Designation: E 358 – 95

AMERICAN SOCIETY FOR TESTING AND MATERIALS
100 Barr Harbor Dr., West Conshohocken, PA 19428
Reprinted from the Annual Book of ASTM Standards. Copyright ASTM
If not listed in the current combined index, will appear in the next edition.

Standard Test Methods for Analysis of Phosphoric Acid[1]

This standard is issued under the fixed designation E 358; 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.

These test methods have been approved for use by agencies of the Department of Defense. Consult the DoD Index of Specifications and Standards for the specific year of issue which has been adopted by the Department of Defense.

1. Scope

1.1 These test methods cover the analysis of furnace grade phosphoric acid.

1.2 The analytical procedures appear in the following order:

	Sections
Assay by Specific Gravity	8 to 16
Iron	17 to 26

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

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 5.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

E 1 Specification for ASTM Thermometers[3]

E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals[4]

E 100 Specification for ASTM Hydrometers[3]

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals[5]

E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis[5]

3. Significance and Use

3.1 These test methods provide for the classification of various grades of phosphoric acid and for the determination of trace amounts of iron. The acid strength and iron level are important factors in many uses of phosphoric acid.

4. 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.[6] 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 *Safety Precautions:*

5.1.1 Phosphoric acid is a corrosive acid and is dangerous if improperly handled. Avoid any skin contact.

5.1.2 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 photometric practice prescribed in these test methods shall conform to Practice E 60.

7. Sampling

7.1 Sampling of phosphoric 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.

ASSAY BY SPECIFIC GRAVITY

8. Scope

8.1 This test method covers the determination of H_3PO_4 in furnace-grade phosphoric acid only, by sp gr at 25°C/15.5°C.

---

[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 Mineral Acids.

Current edition approved Sept. 10, 1995. Published November 1995. Originally published as E 358 – 68. Last previous edition E 358 – 94.

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

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

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

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

[6] *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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

9. Summary of Test Method

9.1 The sample of phosphoric acid is placed in a hydrometer cylinder, and the specific gravity is read from a glass hydrometer placed in the jar. The temperature of the acid is noted and proper corrections applied to the reading.

10. Significance and Use

10.1 The specific gravity can be used to determine the strength of phosphoric acid made from furnace-grade phosphorus.

11. Apparatus

11.1 *Hydrometer*, streamline or torpedo design, precision grade for liquids heavier than water in ranges suitable to the acid strength tested. For specifications, refer to Specification E 100.

ASTM Hydrometer No.	Range	For
136H-62	1.550 to 1.600	75 % acid
137H-62	1.600 to 1.650	80 % acid
138H-62	1.650 to 1.700	85 % acid

Each unit is equivalent to 0.001 sp gr. The distance between each unit is approximately 1.5 mm; overall length is approximately 280 mm (11 in.). The correction factor for each hydrometer should be determined by testing in acid of known specific gravity at 25°C/15.5°C as determined in Section 12 and applied to the hydrometer readings.

11.2 *Thermometer*—ASTM Gravity Thermometer, having a range from −20 to +102°C, and conforming to the requirements of Thermometer 12C as prescribed in Specification E 1.

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

11.4 *Pycnometer*,[7] either 25 or 50-mL capacity of a type either with or without a built-in thermometer. The latter type is superior for precise work.

12. Procedure with Pycnometer

12.1 *Procedure:*

12.1.1 Thoroughly clean the pycnometer, rinse with a volatile solvent such as acetone or methanol, and sparge with dry air.

12.1.2 Weight the clean, dry, assembled pycnometer on an analytical balance and record the weight.

12.1.3 Fill the pycnometer to just above the ground-glass joint with freshly boiled reagent water that has been cooled to a temperature below 25°C.

12.1.4 Carefully insert the top of the pycnometer so that no air remains entrapped. If using a vertical capillary pycnometer, the water will rise in the capillary and overflow. If using a sidearm capillary, the excess water will overflow from the small side arm capillary.

12.1.5 Place the pycnometer in a water bath set at 25°C. In the case of the vertical capillary pycnometer, allow to remain ½ h. If using a sidearm capillary pycnometer, allow to remain until the temperature in the pycnometer is 25°C.

12.1.6 Remove the pycnometer from the water bath, cool to below 25°C, and wipe off the excess water using a chamois or a soft paper towel and lens tissue. Be careful, when wiping, not to wipe directly over the capillary opening because of the capillary action of the paper toweling.

