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Manganese sulfate for battery materials

电池用硫酸锰

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Manganese sulfate for battery materials

1 Scope

This document specifies the classification, requirements, test methods, inspection rules, marking and accompanying documents, packaging, transportation, storage of manganese sulfate for batteries.

This document is applicable to manganese sulfate for batteries.

Note: This product is mainly used to prepare precursors for positive electrode materials of secondary lithium batteries (nickel-cobalt-manganese ternary composite hydroxides, nickel-manganese ternary hydroxides, etc.); it can also be used to manufacture other manganese salts.

2 Normative references

The contents of the following documents constitute essential clauses of this document through normative references in the text. For dated references, only the version corresponding to that date applies to this document; for undated references, the latest version (including all amendments) applies to this document.

GB/T 191-2008 Packaging - Pictorial marking for handling of goods

GB/T 6003.1-2022 Test sieves - Technical requirements and testing - Part 1: Test sieves of metal wire cloth

GB/T 6678 General principles for sampling chemical products

GB/T 6682-2008 Water for analytical laboratory use - Specification and test methods

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

HG/T 2962-2010 Manganous sulphate for industrial use

HG/T 3696.1 Inorganic chemicals for industrial use - Preparations of standard and reagent solutions for chemical analysis - Part 1: Preparations of standard volumetric solutions

HG/T 3696.2 Inorganic chemicals for industrial use - Preparations of standard and reagent solutions for chemical analysis - Part 2: Preparations of standard solutions for impurity

cadmium (Cd), chromium (Cr), potassium (K), sodium (Na), calcium (Ca), magnesium (Mg), nickel (Ni), cobalt (Co), aluminum (Al) prepared according to HG/T 3696.2. Place them in a 100 mL volumetric flask. Use nitric acid solution to dilute it to the mark (see 7.4.2.2). Shake well.

It can also use solutions of certified series of national standard substances for accurate dilution.

The solution is prepared before use.

7.4.2.4 Water: Meet the grade 2 water specifications in GB/T 6682-2008.

7.4.3 Instruments and equipment

Inductively coupled plasma emission spectrometer.

7.4.4 Test steps

7.4.4.1 Drawing of working curve

Pipette 0.00 mL, 1.00 mL, 2.00 mL, 4.00 mL, 8.00 mL, 12.00 mL of the mixed standard solution respectively. Place in six 100 mL volumetric flasks. Use nitric acid solution to dilute it to the mark (see 7.4.2.2). Shake well.

Adjust the inductively coupled plasma emission spectrometer to the optimal working conditions. Introduce the above standard solution into the inductively coupled plasma emission spectrometer. Analyze the spectral line wavelength as shown in Appendix A or select according to the instrument manual. Determine the spectral intensity of each element to be measured in the standard solution. Use the mass concentration ($\mu\text{g/mL}$) of the element to be measured in the standard solution as the abscissa and the corresponding spectral intensity as the ordinate, to draw the working curve of each element to be measured.

7.4.4.2 Preparation of test solution

7.4.4.2.1 Preparation of test solution for solid specimen

Weigh about 1.0 g (accurate to 0.0002 g) of the specimen. Place it in a 100 mL beaker. Moisten it with a small amount of water. Add 4 mL of nitric acid solution (see 7.4.2.1). Cover with a watch glass. Heat at low temperature until almost dry. After cooling, add a small amount of water to dissolve. Transfer the solution into a 100 mL volumetric flask. Use water to dilute to the mark. Shake well. Dilution can be performed if necessary, depending on the sample and instrument conditions.

7.4.4.2.2 Preparation of test solution for liquid specimen

Take 5.00 mL of the specimen. Place it in a 100 mL volumetric flask. Add 4 mL of nitric acid solution (see 7.4.2.1). Use water to dilute to the mark. Shake well. Dilution can be

p_i - The mass concentration of the element to be determined in the test solution found from the working curve, in micrograms per milliliter ($\mu\text{g/mL}$);

p_0 - The mass concentration of the element to be determined in the blank test solution found from the working curve, in micrograms per milliliter ($\mu\text{g/mL}$);

V - The volume of the liquid sample to be transferred, in milliliters (mL).

