Standard Test Method for Determination of Phosphorus in Iron Ores by Phosphomolybdate Coprecipitation and Nitric Acid Titrimetry[1]

This standard is issued under the fixed designation E278; 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.

ε^1 NOTE—Editorial corrections were made in 1.2 and Table 1.

1. Scope

1.1 This test method covers the determination of phosphorus in iron ores, concentrates, and agglomerates.

1.2 This test method covers the determination of phosphorus in the range from 0.01 % to 1.00 %.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this 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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials

E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

E877 Practice for Sampling and Sample Preparation of Iron Ores and Related Materials for Determination of Chemical Composition and Physical Properties

E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology E135.

4. Summary of Test Method

4.1 The sample is dissolved in HCl and HNO_3. After the addition of $HClO_4$, the solution is evaporated to strong fumes to dehydrate the silica. The insoluble residue is filtered off, ignited, and treated for the recovery of any contained phosphorus. Ammonium molybdate is added to precipitate phosphomolybdate. The precipitate is filtered off and washed free from acid. It is then dissolved in an excess of standard sodium hydroxide solution. The excess sodium hydroxide is titrated with a standard solution of HNO_3 using phenolphthalein as an indicator.

5. Significance and Use

5.1 This test method is intended to be used for compliance with compositional specifications for phosphorus content. It is assumed that all who use these procedures will be trained analysts capable of performing common laboratory procedures skillfully and safely. It is expected that work will be performed in a properly equipped laboratory and that proper waste disposal procedures will be followed. Appropriate quality control practices shall be followed, such as those described in Guide E882.

6. Interferences

6.1 Vanadium and arsenic, elements commonly found in iron ores, coprecipitate with the phosphorus. Provisions for their removal or elimination of their interference are included in this test method.

6.2 Titanium tends to form an insoluble compound with phosphorus and thus may cause low values for phosphorus. Provision for its removal is included in this test method.

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[1] This test method is under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and is the direct responsibility of Subcommittee E01.02 on Ores, Concentrates, and Related Metallurgical Materials.

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[2] 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.

7. Reagents and Materials

7.1 *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.[3] Other grades may be used, provided it is first ascertained that the reagent is of sufficient high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of Specification D1193.

7.3 *Ammonium Molybdate Solution* (Acidic).

7.3.1 *Solution No. 1*—Transfer 100 g of molybdic acid (85 % MoO_3) to a 600–mL beaker containing 240 mL of water and mix thoroughly. Add 140 mL of NH_4OH while stirring vigorously. When dissolution is complete, filter through a medium paper, add 60 mL of HNO_3, and cool.

7.3.2 *Solution No. 2*—Add 400 mL of HNO_3 to 960 mL of water in a 2-L beaker and cool.

7.3.3 Add Solution No. 1 to Solution No. 2 while stirring constantly. Add 0.1 g of ammonium phosphate, dibasic ($(NH_4)_2HPO_4$), and let stand at least 24 h before using. Use only the clear supernatant liquid.

7.4 *Ammonium Nitrate* (NH_4NO_3)

7.5 *Ferric Chloride Solution*—Dissolve 0.3 g of pure iron wire in 25 mL of HCl (1 + 1). Oxidize by adding HNO_3 dropwise to the hot solution. Cool, add 25 mL of HCl, dilute to 1 L and mix.

7.6 *Ferrous Sulfate Solution*—Dissolve 100 g of ferrous sulfate ($FeSO_4·7H_2O$) in 1 L of H_2SO_4 (5 + 95).

7.7 *Hydrobromic Acid* (1 + 4)—Mix 20 mL of concentrated hydrobromic acid (HBr, sp gr 1.49) with 80 mL of water.

7.8 *Hydrochloric Acid* (1 + 1)—Mix equal volumes of concentrated HCl (sp gr 1.19) and water.

7.9 *Hydrofluoric Acid* (sp gr 1.15)—Concentrated HF.

7.10 *Nitric Acid, Standard* (0.15 *N*)—Transfer 10 mL of clear and water white concentrated HNO_3 (sp gr 1.42) to a 1-L flask, dilute to the mark, and mix. Standardize this solution against the standard sodium hydroxide (NaOH) solution using phenolphthalein as indicator. If desired, this solution may be made equivalent to the standard sodium hydroxide solution by dilution with water.

7.11 *Nitric Acid, Wash Solution* (1 + 99)—Mix 10 mL of concentrated HNO_3 (sp gr 1.42) with 990 mL of water.

7.12 *Perchloric Acid* (70 %) ($HClO_4$).

7.13 *Phenolphthalein Indicator Solution*—Dissolve 0.2 g of phenolphthalein in 100 mL of ethanol.