12.1.7 Carefully place the pycnometer on the balance pan and weigh. Avoid getting any moisture from the fingers on the glass. Record the weight.

12.1.8 Calculate the volume of the pycnometer at 25°C.

12.1.9 Repeat 12.1.1 through 12.1.8. The calculated volumes should agree within ±0.002 mL.

12.1.10 Using phosphoric acid of proper strength instead of reagent water, repeat 12.1.1 through 12.1.7 twice. The weights of phosphoric acid obtained should agree within ±0.002 g.

12.1.11 Determine two specific gravity readings on the acid using the hydrometer to be standardized. These values should agree within ±0.0002 units. Correct for temperature to 25°C/15.5°C.

12.1.12 If the entire range of the hydrometer is to be used, the hydrometer calibration should be made at two or more points.

12.2 *Calculation:*

12.2.1 Calculate the volume of the pycnometer as follows:

$$\text{Volume of pycnometer} = (W_w - W_o)/D$$

where:

W_w = weight of pycnometer plus water,
W_o = weight of empty pycnometer, and
D = density of water at 25°C = 0.99707.

12.2.2 Calculate the density of acid at 25°C as follows:

$$\text{Density of acid at } 25^\circ\text{C} = (W_a - W_o)/V$$

where:

W_a = weight of pycnometer plus acid,
W_o = weight of empty pycnometer, and
V = volume of pycnometer at 25°C.

12.2.3 Calculate the specific gravity of acid, 25°C/15.5°C, as follows:

$$\text{Sp gr of acid, } 25^\circ\text{C}/15.5^\circ\text{C} = A/W$$

where:

A = density of acid at 25°C, and
W = density of water at 15.5°C.

12.2.4 Hydrometer correction is the number of specific gravity units that must be added to or subtracted from the hydrometer reading to make it equal to the specific gravity obtained by the pycnometer.

12.2.5 Always handle the pycnometer carefully. Any moisture from the fingers will cause an incorrect weight. As an aid in handling, fold a small piece of paper toweling into a narrow strip, place around the neck of the pycnometer, and handle by the extended paper tabs.

13. Procedure with Hydrometer

13.1 Adjust the temperature of the sample to be tested to 20 to 30°C, thoroughly mix the sample, and rinse a clean hydrometer cylinder with the sample.

13.2 Add the sample, and place the cylinder in a vertical position in a location free of air currents.

---

[7] Either a vertical capillary pycnometer (such as Sargent-Welch No. S-9205) or a sidearm capillary pycnometer (such as Sargent-Welch No. S-9195) has been found satisfactory for this purpose.

13.3 Grasp the top of the stem of a clean, dry hydrometer between thumb and forefinger and slowly lower it into the center of the cylinder containing the sample. By sense of feel, gently release it just before it comes to rest. The free fall should be no more than 6 mm. No portion of the hydrometer should touch the cylinder.

13.4 The reading should not be taken until the liquid is free of any air bubbles and the hydrometer is at rest. In taking the reading, the eye should be placed slightly below the plane of the surface of the liquid and then raised slowly until this surface, seen as an ellipse, becomes a straight line. The point at which this line cuts the hydrometer scale should be taken as the reading.

NOTE 1—Record the temperature of the sample to the nearest 0.1°C at the time of reading.

(*1*) If the hydrometer is released at too high a point after insertion into the liquid, it will drop too far past the correct reading, bob up, and the excess liquid on the stem will cause a false, low reading.

(*2*) If any portion of the hydrometer touches the cylinder while immersed it will not sink far enough and a false high reading will result.

14. Calculation

14.1 Determine furnace-grade acid strength opposite the appropriate specific gravity at 25°C/15.5°C in Table 1 using the appropriate temperature coefficient factor in Table 2.

(sp gr at T) + [(T − 25) (temperature coefficient factor)] = sp gr at 25°C/15.5°C

If the temperature of the determination is higher than 25°C, a plus correction will result. If lower than 25°C, a minus correction will result.

