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Standard Test Methods for Determination of Manganese in Iron Ores by Pyrophosphate (Potentiometric) Potentiometry and Periodate (Spectrophotometric) Spectrophotometry Techniques¹

This standard is issued under the fixed designation E314; 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.

^{ε1} NOTE—Editorial changes made throughout E314 in November 2015.

1. Scope

1.1 These test methods cover the determination of manganese in iron ores, concentrates, and agglomerates. The following two test methods are included:

	Sections
Test Method A (Pyrophosphate (Potentiometric))	8 – 15
Test Method B (Periodate (Photometric))	16 – 22
Test Method B (Periodate (Spectrophotometric))	16 – 22

1.2 Test Method A covers the determination of manganese in the range from 2.5 % to 15.0 %. Test Method B covers the determination of manganese in the range of 0.01 % to 5.00 %.

NOTE 1—The lower limit for this test method is set at 50 % relative error for the lowest grade material tested in the interlaboratory study in accordance with Practice E1601.

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

[E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications](#)

[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](#)

[E173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals \(Withdrawn 1997\) \(Withdrawn 1998\)](#)³

[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](#)

[E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method](#)

3. Terminology

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

4. Significance and Use

4.1 This test method is intended to be used for compliance with compositional specifications for manganese content in iron ores, concentrates, and agglomerates. It is assumed that all who use these procedures will be trained analysts capable of performing

¹ These test methods are under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and are 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.

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

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 must be followed such as those described in Guide E882.

5. Reagents and Materials

5.1 *Purity of Reagents*—The purity of the common chemical reagents used shall conform to Practices E50. Special apparatus and reagents required are located in separate sections preceding the procedure.

6. Hazards

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

7. Sampling and Sample Preparation

7.1 The gross sample shall be collected and prepared in accordance with Practice E877.

7.2 The analytical sample shall be pulverized to pass a No. 100 (150- μ m) sieve.

NOTE 2—To facilitate decomposition some ores, such as specular hematites, may require grinding to pass a No. 200 (75- μ m) sieve.

TEST METHOD A—PYROPHOSPHATE (POTENTIOMETRIC) METHOD

8. Summary of Test Method

8.1 The test sample is decomposed by treatment with HCl, HNO₃, HF, and HClO₄. After the addition of sodium pyrophosphate and the adjustment of the acidity, the manganese is determined by oxidation to trivalent manganese with a standard solution of potassium permanganate. The end point is determined potentiometrically.

9. Interferences

9.1 Provision has been made for the removal of chromium which under some conditions is an interfering element.

10. Apparatus

10.1 *pH Meter*—A number of pH meters are commercially available. Many of these instruments can accept a variety of electrodes and therefore can be used also for potential measurements. Although both line- and battery-operated pH meters are manufactured, the former is recommended for laboratory work because this type of pH meter contains an electronic or transistorized potentiometer which makes the emf balancing operation entirely automatic. Electrometer tube input is used on both the electronic and transistorized pH meters.

10.1.1 The pH meter must have electrode standardization (or asymmetry potential) and manual or automatic temperature compensation controls. The dial must read in pH directly, and permit readings that are accurate to at least ± 0.01 pH unit. For higher accuracies it is recommended that a pH meter with an expanded scale be used.

10.1.2 Because there is no accurate method for determining the absolute potential of an individual electrode, two electrodes are used for pH measurements. These are called the reference and indicator electrodes. By international agreement the hydrogen electrode is the standard indicator electrode for pH, but is inconvenient to use and subject to several limitations. The most widely used reference electrode is the saturated calomel electrode. It is most often used as a pencil-type unit that is immersed directly in the solution, but may also be utilized as an external cell (to prevent possible contamination) contacting the solution by means of a salt bridge. The silver-silver chloride reference electrode is also convenient to use, but it is more difficult to prepare than the saturated calomel electrode. The mercurous sulfate reference electrode may be used in solutions in which the chloride ions that diffuse out of the calomel cell might be harmful.

