup>5</sup> This reagent is also described in Practice **E200**.

**TABLE 1 Sample Size For Total Acidity**

HCl, % mass (m/m)	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

where:

- $V$  = corrected mL of NaOH solution required for titration of the sample,  
 $N$  = normality meq/mL ( $N$ ) of the NaOH solution, and  
 $W$  = sample used, g.

## 15. Report

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

## 16. Precision and Bias

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

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

16.1.2 *Laboratory Precision (Within-Laboratory, Between-Days Variability)*—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 % mass (m/m) relative at 25 df. The 95 % limit for the difference between two such averages is 0.48 % mass (m/m) 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 % mass (m/m) relative at 7 df. The 95 % limit for the difference between two such averages is 0.80 % mass (m/m) 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 % mass (m/m) hydrochloric acid. One analyst in each of ten laboratories performed duplicate determinations and repeated one day later, for a total of 120 determinations.<sup>6</sup> Practice **E180** 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 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 *Definitions:*

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

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

<sup>6</sup> Details of the interlaboratory study are available from ASTM International Headquarters. Request Research Report RR:E15-1046.

### 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*,<sup>7</sup> streamline or torpedo design, precision grade, for liquids heavier than water in ranges from 17.5 °Bé to 23 °Bé. The total length shall be approximately 305 mm (12 in.) divided to 0.1 °Bé over a 152 mm (6 in.) (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:

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

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

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

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

### 22. Temperature of Test

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

### 23. Procedure

23.1 Rinse a clean hydrometer cylinder with the sample to be tested, add the sample, and adjust the temperature to 15.5 °C ± 0.3 °C (60 °F ± 0.5 °F). Place the cylinder in a vertical position in a location free of air currents. Insert the hydrometer 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 acceptability of results (see **Note 2**):

<sup>7</sup> See Specification **E100**.

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)*—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.<sup>6</sup> Practice E180 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 % mass (m/m).

### 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 °C ± 25 °C (1472 °F ± 45 °F).

29.3 *Crucible Tongs*.

### 30. Reagent

30.1 *Sulfuric Acid* (1 + 1)—Add slowly with stirring one volume of concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, sp gr 1.84) to one volume of water. (**Warning**—Use goggles when preparing this solution.)

### 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 °C ± 25 °C (1472 °F ± 45 °F) for at least 10 min. Cool in a desiccator to room temperature and weigh the dish to the nearest 0.1 mg (Note 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<sub>2</sub>SO<sub>4</sub>, 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 % mass (m/m) of sulfated ash as follows (Note 6):

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

where:

R = weight of evaporating dish and residue, g,

D = weight of evaporating dish, g, and

W = sample used, g.

NOTE 6—When this value is less than 0.0010 % mass (m/m), report as less than 0.0010 % mass (m/m).

### 33. Report

33.1 Report the % mass (m/m) of sulfated ash to the nearest 0.0001 % mass (m/m).

### 34. Precision and Bias

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

34.1.1 *Repeatability (Single Analyst)*—The standard deviation for a single determination has been estimated to be the

**TABLE 2 Sulfated Ash Precision Values**

Level, % mass (m/m)	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

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)*—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 % mass (m/m) 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.<sup>6</sup> Practice E180 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 % mass (m/m).

### 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 µg/g to 50 µg/g (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.

### 38. Apparatus

38.1 *Photometer*—Any photoelectric spectrophotometer or filter photometer that will measure the absorbance of the solutions in the range from 500 nm 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<sub>3</sub>COONH<sub>4</sub>) in about 600 mL of water, filter, add 200 mL of glacial acetic acid to the filtrate, and dilute to 1 L.<sup>5</sup>

39.2 *Ammonium Hydroxide Solution (1 + 1)*—Dilute 500 mL of ammonium hydroxide (NH<sub>4</sub>OH) with 500 mL of water, and mix.<sup>5</sup>

39.3 *Congo Red Paper*.

39.4 *Hydroxylamine Hydrochloride Solution (100 g/L)*—Dissolve 100 g of hydroxylamine hydrochloride (NH<sub>2</sub>OH·HCl) in about 600 mL of water, filter, and dilute to 1 L.<sup>5</sup>

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.<sup>8</sup>

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.<sup>5</sup>

39.7 *Sulfuric Acid (1 + 1)*—Add slowly with stirring 1 volume of concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, sp gr 1.84) with 1 volume of water. (**Warning**—Use goggles when preparing this solution.)

### 40. Calibration

40.1 To a series of 100 mL volumetric flasks, pipet 0 mL, 2 mL, 4 mL, 8 mL, and 10 mL of standard iron solution. To each flask add the following reagents in order, mixing after addition of each: 20 mL of water, 1 mL of hydroxylamine hydrochloride solution, 5 mL of 1,10-phenanthroline solution, and NH<sub>4</sub>OH (1 + 1) as required to bring the pH to 3.5 to 4.0 (just alkaline to Congo red paper). Add 5 mL of ammonium acetate solution, dilute to the mark with water, mix thoroughly, and allow to stand approximately 15 min.

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 nm to 525 nm, adjusting the photometer to read zero absorbance for the reagent blank.

40.3 Plot on coordinate paper the absorbances 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<sub>2</sub>SO<sub>4</sub> (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.

<sup>8</sup> This reagent is used for calibrating purposes only.