14.1.1 *Examples:*

14.1.1.1

Approximate composition of acid = 75 %
Temperature of acid = 24°C
Sp gr at 24°C = 1.5818
Sp gr temperature coefficient (Table 2) = 0.00075
1.5818 + [(24 − 25)(0.0075)] =
1.5818 + [(− 1)(0.00075)] =
1.5818 − 0.00075 = 1.5810 sp gr at 25°C/15.5°C, which is equivalent to 75.6 % H_3PO_4

14.1.1.2

Approximate composition of acid = 85 %
Temperature of acid = 27.6°C
sp gr at 27.6 = 1.6902
sp gr temperature coefficient (Table 2) = 0.00078
1.6902 + [(27.6 − 25.0)(0.00078)] =
1.6902 + [(2.6)(0.00078)] =
1.6902 + 0.0020 = 1.6922 sp gr at 25°C/15.5°C, which is equivalent to 85.5 % H_3PO_4

15. Report

15.1 Report the specific gravity to the nearest 0.0001 unit.

16. Precision and Bias

16.1 *Precision*—The following criteria should be used for judging the acceptability of results (Note 2):

16.1.1 *Repeatability* (*Single Analyst*)—The standard deviation for a single determination has been estimated to be 0.0002 unit at 16 df. The average 95 % limit for the difference between two such runs is 0.0006 unit.

16.1.2 *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 0.0004 unit at 9 df. The 95 % limit for the difference between two such averages is 0.0011 unit.

16.1.3 *Reproducibility* (*Multilaboratory*)—The standard deviation of results (each the average of duplicates), obtained by analysts in different laboratories, has been estimated to be 0.00046 unit at 4 dF. The 95 % limit for the difference between two such averages is 0.0013 unit.

NOTE 2—The precision estimates in 16.1.1 to 16.1.3 are based on an interlaboratory study on two samples containing approximately 75 and 85 % H_3PO_4. One analyst in each of five laboratories performed duplicate determinations and repeated at least one day later for a total of 40 determinations. Practice E 180 was used in developing these precision estimates.

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

IRON

17. Scope

17.1 This test method is a colorimetric estimation of iron in furnace-grade phosphoric acid, covering a range from 0 to 40 ppm, based on 5-g sample.

18. Summary of Test Method

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

19. Interferences

19.1 *Anions*—There is discussion in the literature of the interference of orthophosphate. However, this test method compensates for this by using standards and samples with equivalent amounts of P_2O_5. Generally, colored ions, strong oxidizing agents, ions that will precipitate at the pH of the test, and ions that will complex the iron must be absent. Suggested limits for some of these are:

CN^-	10 ppm
$Cr_2O_7^=$	100 ppm
ClO_4^-	100 ppm
SiO_3^-	100 ppm
F^-	500 ppm

19.2 *Cations*—Ions that will precipitate as either the phosphate or the hydroxide at the pH of the test must be absent. Ions that complex with 1,10-phenanthroline must also be absent. Copper, nickel, chromium, and cobalt all interfere to some degree. Suggested maximum concentrations of some of the metal ions are as follows:

Cadmium	50 ppm
Mercury	1 ppm
Zinc	10 ppm
Copper	10 ppm
Nickel	2 ppm
Cobalt	10 ppm
Tin	20 ppm
Chromium	10 ppm
Antimony	30 ppm

20. Apparatus

20.1 *Photometer*—Any photoelectric spectrophotometer

TABLE 1 o-Phosphoric Acid Solutions—Specific Gravity at 25°C/15.5°C Versus Concentration[A]