7.14 *Potassium Nitrate, Wash Solution* (10 g/L)—Dissolve 10 g of potassium nitrate (KNO_3) in water, dilute to 1 L, and mix.

7.15 *Potassium Permanganate Solution* (25 g/L)—Dissolve 25 g of potassium permanganate ($KMnO_4$) in water and dilute to 1 L.

7.16 *Sodium Carbonate* (Na_2CO_3).

7.17 *Sodium Hydroxide, Stock Solution*—Dissolve 300 g of NaOH in 1 L of water. Add a slight excess of barium hydroxide ($Ba(OH)_2$) to precipitate any carbon dioxide (CO_2). Allow any precipitate to settle out. Store the solution in a polyethylene container.

7.18 *Sodium Hydroxide, Standard Solution* (0.15 *N*)—Transfer 20 mL of the clear, supernatant stock solution to a 1-L flask. Dilute to the mark with freshly boiled and cooled water and mix thoroughly. Standardize this solution against potassium acid phthalate. It is convenient to adjust the normality of this standard solution to 0.148 *N* (1 mL = 0.0002 g P). Confirm the phosphorus value by analyzing a standard of a known phosphorus content, preferably an iron ore of similar composition. Protect the NaOH solution from CO_2 by means of a soda-lime or soda-asbestos tube.

7.19 *Sulfurous Acid* (H_2SO_3).

8. Hazards

8.1 For precautions to be observed in this test method, refer to Practices E50.

9. Sampling and Sample Preparation

9.1 *Sampling*—The gross sample shall be collected and prepared in accordance with Practice E877.

9.2 *Sample Preparation*—The laboratory sample shall be pulverized to pass a No. 100 (150-µm) sieve.

NOTE 1—Some ores, such as specular hematites, may require finer grinding to pass a No. 200 (75-µm) sieve.

9.3 *Sample Weight*—Weigh approximately (within ± 25 mg) an amount of sample specified as follows:

Content of Phosphorus, %	Weight of Sample, g
0.01 to 0.10	2.0
0.11 to 0.50	1.0
0.51 to 1.00	0.5

10. Procedure

10.1 Transfer the test sample to a small dry weighing bottle and place in a drying oven. After drying at 105 °C to 110 °C for 1 h, cap the bottle, and cool to room temperature in a desiccator. Momentarily release the cap to equalize pressure and weigh the capped bottle to the nearest 0.1 mg. Repeat the drying and weighing until there is no further weight loss. Transfer the test sample to a 400-mL beaker and reweigh the capped bottle to the nearest 0.1 mg. The difference between the two weights is the weight of the test sample.

10.2 Moisten the test sample with a few milliliters of water and add 25 mL of HCl for each gram of test sample. Cover and digest below the boiling point until all soluble minerals are in

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[3] *Reagent Chemicals, American Chemical Society Specifications,* American Chemical Society, Washington, DC, www.chemistry.org. For suggestions on the testing of reagents not listed by the American Chemical Society, see the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD, http://www.usp.org.

solution. Add 5 mL of HNO_3 and 20 mL of $HClO_4$ and evaporate to strong fumes to dehydrate the silica. Cool, add 50 mL of water, and warm until soluble salts are in solution. Filter and collect the filtrate in a 300-mL Erlenmeyer flask. Wash the residue with HNO_3 (1 + 99), and finally with hot water until free from perchlorates. Evaporate the filtrate using a low heat.

10.3 Ignite the paper and residue in a platinum crucible. Cool, moisten with several drops of water and add 2 mL of $HClO_4$ and 5 mL of HF, and evaporate to complete dryness. Fuse the residue with 3 g of Na_2CO_3. Place the crucible in a 250-mL beaker and add 100 mL of water. Heat to disintegrate the melt and to dissolve all soluble salts. Remove, wash, and police the crucible. Filter the alkaline solution through a medium-texture paper and collect the filtrate in the 400-mL beaker. Wash the residue with hot water and discard. Acidify the filtrate with HCl, add 5 mL of the ferric chloride ($FeCl_3$) solution, and render the solution alkaline to litmus with NH_4OH. Boil for 1 min to coagulate the precipitate. Filter and wash the residue with hot water. Discard the filtrate. Place the flask containing the evaporated filtrate from 10.2 underneath the funnel. Dissolve the residue through the paper with 10 mL of warm HCl (1 + 1) and wash with hot water. Discard the paper and evaporate the solution to fumes of $HClO_4$.

NOTE 2—If the test sample is high in manganese, manganese dioxide (MnO_2) may precipitate when the solution is evaporated to $HClO_4$ fumes. If this occurs, the MnO_2 can be redissolved by the addition of a crystal of sodium nitrite ($NaNO_2$) when the perchlorates are dissolved in water.