The arithmetic mean of the parallel determination results is taken as the determination result; the absolute difference between the two parallel determination results is not greater than 20% of the arithmetic mean.

7.5 Determination of lead content - Atomic absorption method (arbitration method)

7.5.1 Reagents or materials

7.5.1.1 Chloroform.

7.5.1.2 Hydrochloric acid.

7.5.1.3 Nitric acid.

7.5.1.4 Nitric acid solution: 2 + 98.

7.5.1.5 Sodium hydroxide solution: 250 g/L.

7.5.1.6 Ammonium pyrrolidine dithiocarbamate (APDC) solution: 20 g/L.

Filter before use.

7.5.1.7 Lead standard solution: 1 mL of solution contains 0.010 mg of lead (Pb).

Pipette 1.00 mL of the lead (Pb) standard solution prepared according to HG/T 3696.2 into a 100 mL volumetric flask. Use nitric acid solution to dilute it to the mark. Shake well.

It can also use the solution of the certified series of national standard substances for accurate dilution.

The solution is prepared before use.

7.5.1.8 Water: Meet the grade 2 water specification in GB/T 6682-2008.

7.5.2 Instruments and equipment

Atomic absorption spectrophotometer: Equipped with a lead hollow cathode lamp.

7.5.3 Test steps

7.6.1.2.1 Ethanol.**7.6.1.2.2 Nitric acid solution: 1+1.****7.6.1.2.3 Silver nitrate solution: 17 g/L.****7.6.1.2.4 Chloride standard solution: 1 mL of solution contains 0.02 mg of chlorine (Cl).**

Use a pipette to transfer 2 mL of the chloride (as Cl) standard solution prepared according to HG/T 3696.2. Place it in a 100 mL volumetric flask. Use water to dilute to the mark. Shake well.

This solution is prepared immediately before use.

7.6.1.3 Instruments and equipment

Visible spectrophotometer: Equipped with a 2 cm cuvette.

7.6.1.4 Test steps**7.6.1.4.1 Drawing of working curve**

Pipette 0.00 mL, 0.50 mL, 1.00 mL, 2.00 mL, 3.00 mL, 4.00 mL of chloride standard solution. Place them in six 50 mL volumetric flasks respectively. Add 5 mL of nitric acid solution and 2 mL of silver nitrate solution in turn. Then add 1 mL ~ 2 mL of ethanol. Use water to dilute it to the mark. Shake well. Place in the dark for 10 min.

Pipette part of the solution into a 2 cm cuvette. Use water as a reference, to measure its absorbance at a wavelength of 380 nm on the spectrophotometer. Draw a working curve with the mass concentration of chlorine as the abscissa and the absorbance as the ordinate.

7.6.1.4.2 Preparation of test solution**7.6.1.4.2.1 Preparation of solid specimen test solution**

Weigh 2.5 g (accurate to 0.0002 g) of solid specimen. Dissolve it in water. Transfer it to a 100 mL volumetric flask. Use water to dilute it to the mark. Shake it well. Dry filter the solution with medium-speed quantitative filter paper. Discard the initial filtrate. Retain the middle filtrate.

Pipette 5.00 mL of filtrate respectively and place it in two 50 mL volumetric flasks. Add 5 mL of nitric acid solution and 1 mL ~ 2 mL of ethanol to one part. Use water to dilute it to the mark. Shake well. Use it as a reagent blank solution. Place it in a dark place for 10 min. Add 5 mL of nitric acid solution and 2 mL of silver nitrate solution to the other part. Then add 1 mL ~ 2 mL of ethanol. Use water to dilute it to the mark. Shake well. Place it in a dark place for 10 min.

ρ_1 - The mass concentration of chlorine in the test solution found from the working curve, in micrograms per milliliter ($\mu\text{g/mL}$);

ρ_0 - The mass concentration of chlorine in the blank test solution found from the working curve, in micrograms per milliliter ($\mu\text{g/mL}$);

V - The volume of the liquid sample transferred, in milliliters (mL).

