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Manganese ores - Determination of calcium and magnesium contents - EDTA titrimetric method

锰矿石 钙和镁含量的测定 EDTA 滴定法

(ISO 6233:1983, Manganese ores and concentrates - Determination of calcium and magnesium contents - EDTA titrimetric method, MOD)

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Manganese ores - Determination of calcium and magnesium contents - EDTA titrimetric method

WARNING – The personnel who uses this Standard shall have hands-on experience in formal laboratory work. This Standard does not address all possible security issues. It is the responsibility of the user to take appropriate safety and health measures and to ensure compliance with the conditions which are set by the relevant national regulations.

1 Scope

This Standard specifies the determination of calcium and magnesium contents in manganese ores by EDTA titration.

This Standard applies to the determination of calcium and magnesium contents in manganese ores. The determination range (mass fraction): 0.75% ~ 18.00% for calcium, and 1.50% ~ 6.00% for magnesium.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

GB/T 2011, Method of sampling and sample preparation of manganese ores in bulk (GB/T 2011-1987,neq ISO 3081:1983)

GB/T 6682, Water for analytical laboratory use - Specification and test methods (GB/T 6682-2008, ISO 3696:1987, MOD)

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

GB/T 14949.8, Manganese ores - Determination of hygroscopic moisture content - Gravimetric method (GB/T 14949.8-1994, eqv ISO 310:1981)

3 Principle

For the sample, use acid to decompose, and use sodium carbonate to melt the residue; use hexamethylenetetramine and copper reagent to dissolve the

interfering elements such as manganese, iron, aluminum, titanium, copper, nickel, vanadium and chromium. Divide part of the test solution in a solution of pH≥12; in the presence of calcein indicator, use EDTA standard solution to titrate calcium content; take another part of the solution in a solution of pH=10; use chrome black T as indicator; use EDTA standard titration solution for titration of calcium and magnesium contents.

4 Reagents and materials

In the analysis process, only use the approved analytical reagents and water of grade 3 and above in accordance with the provisions of GB/T 6682.

4.1 Anhydrous sodium carbonate, solid.

4.2 Nitric acid, ρ = 1.42 g/mL.

4.3 Hydrochloric acid, ρ = 1.19 g/mL.

4.4 Hydrofluoric acid, ρ = 1.15 g/mL.

4.5 Sulfuric acid, ρ = 1.84 g/mL.

4.6 Ammonia, ρ = 0.91 g/mL.

4.7 Sulfuric acid, 1+1.

4.8 Hydrochloric acid, 1+1.

4.9 Hydrochloric acid, 1+4.

4.10 Hydrochloric acid, 1+50.

4.11 Potassium hydroxide, 200 g/L, stored in a plastic bottle.

4.12 Sodium diethyldithiocarbamate, 100 g/L. It is abbreviated as copper reagent solution, and prepared when used.

4.13 Sucrose solution: 40 g/L.

4.14 Ammonium sulfate solution, 50 g/L.

4.15 Hexamethylenetetramine solution, 100 g/L.

4.16 Buffer solution, pH = 10. Weigh 35 g of ammonium chloride and dissolve it in 200 mL of ammonia water (ρ = 0.91 g/mL); use water to dilute to 500 mL; mix well.

4.22 Calcein indicator, calcein: thymolphthalein: sodium chloride = 1:1:100, mixed and ground finely.

5 Instruments

Laboratory instruments and equipment which are commonly used in the analysis.

6 Sampling

Take and prepare samples according to the provisions of GB/T 2011; the particle size of the sample shall be no more than 0.080 mm.

7 Analysis steps

7.1 Number of analyses

Perform at least two repeatability analyses on the same sample.

7.2 Sample mass

Weigh 0.50 g of air-dried sample, accurate to 0.000 1 g. According to GB/T 14949.8, determine the moisture content at the same time.

7.3 Blank test

Perform a blank test along with the sample.

7.4 Determination

7.4.1 Put the sample (see 7.2) in a 250 mL beaker; add 15 mL ~ 20 mL of hydrochloric acid (see 4.3); after heating to dissolve the sample, add 10 mL of nitric acid (see 4.2) and heat until no small bubbles are generated; remove and cool; then, add 10 mL of sulfuric acid (see 4.7); heat at low temperature until sulfuric acid smoke is emitted; remove and cool.

