GB

NATIONAL STANDARD OF THE

PEOPLE'S REPUBLIC OF CHINA

ICS 73.060.20
D 32

GB/T 1506-2016

Replacing GB/T 1506-2002

Manganese ores - Determination of manganese content - Potentiometric method and ammonium iron (II) sulphate titrimetric method

Issued on: August 29, 2016 **Implemented on: July 01, 2017**

Issued by: General Administration of Quality Supervision, Inspection and Quarantine;

Standardization Administration of PRC.

Table of Contents

Foreword

This standard was drafted in accordance with the rules given in GB/T 1.1-2009.

This standard replaces GB/T 1506-2002 “Manganese ores - Determination of manganese content - Potentiometric method and ammonium iron (II) sulphate titrimetric method”.

As compared with GB/T 1506-2002, the main technical changes are as follows:

- ADD the content of normative references;
- MODIFY the expression of requirements for the reagents and water used;
- ADD the contents of the reagents used;
- ADD the provisions on the number of determinations;
- MODIFY the operational statement of the blank value determination;
- MODIFY the added water volume for the preparation of N-phenyl anthranilic acid indicator solution (0.2 g/L);
- MODIFY the operational statement of the dissolution of the sample by ammonium nitrate oxidation;
- MODIFY the operational statement of the dissolution of the sample by perchloric acid oxidation;
- MODIFY the amount of nitric acid added when the sample is dissolved by perchloric acid oxidation;
- ADD notes on the applicability of the two sample dissolution methods;
- MODIFY the operational statement before titration with ammonium ferrous sulfate standard solution;
- ADD the acceptance of the analytical value of the standard sample;
- ADD the calculation of the final result;
- ADD the requirements for the test report;
- ADD Appendix A.

This standard was proposed by the China Iron and Steel Association.

This standard shall be under the jurisdiction of the National Standards

Manganese ores - Determination of manganese content - Potentiometric method and ammonium iron (II) sulphate titrimetric method

Warning - The personnel using this standard shall have practical experience in formal laboratory work. This standard does not address all possible safety issues. It is the responsibility of the user to take appropriate safety and health measures and to ensure compliance with the conditions set by the relevant national regulations.

1 Scope

This standard specifies the determination of manganese in manganese ore by potentiometric method and ammonium iron (II) sulphate titrimetric method.

This standard is applicable to the determination of manganese content in manganese ore and manganese concentrates with vanadium content (mass fraction) not more than 0.05%, the determination range (mass fraction) is as follows: manganese content of potentiometric titration ≥ 15.00%; manganese content of ammonium iron (II) sulphate titrimetric method is 8.00% ~ 60.00%.

2 Normative references

The following documents are essential to the application of this document. For the dated documents, only the versions with the dates indicated are applicable to this document; for the undated documents, only the latest version (including all the amendments) are applicable to this standard.

GB/T 2011 Method of sampling and sample preparation of manganese ores in bulk

GB/T 6682 Water for analytical laboratory use - Specification and test methods

GB/T 8170 Rules of rounding off for numerical values & expression and judgement of limiting values

GB/T 14949.8 Method for chemical analysis of manganese ore - Determination of moisture storage

into the filter type crucible with glass core, PERFORM suction filtering on a suction device. REPEAT the crystallization process.

After sufficient suction filtration, TRANSFER the obtained crystals to a glass dish or a porcelain dish, ALLOW it to air dry in the dark, PAY attention to avoid dust. USE a glass rod to grind it. When the crystal is no longer in a block, PLACE it in a drying oven at 80 °C ~ 100 °C to dry it for 2 h ~ 3 h, then PUT it in a brown glass bottle. PERFORM recrystallization to obtain the manganese content (mass fraction) of potassium permanganate, which is 34.76%.

3.2.12 Manganese standard solution:

WEIGH 10 g of electrolytic manganese (purity greater than 99.95%) in a 400 mL beaker, ADD 50 mL of water and 5 mL of nitric acid (ρ = 1.42 g/mL), LEAVE for a few minutes until the manganese surface becomes bright. USE water to wash it for 6 times, then USE acetone to wash it, DRY it at 100 °C for 10 min.

WEIGH 1.0000 g of the treated manganese in a 400 mL beaker, ADD 20 mL of sulfuric acid (1 + 1) and about 100 mL of water. BOIL the solution until it is clear, COOL it down, TRANSFER it into a 1000 mL volumetric flask, USE water to dilute it to the mark, MIX it uniformly. This solution contains 1.00 mg of manganese per millimeter.

3.2.13 Potassium permanganate standard titration solution, $c(1/5\ KMnO_4) \approx 0.1$ mol/L

3.2.13.1 Preparation

WEIGH 3.20 g of potassium permanganate, DISSOLVE it in 1000 mL of water, PLACE it for 6 d, USE glass wool or filter glass with glass sand core to filter it into a brown glass bottle, MIX it uniformly.

3.2.13.2 Calibration

3.2.13.2.1 Calibration with manganese standard solution

PIPETTE 100.00 mL of manganese standard solution (see 3.2.12) in a 500 mL beaker, ADD 250 mL of sodium pyrophosphate solution (see 3.2.9) whilst stirring it, USE hydrochloric acid (see 3.2.7) or sodium carbonate solution (see 3.2.8) to adjust the pH of the solution to 7.0 [USE the pH meter or bromothymol blue indicator (see 3.2.14) to check the pH value]. On the potentiometric titrator (see 3.3.2), USE potassium permanganate standard titration solution (see 3.2.13) to titrate it, until the potentiometric titrator (see 3.3.2) has obvious potential sharp change or pointer deflection, as the end point.