The arithmetic mean of the parallel determination results is taken as the determination result. The absolute difference between the two parallel determination results shall not exceed 20% of the arithmetic mean.

7.6.2 Ion chromatography

7.6.2.1 Principle

The specimen is dissolved in water, separated by anion exchange column using an ion chromatograph, detected by suppressed conductivity method, quantified by external standard method (peak area/peak height). The mass concentration of chlorine is found from the working curve and its content is calculated.

7.6.2.2 Reagents or materials

7.6.2.2.1 Water: Deionized water with a resistivity (25 °C) of not less than 18.2 M Ω ·cm.

7.6.2.2.2 Chloride standard solution: 1 mL of solution contains 50 μg of chlorine (Cl).

Take 5.00 mL of the chloride (as Cl) standard solution prepared according to HG/T 3696.2. Place it in a 100 mL volumetric flask. Use water to dilute to the mark. Shake well.

7.6.2.3 Instruments and equipment

7.6.2.3.1 Ion chromatograph: Equipped with conductivity detector.

7.6.2.3.2 Microporous filter membrane: Recommended pore size 0.22 μm ~ 0.45 μm .

7.6.2.3.3 Chromatographic column: Anion chromatographic column, where the separation between the detected anion and the adjacent ion R is ≥ 1.5 .

7.6.2.4 Test steps

7.6.2.4.1 Drawing of working curve

Pipette 0.00 mL, 0.50 mL, 1.00 mL, 2.00 mL, 4.00 mL, 5.00 mL of chloride standard solution into six 100 mL volumetric flasks. Use water to dilute it to the mark. Shake well. Pass this series of standard solutions through the microporous filter membrane in order from low to high mass concentration. Discard the initial 10 mL of filtrate.

7.8 pH determination

7.8.1 Instruments and equipment

Acidity meter: The graduation value is 0.1 pH unit; it is equipped with pH electrode and calomel electrode.

7.8.2 Test steps

Solid product: Determine according to the method specified in 5.8 of HG/T 2962-2010.

Solution product: Take 50 mL of liquid specimen. Place it in a dry beaker. Determine the pH with an acidity meter.

7.9 Determination of fineness

7.9.1 Instruments and equipment

Test sieve: $\phi 200 \times 50-0.4/0.25$ GB/T 6003.1-2022, equipped with sieve cover and sieve bottom.

7.9.2 Test steps

Weigh about 50 g of specimen. Place it in the test sieve. Install the sieve cover and sieve bottom. Perform manual sieving. If there is no residue on the sieve, it means that all the samples have passed.

7.10 Determination of silicon content

7.10.1 Principle

The specimen is treated with sulfuric acid. The silicic acid and ammonium molybdate generate silicomolybdic heteropoly acid. Hydrofluoric acid is added to dissolve silicon and eliminate the influence of some impurities. Ammonium ferrous sulfate is used to reduce and generate silicon-molybdenum blue. The absorbance is measured at a wavelength of 810 nm on a spectrophotometer.

7.10.2 Reagents or materials

7.10.2.1 Sulfuric acid solution: 6+94.

7.10.2.2 Hydrofluoric acid solution: 1+9.

7.10.2.3 Ammonium molybdate solution: 75 g/L.

Weigh 75 g of ammonium molybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$. Dissolve in warm water. Cool and dilute to 1000 mL with water. Filter before use.

7.10.2.4 Ammonium ferrous sulfate solution: 150 g/L.

Weigh 150 g of ammonium ferrous sulfate $[(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}]$. Dissolve in 500 mL of water. Add 100 mL of sulfuric acid solution (1+9). Use water to dilute to 1000 mL. Shake well.

7.10.2.5 Silicon standard solution: 1 mL of solution contains 0.010 mg of silicon (Si).

Pipette 1.00 mL of silicon (Si) standard solution prepared according to HG/T 3696.2. Place it in a 100 mL plastic volumetric flask. Use water to dilute it to the mark. Shake well.

