Designation: E248 – 12

Standard Test Method for Determination of Manganese in Manganese Ores by Pyrophosphate Complexed Permanganate Potentiometric Titrimetry[1]

1. Scope

1.1 This definitive test method covers the determination of manganese in manganese ore in the range from 15 % to 60 %.

1.2 *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
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 test sample is decomposed by treatment with HCL, HNO_3, HF, and $HClO_4$. After the addition of sodium pyrophosphate and 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.

5. Significance and Use

5.1 This definitive test method is intended to be used as a referee method for compliance with compositional specifications for manganese 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 must be followed such as those described in Guide E882.

6. Interferences

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

7. Apparatus

7.1 *pH Meter* equipped with calomel and glass electrodes.

7.2 *Potentiometric Titration Apparatus* equipped with calomel and platinum electrodes. A suitable pH meter may be used for this purpose.

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

8. Reagents

8.1 *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.[3] Other grades may be used, provided it is first ascertained that the reagent is of

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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.

[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.

sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type I or II of Specification D1193. Type III or IV may be used if they effect no measurable change in the blank or sample.

8.3 *Hydrogen Peroxide (3 %)*—Mix 1 volume of concentrated hydrogen peroxide (H_2O_2, 30 %) with 9 volumes of water.

8.4 *Potassium Permanganate, Standard Solution (0.1 N)*

NOTE 1—The 0.1 normality of the $KMnO_4$ solution used (3.1606 g/L) is based on the usual valence change of manganese in acid solution from 7 to 2. In this test method, the manganese in the sample is oxidized from Mn(II) to Mn(III) while the $KMnO_4$ is reduced from Mn(VII) to Mn(III) The factor 0.0439 used in Section 12, therefore, is based on the following calculation: 4/5 × 0.05494 (Mn equivalent of $KMnO_4$ in 7 to 2 valence change).

8.4.1 *Preparation*—Dissolve 3.2 g of potassium permanganate ($KMnO_4$) in 1 L of water. Let stand in the dark for 2 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.

8.4.2 *Standardization*—Dry a portion of the National Institute of Standards and Technology (NIST) standard sample, or equivalent, of sodium oxalate at 105 °C. Transfer 0.3000 g of the sodium oxalate to a 600-mL beaker. Add 250 mL of H_2SO_4 (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 of the $KMnO_4$ solution (8.4.1), at a rate of 25 mL/min to 35 mL/min, while stirring slowly. Let stand until the pink color disappears (about 45 s). Heat to 55 °C to 60 °C and complete the titration by adding $KMnO_4$ solution (8.4.1), 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 H_2SO_4 (5 + 95), treated as above, with $KMnO_4$ solution (8.4.1) to a faint pink color. The blank correction is usually equivalent to 0.03 × 0.05 mL.

8.5 *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.

8.6 *Sodium Pyrophosphate*—($Na_4\,P_2O_7{\cdot}10H_2O$), *Saturated Solution*—This reagent shall be tested in the titration of a known amount of manganese and only lots which rapidly provide steady potentials shall be used.

9. Hazards

9.1 For precautions to be observed in this method, refer to Practice E50.

10. Sample Preparation

10.1 The laboratory sample shall be pulverized, if necessary, so that 100 % passes a No. 100 (150-µm) sieve.

11. Procedure

11.1 Transfer approximately 0.40 g (or 0.30 g if the manganese content exceeds 50 %) of the prepared sample to a small weighing bottle. Place into a drying oven and dry at 120 °C for 1 h. Cap the bottle and cool to room temperature in a desiccator. Loosen the stopper momentarily and weigh the capped bottle and test sample to the nearest 0.1 mg. Dry the test sample for an additional 30 min. Cap the bottle, cool in a desiccator, and reweigh. Repeat the drying and weighing until constant weight is obtained. Transfer the sample to a 600-mL beaker and reweigh the capped bottle to the nearest 0.1 mg. The difference between the last two weights is the mass of the sample.

11.2 To the 600-mL beaker add 10 mL of concentrated HCl, 10 mL of HNO_3, 4 mL to 5 mL of HF, and 10 mL of $HClO_4$ and heat to affect solution. Evaporate to fumes of $HClO_4$. Cool and rinse down the sides of the beaker. If complete decomposition has not been effected, add more HCl, HNO_3, and HF. Evaporate to fumes again and fume strongly (Note 1). Withdraw the cover slightly and volatilize any chromium present by dropwise addition of HCl. When chromyl chloride has been expelled, as evidenced by the disappearance of any orange vapor upon HCl addition, replace the cover and evaporate to a volume of 2 mL to 3 mL or until the first appearance of salt formation on the bottom of the beaker. Cool, add 10 mL of HCl (1 + 1), and 1 mL of H_2O_2, hydrogen peroxide (3 %) (8.3) and boil for 4 min to 5 min.

NOTE 2—In rare instances there may be a small amount of black residue at this point. If such is the case, the cool solution shall be diluted with water and the residue filtered on a small medium-texture paper and washed alternately with hot HCl (1 + 1) and hot water until perchlorates are removed. The paper and precipitate shall be placed in a platinum crucible, inserted into a muffle furnace, and heated to destroy the carbonaceous matter. The residue shall then be fused with a minimum amount of sodium carbonate, cooled, and dissolved in a little water. The solution of this melt shall then be added to the filtrate and the solution again evaporated to fumes of $HClO_4$.

11.3 To the test solution add 250 to 300 mL of a cold saturated solution of $Na_4P_2O_7$. Adjust the pH to 6.5 (using calomel and glass electrodes on the pH meter and a magnetic stirring device) with NaOH solution (8.5) and HCl. The test solution should be clear and colorless. If a precipitate forms, dilute further with the $Na_4P_2O_7$ solution (8.6) until a clear solution is obtained, maintaining a pH of 6.5. Cool from 10 °C to 20 °C and titrate the manganese potentiometrically with the 0.1 *N* $KMnO_4$ solution (8.4). 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 3—If any pink coloration in the solution is evident at this point, the sample shall be discarded and the analysis repeated.

12. Calculation

12.1 Calculate the percentage of manganese as follows (Note 1):

$$Manganese,\ \% = \frac{4.3965AB}{C}$$

where:

A = $KMnO_4$ solution (8.4) required for titration of the sample, mL

B = normality of the $KMnO_4$ solution (8.4), and

C = sample used, g.

13. Precision and Bias[4]

13.1 *Precision*—Six laboratories cooperated in testing this test method and obtained the data summarized in Table 1.

13.2 *Bias*—The bias of this test method may be judged by comparing accepted reference values with the corresponding arithmetic average obtained by interlaboratory testing. The *h* and *k* statistical values computed by Practice E691 did not exceed a critical value, which would have suggested a bias in the results of a participating laboratory. All of the data seem consistent, and there is no evidence that the test method gave biased results.

TABLE 1 Statistical Information—Manganese—Titrimetric Method

Test Material	Mn Found, %	*r*, E691	*R*, E691
Mn Ore (CMSI No. 1721, 27.74 % Mn)	27.60	0.44	0.63
Mn Ore (NIST SRM 25c, 57.85 % Mn)	57.69	0.23	0.57

14. Keywords

14.1 manganese content; manganese ores; titrimetry

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[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1033.

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