10.1.3 The most commonly employed indicator electrode is the glass electrode. The quinhydrone and antimony-antimonous oxide electrodes are used to a much lesser extent. Combination electrodes containing both the indicator and reference units are also available. The tips of the electrodes containing solutions must be covered with rubber caps when the electrodes are disconnected from the meter and stored. When pH measurements are not being made the electrodes connected to the pH meter should be kept in a beaker containing water. Prior to measuring the pH of a solution the electrodes must be thoroughly washed with water especially if they have been left standing for a long period of time.

10.2 *Potentiometric Titration Apparatus*—Instruments for detecting the end points in pH (acid-base), oxidation-reduction, precipitation, and complexation titrations consist of a pair of suitable electrodes, a potentiometer, a buret, and a motor-driven stirrer. Titrations are based on the fact that when two dissimilar electrodes are placed in a solution there is a potential difference between them. This potential difference depends on the composition of the solution and changes as the titrant is added. A high-impedance electronic voltmeter follows the changes accurately. The end point of the titration may be determined by adding the titrant until the potential difference attains a predetermined value or by plotting the potential difference versus the titrant volume, the titrant being added until the end point has been passed.

10.2.1 An elaborate or highly sensitive and accurate potentiometer is not necessary for potentiometric titrations because the absolute cell voltage needs to be known only approximately, and variations of less than 1 mV are not significant. Such instruments should have a range of about 1.5 V and a readability of about 1 mV. Many of the pH meters are also suitable for potentiometric titrations.

10.2.2 The electrode system must consist of a reference electrode and an indicator electrode. The reference electrode maintains a constant, but not necessarily a known or reproducible potential during the titration. The potential of the indicator electrode does change during the titration; further, the indicator electrode must be one that will quickly come to equilibrium. A platinum indicator electrode and reference electrode are required for this method.

10.2.3 Initially, a titration of the constituent in question is performed manually, and the volumes of titrant added and the corresponding potential differences are noted. By use of established techniques the end point potential is determined. For the analytical determinations, titration may be continued to a preset potential, the end point being signaled by a null meter, with or without automatic termination of the titration. This technique is applicable to reasonably rapid reactions involving strong oxidants and reductants, precipitates not more soluble than silver chloride, and ionization constants greater than that of boric acid.

10.2.4 Other techniques may be used for both slow and fast reactions. These include automatic recording of the titration curve on a strip chart, and the recording of the titrant end point volume on a tape. In the latter, an adjustable print-out delay prevents undertitrating when the reaction is slow.

10.3 *Magnetic Stirrer*—Use of a TFE-fluorocarbon-covered stirring bar is recommended.

11. Reagents

11.1 *Hydrochloric Acid* (sp gr 1.19)—Concentrated.

11.2 *Hydrochloric Acid* (1 + 1)—Mix one volume of concentrated HCl (sp gr 1.19) with one volume of water.

11.3 *Hydrochloric Acid* (1 + 10)—Mix one volume of concentrated HCl (sp gr 1.19) with ten volumes of water.

11.4 *Hydrofluoric Acid* (48 %)—Concentrated.

11.5 *Hydrogen Peroxide* (3 %)—Mix one volume of concentrated hydrogen peroxide (H₂O₂, 30 %) with nine volumes of water.

11.6 *Nitric Acid* (sp gr 1.42)—Concentrated HNO₃ (1.42)—Concentrated.

11.7 *Perchloric Acid* (70 %).

11.8 *Potassium Permanganate, Standard Solution* (0.1 N).

11.8.1 *Preparation*—Dissolve 3.2 g of potassium permanganate (KMnO₄) in 1 L of water. Let stand in the dark for two weeks. Filter, without washing, through a Gooch crucible or a fine porosity fritted-glass crucible. Avoid contact with rubber or other organic material. Store in a dark-colored glass-stoppered bottle.