The solution is prepared immediately before use.

7.10.3 Instruments and equipment

7.10.3.1 Spectrophotometer: Equipped with a cuvette which has a pathlength of 3 cm.

7.10.3.2 Constant temperature water bath: The temperature can be controlled at $50\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$.

7.10.3.3 Beaker: Made of polytetrafluoroethylene.

7.10.3.4 Volumetric flask: Made of polytetrafluoroethylene.

7.10.4 Test steps

7.10.4.1 Drawing of working curve

Pipette 0.00 mL, 1.00 mL, 2.00 mL, 4.00 mL, 8.00 mL, 12.00 mL of silicon standard solution respectively. Place in six 100 mL volumetric flasks. Add 9 mL of sulfuric acid solution respectively. Use water to dilute it to about 40 mL. Place in a $50\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ constant temperature water bath. After 5 minutes, add 10 mL of ammonium molybdate solution while shaking. Use a small amount of water, to rinse the ammonium molybdate solution attached to the inner wall of the bottle. Keep warm in a $50\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ constant temperature water bath for 5 minutes. Shake from time to time. Remove and cool to room temperature with running water. Add 15 mL of hydrofluoric acid solution. Mix well. Add 5 mL of ammonium ferrous sulfate solution within 30 seconds. Mix well. Use water to dilute to the mark. Let stand for 15 minutes.

Transfer to a set of cuvettes. Use the blank solution as a reference, to measure its absorbance at a wavelength of 810 nm. Draw a working curve with the mass concentration of silicon (mg/L) as the abscissa and the absorbance as the ordinate.

7.10.4.2 Preparation of test solution

7.10.4.2.1 Preparation of solid specimen test solution

Weigh about 2.0 g (accurate to 0.0002 g) of solid specimen. Place it in a 200 mL beaker. Add 50 mL of water. Cover with a watch glass. Heat at low temperature in a water bath

Pipette 1.00 mL of fluorine standard solution prepared according to HG/T 3696.2. Place it in a 100 mL volumetric flask. Use water to dilute it to the mark. Shake well.

The solution is prepared before use.

7.11.1.2.6 Bromocresol green indicator: 1 g/L.

7.11.1.3 Instruments and equipment

7.11.1.3.1 Fluoride ion selective electrode.

7.11.1.3.2 Saturated calomel electrode.

7.11.1.3.3 Potentiometer.

7.11.1.3.4 Electromagnetic stirrer and stirring bar.

7.11.1.4 Test steps

7.11.1.4.1 Drawing of working curve

According to the fluorine content in the specimen, pipette an appropriate amount of fluorine standard solution; place it in a set of 50 mL volumetric flasks. Add 1 mL of hydrochloric acid solution, 5 drops of buffer solution, 2 drops of bromocresol green indicator. Use sodium hydroxide solution and nitric acid solution to adjust the solution to yellow. Add 20 mL of buffer solution. Use water to dilute it to the mark. Shake well.

Pour the solution into a clean and dry 50 mL beaker. Place it on an electromagnetic stirrer. Put in a stirring bar. Insert the fluorine ion selective electrode and saturated calomel electrode connected to the potentiometer into the solution. Start the stirrer. Measure the potential value of the solution. Record the potential value at equilibrium. Draw a working curve, using the logarithm of the mass concentration of fluorine as the abscissa and the corresponding potential value as the ordinate.

7.11.1.4.2 Preparation of test solution

7.11.1.4.2.1 Preparation of solid specimen test solution

Weigh about 0.5 g (accurate to 0.0002 g) of solid specimen. Place it in a 50 mL beaker. Add 10 mL of water to dissolve the sample. Transfer it to a 50 mL volumetric flask.

7.11.1.4.2.2 Preparation of liquid specimen test solution

Pipette 10.00 mL of liquid specimen. Place it in a 50 mL volumetric flask.