7.4.2 Add 10 mL ~ 15 mL of hydrochloric acid (see 4.3); heat for 3 min ~ 5 min to dissolve salts; add 30 mL ~ 40 mL of hot water; heat to boil; cool; use a fast filter paper containing pulp to filter; use hydrochloric acid (see 4.10) to wash the residue and filter paper 3 ~ 4 times; then, use hot water to wash 3 ~ 4 times; retain the filtrate; steam the filtrate to about 100 mL.

7.4.3 Transfer the filter paper with the residue into a platinum crucible; dry and carbonize at low temperature; then, put it at 500 °C ~ 600 °C for ashing; take it out to cool slightly; use 2 ~ 3 drops of water to wet the residue; add 2 ~ 3 drops

of sulfuric acid (see 4.7), 5 mL ~ 7 mL of hydrofluoric acid (see 4.4); heat and evaporate to dryness; burn at 500 °C ~ 600 °C; after cooling, add 1 g ~ 2 g of anhydrous sodium carbonate (see 4.1) to melt at 900 °C ~ 1 000 °C for 5 min; cool; add dropwise hydrochloric acid (see 4.8) in portions; heat until the frit is separated from the platinum crucible; combine this solution with the main solution (see 7.4.2).

7.4.4 Boil the mixed solution (see 7.4.3) to 40 mL ~ 50 mL; add ammonia water (see 4.6) dropwise and shake until stable ferric hydroxide precipitate appears; use hydrochloric acid (see 4.8) to dissolve until the precipitate just disappears. When neutralizing the blank test solution, the amount of ammonia water (see 4.6) and hydrochloric acid (see 4.8) used shall be the same as the consumption of the test solution. Add 5 mL of ammonium sulfate solution (see 4.14); add 30 mL of hexamethylenetetramine solution (see 4.15); heat the solution to 80 °C ~ 90 °C in a water bath, and keep it for 15 min ~ 20 min; cool it down; add 80 mL of copper reagent solution (see 4.12); transfer it into a 200 mL volumetric flask; use water to dilute it to the mark; mix well; use a double-layer medium-speed filter paper to filter it in a dry 500 mL conical flask; discard the initial filtrate. If the solution is heavily cloudy, use the double-layer filter paper to filter it once more.

7.4.5 Pipette 50.00 mL of filtrate (see 7.4.4) in two parts into 250 mL conical flasks, and one part is used for titration of calcium content. Use water to dilute to a volume of about 150 mL; add 5 mL of sucrose solution (see 4.13); add 1 drop ~ 2 drops of malachite green solution (see 4.20); the solution is blue-green at this time; then, use potassium hydroxide solution (see 4.11) to adjust the solution to colorless, and exceed for 10 mL; add an appropriate amount of calcein indicator (see 4.22); use EDTA standard titration solution (see 4.19) to titrate until the green fluorescence in the solution disappears as the end point. The other is used to titrate the combined calcium and magnesium contents. Use water to dilute to about 150 mL; add 15 mL of buffer solution (see 4.16); add an appropriate amount of chrome black T indicator (see 4.21); use EDTA standard titration solution (see 4.19) to titrate until the solution changes from wine red to pure blue as the end point.

8 Calculation of analysis results

8.1 Calculation of calcium content

Calculate the calcium content (mass fraction) w_{Ca} in the sample according to Formula (3); express in %:

$$w_{Ca} = \frac{(V_7 - V_8) \times T_2}{m_1 \times r} \times 100 \times \frac{100}{100 - A} \quad \cdots\cdots (3)$$

Where:

y – assay value of the standard sample;

μ_0 – determined standard value of the standard sample;

k_3 – 0.7, critical difference coefficient;

R – allowable difference.

If the assay value of the standard sample does not meet Formula (7), it needs to be re-analyzed together with the sample.

If the range of the two values of the sample exceeds the allowable difference limits that are given in Table 1 and Table 2, one or more additional analyses shall be performed simultaneously with the standard sample of the same type of ore according to the flow chart in Appendix A.

In any case, the acceptability of the assay value of the test sample shall depend on the acceptability of the analytical value of the standard sample.

8.4.3 Calculation of the final result

The final result is the arithmetic mean of the acceptable values of the sample, or the final result that is obtained by operating in accordance with the procedures specified in Appendix A. The rounding of numerical values shall be carried out in accordance with the provisions of GB/T 8170, and the result shall be rounded to two decimal places.

9 Test report

The test report shall include the following contents:

a) name and address of the testing laboratory;

b) date of release of the test report;

c) number of this Standard;

d) the necessary detailed description of the sample itself;

e) analysis results;

f) any abnormal characteristics in the determination process and any operations that may affect the analysis results of the sample or standard sample that are not specified in this Standard.

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