11.8.2 *Standardization*—Dry a portion of a sample of sodium oxalate at 105 °C. Transfer 0.3000 g of the sodium oxalate to a 600-L beaker. Add 250 mL of H₂SO₄ (5 + 95) previously boiled for 10 min to 15 min and then cooled to 27 °C ± 3 °C, and stir until the oxalate has dissolved. Add 39 mL to 40 mL (Note 3) of the KMnO₄ solution, at a rate of 25 mL/min to 35 mL/min, while stirring slowly. Let stand until the pink color disappears (about 45 s) (Note 4). Heat to 55 °C to 60 °C and complete the titration by adding KMnO₄ solution until a faint pink color persists for 30 s. Add the last 0.5 mL to 1 mL dropwise, allowing each drop to become decolorized before adding the next drop. To determine the blank: Titrate 250 mL of H₂SO₄ (5 + 95), treated as above, with KMnO₄ solution to a faint pink color. The blank correction is usually equivalent to 0.03 mL to 0.05 mL.

NOTE 3—A 0.3000-g portion of sodium oxalate requires 44.77 mL of KMnO₄ solution (0.1 N).

NOTE 4—If the KMnO₄ solution is too strong, the pink color will not fade at this point; begin again, adding a few millilitres less of the KMnO₄ solution.

11.9 *Potassium Permanganate, Standard Solution* (0.05 N) (Note 5)—Dilute one volume of 0.1 N potassium permanganate solution with one volume of water. Standardize using 0.1500 g of sodium oxalate as described under 11.8.2. Confirm the standardization against an ore of known manganese content by carrying the known sample through all steps of the procedure.

NOTE 5—The 0.05 normality of the potassium permanganate (KMnO₄) solution used (1.5803 g/L) is based on the usual valence change of manganese in acid solution from 7 to 2. In the test method described, the manganese in the sample is oxidized from Mn (II) to Mn (III) while the KMnO₄ is reduced from Mn (III) to Mn (VII). The factor 0.04395 mentioned in Section 13, therefore, is based on the following calculation: $\frac{4}{5} \times 0.05494$ (Mn equivalent of KMnO₄ in the (7 to 2) valence change).

11.10 *Sodium Carbonate* (Na₂CO₃).

11.11 *Sodium Hydroxide Solution* (200 g/L)—Dissolve 200 g of sodium hydroxide (NaOH) in 500 mL to 600 mL of water and dilute to 1 L.

11.12 *Sodium Pyrophosphate* (Na₄P₂O₇·10H₂O), *Saturated Solution*—This reagent shall be tested in the titration of a known amount of manganese. Only lots which rapidly provide steady potentials shall be used.

12. Procedure

12.1 Transfer approximately 0.5000 g of prepared sample to a small dry weighing bottle and place in a drying oven. After drying at ~~105 °C to~~ 110 °C (Note 6) 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 0.0001 g. Repeat the drying and weighing until there is no further weight loss. Transfer the test sample to a 600-mL beaker and reweigh the capped bottle to the nearest 0.0001 g. The difference between the two weights is the weight of the test sample.

NOTE 6—Most ores yield their hygroscopic moisture at the specified temperature. However, in the case of some ores, higher drying temperatures may be required.

12.2 Moisten the test sample with a few millilitres of water, add 20 mL of HCl, cover, and heat below boiling. When all soluble minerals are decomposed, add 10 mL of HNO₃, 4 mL to 5 mL of HF, and 15 mL of HClO₄ and evaporate without a cover to copious fumes of HClO₄. Cool, and rinse down the sides of the beaker and dissolve the salts in 10 mL of water (water, Note 7). ~~Cover and again evaporate to fumes of HClO₄ and fume strongly for 1 min. Withdraw the cover slightly and volatilize any chromium present by the drop-wise addition of HCl. When chromyl chloride has been expelled, as indicated by the absence of orange vapor on the addition of HCl, replace the cover and evaporate to about 3 mL or until the salts form on the bottom of the beaker. Cool, add 10 mL of HCl (1 + 1) and 1 mL of H₂O₂, and boil for about 5 min.~~