H_3PO_4, %	P_2O_5, %	sp gr 25°C/15.5°C	H_3PO_4, %	P_2O_5, %	sp gr 25°C/15.5°C
74.0	53.59	1.563	81.0	58.66	1.640
74.5	53.96	1.569	81.1	58.74	1.641
74.6	54.03	1.570	81.2	58.81	1.643
74.7	54.10	1.571	81.3	58.88	1.644
74.8	54.17	1.572	81.4	58.95	1.645
74.9	54.25	1.573	81.5	59.03	1.646
			81.6	59.10	1.647
75.0	54.32	1.574	81.7	59.17	1.648
75.1	54.39	1.575	81.8	59.24	1.649
75.2	54.46	1.576	81.9	59.32	1.650
75.3	54.54	1.577			
75.4	54.61	1.578	82.0	59.39	1.652
75.5	54.68	1.580	82.1	59.46	1.653
75.6	54.75	1.581	82.2	59.53	1.654
75.7	54.82	1.582	82.3	59.60	1.655
75.8	54.90	1.583	82.4	59.68	1.656
75.9	54.97	1.584	82.5	59.75	1.657
			82.6	59.82	1.658
76.0	55.04	1.585	82.7	59.89	1.660
76.1	55.11	1.586	82.8	59.97	1.661
76.2	55.19	1.587	82.9	60.04	1.662
76.3	55.26	1.588			
76.4	55.33	1.589	83.0	60.11	1.663
76.5	55.40	1.590	83.1	60.18	1.664
76.6	55.48	1.591	83.2	60.26	1.665
76.7	55.55	1.593	83.3	60.33	1.666
76.8	55.62	1.594	83.4	60.40	1.668
76.9	55.69	1.595	83.5	60.47	1.669
			83.6	60.55	1.670
77.0	55.77	1.596	83.7	60.62	1.671
77.1	55.84	1.597	83.8	60.69	1.672
77.2	55.91	1.598	83.9	60.76	1.673
77.3	55.98	1.599			
77.4	56.06	1.600	84.0	60.84	1.674
77.5	56.13	1.601	84.1	60.91	1.676
77.6	56.20	1.602	84.2	60.98	1.677
77.7	56.27	1.603	84.3	61.05	1.678
77.8	56.35	1.605	84.4	61.13	1.679
77.9	56.42	1.606	84.5	61.20	1.680
			84.6	61.27	1.681
78.0	56.49	1.607	84.7	61.34	1.683
78.1	56.56	1.608	84.8	61.42	1.684
78.2	56.64	1.609	84.9	61.49	1.685
78.3	56.71	1.610			
78.4	56.78	1.611	85.0	61.56	1.686
78.5	56.85	1.612	85.1	61.63	1.687
78.6	56.93	1.613	85.2	61.71	1.688
78.7	57.00	1.615	85.3	61.78	1.690
78.8	57.07	1.616	85.4	61.85	1.691
78.9	57.14	1.617	85.5	61.92	1.692
			85.6	61.99	1.693
79.0	57.21	1.618	85.7	62.07	1.694
79.1	57.29	1.619	85.8	62.14	1.695
79.2	57.36	1.620	85.9	62.21	1.697
79.3	57.43	1.621	86.0	62.28	1.698
79.4	57.50	1.622	86.5	62.65	1.704
79.5	57.58	1.623	87.0	63.01	1.710
79.6	57.65	1.625	87.5	63.37	1.716
79.7	57.72	1.626			
79.8	57.79	1.627	88.0	63.73	1.721
79.9	57.87	1.628	88.5	64.10	1.727
80.0	57.94	1.629	89.0	64.46	1.733
80.1	58.01	1.630	89.5	64.82	1.739
80.2	58.08	1.631			
80.3	58.16	1.632	90.0	65.18	1.745
80.4	58.23	1.634			
80.5	58.30	1.635			
80.6	58.37	1.636			
80.7	58.45	1.637			
80.8	58.52	1.638			
80.9	58.59	1.639			

[A] Christensen and Reed, *Industrial and Engineering Chemistry*, IECHA, Vol 47, 1955, p. 1277.

Examples of Specific Gravity Conversion:

(*1*) (density at 25°C)/(density of water at 25°C) = sp gr at 25°C/25°C

(*2*) sp gr at 25°C/25°C × (density of water at 25°C)/(density of water at 15.5°C) = sp gr at 25°C/15.5°C

(*3*) sp gr at 25°C/15.5°C + [(25°C–15.5°C) (temperature coefficient)] = sp gr at 15.5°C/15.5°C

(*4*) To convert to Baumé, use the following equation: Baumé = 145 − 145/sp gr

TABLE 2 Specific Gravity Temperature Coefficient[A]

H_3PO_4, %	Solution Temperature, °C		
	15	25	40
75	0.00074	0.00075	0.00076
80	0.00076	0.00077	0.00078
85	0.00078	0.00078	0.00080

[A] Egan, E. P., and Luff, B. B., "Density of Aqueous Solutions of Phosphoric Acid, Measurements at 15 to 80 C," *Industrial and Engineering Chemistry*, IECHA, Vol 47, 1955, p. 1280.

or filter photometer that will measure the absorbance of the solutions in the range from 500 to 525 nm.

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

20.3 *pH Meter*.

NOTE 3—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.

21. Reagents

21.1 *Ammonium Acetate Solution*—See Practice E 200.