NOTE 3—If arsenic is known to be present, concentrate the solution in the Erlenmeyer flask to approximately 75 mL, add 20 mL of HBr (1 + 4), and evaporate to strong fumes. Cool, wash down the sides of the flask with 20 mL of water and again evaporate to fumes.

10.4 Cool, add 50 mL of water, and warm to dissolve the salts. Add an excess of several drops of $KMnO_4$ solution and boil the solution for several minutes. Add, dropwise, enough of a solution of H_2SO_3 to reduce any $KMnO_4$ or precipitated MnO_2. Boil to expel the SO_2, cool, and add NH_4OH until a small precipitate of ferric hydroxide ($Fe(OH)_3$) persists on shaking or stirring. Add HNO_3 until the precipitate just dissolves on shaking, then 3 mL to 5 mL in excess. Add 10 g of NH_4NO_3 and shake to dissolve the salts.

10.5 *Absence of Vanadium*—Adjust the volume to 150 mL and the temperature to 20 °C and add 50 mL of the ammonium molybdate solution. Shake vigorously for 5 min and let stand 20 min or until the yellow precipitate has settled.

TABLE 1 Statistical Summary[A]

Average,[B] %	Standard Deviation		Reproducibility, R^C	Number of Participating Laboratories
	Within-Laboratory	Between-Laboratories		
0.009	0.0007	0.0008	0.0021	5
0.028	0.0008	0.0008	0.0024	7
0.031	0.0012	0.0016	0.0045	7
0.044	0.0017	0.0018	0.0051	7
0.086	0.0014	0.0027	0.0075	7
0.596	0.0106	0.0106[D]	0.0300	7

[A] Calculations based on Practice E691.

[B] Each percentage represents a different kind of iron ore.

[C] Reproducibility factor, R, obtained by multiplying the between-laboratory standard deviation by $2\sqrt{2}$.

[D] Provisional calculation of between-laboratories standard deviation was 0.0089.

NOTE 4—If the precipitate is small it is advisable to allow it to stand 4 h or overnight.

10.6 *Presence of Vanadium*—Adjust the volume of the solution to 100 mL, cool to 15 °C, add 5 mL of the $FeSO_4$ solution and swirl the flask to reduce the vanadium. Add 50 mL of the ammonium molybdate solution, shake vigorously for 10 min, and let stand for 1 h or until the yellow precipitate has settled (Note 4).

10.7 Filter the precipitate obtained in accordance with 10.5 or 10.6 on a close textured paper (Note 5). Wash the flask and precipitate three times with 5-mL portions of the HNO_3 wash solution, and then with the KNO_3 wash solution until free from acid, as indicated by a litmus paper test. Since the yellow precipitate tends to climb, direct the jet of the wash solution around the edge of the paper and spirally down.

NOTE 5—A filtering crucible or smooth funnel plus perforated disk with a macerated paper pulp pad may be used if desired.

10.8 Return the paper and precipitate to the Erlenmeyer flask, add 25 mL of water (CO_2-free), and an excess of 5 mL of 0.15 N NaOH solution. Shake or stir to break up the paper and to dissolve the precipitate. Wash down the sides of the flask, add three drops of the phenolphthalein indicator solution, and titrate the excess NaOH with the 0.15 N HNO_3.

10.9 *Blank*—Carry along with the test sample a reagent blank through all the steps of the procedure using the same amounts of all reagents.

11. Calculation

11.1 Calculate the percent of phosphorus as follows:

$$\text{Phosphorus, } \% = 100\,\frac{[(A - BC) - (D - EC)]F}{G} \quad (1)$$

where:

A = standard NaOH solution used, mL,
B = standard HNO_3 required for titration of the excess of NaOH in the test sample, mL,
C = standard NaOH solution equivalent to 1 mL of the standard HNO_3, mL,
D = standard NaOH solution required for blank determination, mL,
E = standard HNO_3 required for titration of the excess NaOH in blank determination, mL,
F = phosphorus equivalent of the standard NaOH solution, g/mL, and
G = weight of test sample used.

12. Precision and Bias[4]

12.1 *Precision*—Table 1 indicates the precision of the test method as determined by Practice E691. To interpolate for reproducibility factors, R, between 0.009 % and 0.60 % phosphorus (P), the following relationship may be used:

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[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E16-174.

$$R = 0.013 + 0.0781(\%\,P) - 0.0504(\%\,P)^2 \qquad (2)$$

12.2 *Bias*—There was no significant bias in the determinations made for an NIST certified reference material, NBS 27d, certified at 0.028 % phosphorus. An additional CRM, NBS 27c, certified as having 0.042 % phosphorus, was analyzed by two laboratories as having 0.038 % or 0.041 % phosphorus.

13. Keywords

13.1 agglomerates; concentrates; iron ore; phosphorus; related materials; titrimetric phosphorus

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