NOTE 7—At this point manganese, which may have separated as manganese dioxide (MnO₂), should be dissolved by the dropwise addition of H₂O₂. If any residue remains, dilute with 50 mL of hot water and filter the solution through a medium-texture paper. Wash alternately with HCl (1 + 10) and hot water until the paper is free of iron stain, and then with hot water until perchlorates are removed. Reserve the filtrate. Place the paper and residue in a platinum crucible. Dry and ignite to destroy all carbonaceous matter. Add 1 g of Na₂CO₃ to the crucible and fuse until a clear melt is obtained. Cool and dissolve the melt in a small amount of water containing 5 mL of HCl and a few drops of H₂O₂. Rinse and remove the crucible and add the solution to the reserved filtrate. Proceed with evaporation to fumes of HClO₄.

12.2.1 At this point manganese, which may have separated as manganese dioxide (MnO₂), should be dissolved by the dropwise addition of H₂O₂. If any residue remains, dilute with 50 mL of hot water and filter the solution through a medium-texture paper. Wash alternately with HCl (1 + 10) and hot water until the paper is free of iron stain, and then with hot water until perchlorates are removed. Reserve the filtrate. Place the paper and residue in a platinum crucible. Dry and ignite to destroy all carbonaceous matter. Add 1 g of Na₂CO₃ to the crucible and fuse until a clear melt is obtained. Cool and dissolve the melt in a small amount of water containing 5 mL of HCl and a few drops of H₂O₂. Rinse and remove the crucible and add the solution to the reserved filtrate.

12.2.2 Cover and again evaporate to fumes of HClO₄ and fume strongly for 1 min. Withdraw the cover slightly and volatilize any chromium present by the drop-wise addition of HCl. When chromyl chloride has been expelled, as indicated by the absence of orange vapor on the addition of HCl, replace the cover and evaporate to about 3 mL or until the salts form on the bottom of the beaker. Cool, add 10 mL of HCl (1 + 1) and 1 mL of H₂O₂, and boil for about 5 min.

12.3 To the solution add 250 mL to 300 mL of a cold, saturated solution of Na₄P₂O₇. Adjust the pH to 6.5 (using calomel and glass electrodes and a magnetic stirring device) with NaOH solution and HCl (1 + 1). The solution should be clear and colorless (colorless, Note 8). ~~If a~~ If at this point a pink coloration appears, the analysis must be repeated. If a precipitate forms, dilute further with the Na₄P₂O₇ solution until a clear solution is obtained, maintaining a pH of 6.5. Cool to 10 °C to 20 °C and titrate the manganese potentiometrically with the 0.05 N KMnO₄ solution. Add the titrant rapidly until the first deflection of the galvanometer is noted and then dropwise to the equivalence point. The drop giving the largest potential change shall be taken as the end point.

NOTE 8—~~If at this point a pink coloration appears, the analysis must be repeated.~~

TABLE 1 Precision Data

Average, ^A %	Relative Standard Deviation, ^B %	Number of Determinations	Number of Participating Laboratories
2.80	± 1.87	14	7
4.12	± 1.75	14	7
5.53	± 1.16	14	7
7.81	± 0.68	14	7
10.09	± 1.02	14	7

^A Each percentage represents a different kind of iron ore.

^B Relative Standard Deviation, *RSD*, in this test method is calculated as follows:

$$RSD = (100/\bar{X}) \sqrt{\sum d^2 / (n - 1)}$$

where:

\bar{X} = average, %,

d = difference of the determination from the mean, and

n = number of determinations, and in this case *n* = 7 as each value used is the average of two determinations from each laboratory.