21.2 *Ammonium Hydroxide Solution* (1+1)—See Practice E 200.

21.3 *Disodium Phosphate*—Recrystallize disodium phosphate from water to reduce the iron content below 1 ppm as follows:

21.3.1 Make a 50 % solution of disodium phosphate at 100°C.

21.3.2 Cool to 25°C. The crystals that separate will be a mixture of $Na_2HPO_4 \cdot 12H_2O$ and $Na_2HPO_4 \cdot 7H_2O$. The solubility of disodium phosphate is about 10 % at 25°C.

21.3.3 Filter the crystals and wash with cold (10°C) water.

21.3.4 Air-dry the crystals and determine the water loss at 110°C to obtain the percent anhydrous disodium phosphate in the crystals.

21.3.5 Calculate the amount of recrystallized disodium phosphate necessary to equal 8.0 g of $Na_2HPO_4 \cdot 7H_2O$ and use for the standard curve.

21.4 *Hydrochloric Acid* (1+1)—Mix 1 volume of concentrated hydrochloric acid (HCl, sp gr 1.19) with 1 volume of water.

21.5 *Hydroxylamine Hydrochloride Solution* (100 g/L)—See Practice E 200.

21.6 *1,10-Phenanthroline Monohydrate* (3 g/L)—See Practice E 200.

21.7 *Iron, Standard Solution* (1 mL = 0.01 mg Fe)—See Practice E 200.

22. Preparation of Standard Curve

22.1 Into a series of 150-mL beakers pipet 0, 2, 5, 10, 15, and 20 mL of the standard iron solution.

22.2 Add the amount of recrystallized disodium phosphate equivalent to 8.0 g of $Na_2HPO_4 \cdot 7H_2O$ (calculated in 21.3.5) to each beaker.

22.3 Dilute to about 40 mL, add 6 mL of hydroxylamine hydrochloride solution, and stir until solution is effected. Let stand 5 min.

22.4 Add 4 mL of 1,10-phenanthroline solution, 10 mL of ammonium acetate solution, and adjust the pH to 6.0 ± 0.1 if necessary, with NH_4OH (1+1) or HCl (1+1) using a pH meter.

22.5 Transfer the solutions to 100-mL volumetric flasks, cool, dilute to the mark, mix well, and allow color to develop for 30 min.

22.6 Within 30 to 45 min, transfer the solutions to a 2-cm inside diameter cell, and measure their absorbances using a photometer with a wavelength setting of 510 nm or in a filter photometer equipped with a filter in the range from 500 to 525 nm, adjusting the photometer to read 0 absorbance for the reagent blank.

22.7 Plot on coordinate paper the absorbances of the calibration solutions against milligrams of iron present.

23. Procedure

23.1 Accurately weigh about 5 g of phosphoric acid and continue the analysis beginning with 22.3.

23.2 Prepare a blank solution using all the reagents, but omitting the sample, and carry through the same procedure beginning with 22.3.

23.3 Determine the absorbance of the sample after adjusting the photometer to read 0 absorbance with the blank.

23.4 Determine the milligrams of iron present in the sample from the standard curve.

24. Calculation

24.1 Calculate the amount of iron present as follows:

$$\text{Fe, ppm} = (M \times 1000)/W$$

where:

M = Fe found from calibration curve, mg, and
W = sample, g.

25. Report

25.1 Report the values of iron to the nearest 0.1 ppm.

26. Precision and Bias

26.1 *Precision*—The following criteria should be used for judging the acceptability of results (Note 4):

26.1.1 *Repeatability* (*Single Analyst*)—The standard deviation for a single determination has been estimated to be 0.14 ppm absolute at 20 df. The average 95 % limit for the difference between two such runs is 0.4 ppm..

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 0.4 ppm at 10 df. The 95 % limit for the difference between two such averages is 1.1 unit.

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 0.6 ppm at 4 df. The 95 % limit for the difference between two such averages is 1.7 ppm.

NOTE 4—The precision estimates in 26.1.1 to 26.1.3 are based on an interlaboratory study on two samples containing approximately 5 and 10 ppm iron. One analyst in each of five laboratories performed duplicate determinations and repeated at least one day later for a total of 40 determinations. Practice E 180 was used in developing these precision estimates.

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

27. Keywords

27.1 assay; iron; phosphoric acid; specific gravity