7.11.1.4.2.3 Preparation of blank test solution

At the same time, perform a blank test. Except for not adding the specimen to the blank

p_0 - The mass concentration of fluorine in the blank test solution found and obtained from the working curve, in micrograms per milliliter ($\mu\text{g/mL}$);

V_0 - The volume of the liquid sample pipetted, in milliliters (mL).

The arithmetic mean of the parallel determination results is taken as the determination result. The absolute difference between the two parallel determination results shall not exceed 20% of the arithmetic mean.

7.11.2 Ion chromatography

7.11.2.1 Principle

The specimen is dissolved in water and separated by anion exchange column using an ion chromatograph, detected by the suppressed conductivity method, quantified by the external standard method (peak area/peak height). The mass concentration of fluorine is found from the working curve and its content is calculated.

7.11.2.2 Reagents or materials

7.11.2.2.1 Water: Deionized water at a resistivity ($25\text{ }^{\circ}\text{C}$) of not less than $18.2\text{ M}\Omega\cdot\text{cm}$.

7.11.2.2.2 Fluorine standard solution: 1 mL of solution contains 0.050 mg of fluorine.

Pipette 5.00 mL of the fluorine standard solution prepared according to HG/T 3696.2. Place it in a 100 mL volumetric flask. Use water to dilute it to the mark. Shake well.

7.11.2.3 Instruments and equipment

7.11.2.3.1 Ion chromatograph: Equipped with a conductivity detector.

7.11.2.3.2 Microporous filter membrane: Recommended pore size $0.22\text{ }\mu\text{m} \sim 0.45\text{ }\mu\text{m}$.

7.11.2.3.3 Chromatographic column: Anion chromatographic column, the separation degree R between the detected anion and the adjacent ion is ≥ 1.5 .

7.11.2.4 Test steps

7.11.2.4.1 Drawing of working curve

Pipette 0.00 mL, 1.00 mL, 2.00 mL, 4.00 mL, 6.00 mL, 8.00 mL of fluorine standard solution respectively. Place them in six 100 mL volumetric flasks. Use water to dilute it to the mark. Shake well. Pass this series of standard solutions through the microporous filter membrane in order from low to high mass concentration. Discard the initial 10 mL of filtrate.

Adjust the ion chromatograph to the best working state (see Appendix B for recommended instrument operating conditions). Record the peak height or peak area.

Where:

ρ_2 - The value of the mass concentration of fluorine in the test solution B found from the working curve, in micrograms per milliliter ($\mu\text{g/mL}$);

V - The value of the volume of the liquid sample, in milliliters (mL).

The arithmetic mean of the parallel determination results is taken as the determination result. The relative deviation of the two parallel determination results is not greater than 20%.

7.12 Determination of magnetic foreign matter content

7.12.1 Principle

The magnetic material in the specimen is adsorbed by a magnetic rod and dissolved with aqua regia. The working curve method is used, to determine the nickel, iron, zinc chromium contents with an inductively coupled plasma emission spectrometer; the magnetic foreign matter content is obtained by calculation.

7.12.2 Reagents or materials

7.12.2.1 Aqua regia.

Prepared with high-grade pure reagent hydrochloric acid and high-grade pure reagent nitric acid.

7.12.2.2 Nitric acid solution: 1+1.

Prepared with high-grade pure reagent.

7.12.2.3 Mixed standard solution: 1 mL of solution contains 0.010 mg each of nickel (Ni), iron (Fe), zinc (Zn), chromium (Cr).

Use a pipette to take 1 mL of the nickel, iron, zinc, chromium standard solutions prepared according to HG/T 3696.2. Place them in the same 100 mL volumetric flask. Use water to dilute it to the mark. Shake well.

Or use a mixed solution or single standard solution of a certified series of national standard substances for accurate dilution.

This solution shall be prepared immediately before use.

7.12.2.4 Water: Grade 2 water as specified in Table 1 of GB/T 6682-2008.

7.12.3 Instruments and equipment

7.12.3.1 Jar mill: As shown in Figure 1, or other mixing devices with the same mixing

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