PERFORM blank determination together with the calibration.

USE the formula (1) to calculate the titer T_1 of manganese in the potassium

4.2.1 Ammonium nitrate, solid.

4.2.2 Phosphoric acid, ρ = 1.70 g/mL.

4.2.3 Nitric acid, ρ = 1.42 g/mL.

4.2.4 Hydrochloric acid, ρ= 1.19 g/mL.

4.2.5 Perchloric acid, ρ = 1.67 g/mL.

4.2.6 Sulfuric acid, 1 + 1.

4.2.7 Sulfuric acid, 5 + 95.

4.2.8 Sulfuric acid, 1 + 4.

4.2.9 Potassium dichromate standard solution [c (1/6 $K_2Cr_2O_7$) = 0.04000 mol/L]: WEIGH 1.9615 g of reference potassium dichromate (pre-dried at 150 °C for 2 h and cooled to room temperature in a desiccator), PLACE it in a 250 mL beaker, ADD an appropriate amount of water to dissolve it, TRANSFER it into a 1000 mL volumetric flask. USE water to dilute it to the mark, MIX it uniformly.

4.2.10 Ammonium ferrous sulfate standard titration solution, c [$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$] ≈ 0.040 mol/L.

4.2.10.1 Preparation

WEIGH 15.68 g of ammonium iron (II) sulphate, DISSOLVE it in 1000 mL of sulfuric acid (5 + 95) solution, MIX it uniformly.

4.2.10.2 Calibration

PIPETTE 25.00 mL of potassium dichromate standard solution (see 4.2.9) into a 250 mL conical flask, ADD 40 mL of sulfuric acid (see 4.2.8) and 5 mL of phosphoric acid (see 4.2.2), USE the ammonium iron (II) sulphate standard titration solution (see 4.2.10) to titrate it until the orange color disappears, ADD 2 drops of the N-benzoanthranilic acid indicator solution (see 4.2.11), CONTINUE adding it until the solution becomes green, which is the end point.

CALCULATE the titer T_3 of manganese in the ammonium iron (II) sulphate standard titration solution in accordance with formula (5), in grams per milliliter (g/mL):

$$T_3 = \frac{c \times V_7 \times m_4 \times 10^{-3}}{V_8 - V_9} \qquad \cdots\cdots(5)$$

Where:

c - The concentration of potassium dichromate standard solution, in moles

WEIGH 0.20 g of the air-dried sample to the nearest 0.0001 g. DETERMINE the wet moisture content in accordance with GB/T 14949.8 whilst weighing the sample.

4.5.3 Blank test

PERFORM the blank test along with the sample, MAKE titration in accordance with 4.2.10.3, DO not add sulfuric acid and phosphoric acid, RECORD V_{12}.

4.5.4 Determination

4.5.4.1 PLACE the sample (see 4.5.2) (when the sample contains a large amount of carbon and organic matter, PLACE the sample in a porcelain crucible and BURN it at 700 °C for 10 min) in a 250 mL conical flask, USE a small amount of water to wet the specimen, SHAKE it carefully to scatter the specimen. Based on the manganese content, SELECT one of the following methods for operation:

4.5.4.1.1 Ammonium nitrate oxidation method

ADD 5 mL of sulfuric acid (see 4.2.6), SHAKE it uniformly. ADD 20 mL of phosphoric acid (see 4.2.2), SHAKE it uniformly. Then HEAT to dissolve it, after it is slightly boiling, ADD 3 mL ~ 5 mL of nitric acid (see 4.2.3), CONTINUE heating to oxidize carbon and organic matter, after the large bubble and yellow smoke disappear and the surface is calm, HEAT to make the sulfur trioxide produce white smoke for 3 min ~ 5 min (the white smoke release duration is related to the temperature of the electric furnace, generally about 5 minutes on the 1000 W electric furnace). REMOVE it, when observing the appearance of slight white smoke in the flask, immediately ADD 2 g ~ 3 g of ammonium nitrate (see 4.2.1) (the temperature at which the ammonium nitrate is added shall be between 220 °C and 240 °C), fully SHAKE the conical flask whilst adding it to completely oxidize the divalent manganese, DRIVE off the yellow nitrous oxide gas (which can be blown by the rubber suction bulb).

Note: This method is suitable for samples with a manganese content of less than 25%.

4.5.4.1.2 Perchloric acid oxidation

ADD 5 mL of hydrochloric acid (see 4.2.4), SHAKE it uniformly. ADD 20 mL of phosphoric acid (see 4.2.2), SHAKE it uniformly. Then HEAT to dissolve it to slight boiling, ADD 5 mL of nitric acid (see 4.2.3) while it is hot, SHAKE it in the process of addition, after addition, SHAKE the conical flask sufficiently to destroy the carbon and organic matter, HEAT it to the occurrence of slight phosphoric acid smoke (the liquid level is calm). TAKE it off, ADD 2 mL of perchloric acid (see 4.2.5), SHAKE it in the process of addition, HEAT it until the solution level is calm to completely oxidize the divalent manganese, TAKE

This is an excerpt of the PDF (Some pages are marked off intentionally)

------ The End ------