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NONFERROUS METALS INDUSTRY STANDARD OF THE PEOPLE'S REPUBLIC OF CHINA

YS/T 1658.1-2023

Methods for chemical analysis of crude nickel cobalt hydroxide - Part 1: Determination of nickel content - Dimethylglyoxime gravimetric method

粗氢氧化镍钴化学分析方法 第1部分：镍含量的测定 丁二酮肟重量法

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Introduction

Crude nickel cobalt hydroxide is a binary hydrometallurgical intermediate containing nickel and cobalt, obtained from spent lithium-ion battery material by acid dissolution, impurity removal, alkaline precipitation and other hydrometallurgical concentration processes. It is a product of considerable value and can serve as the raw material for nickel manganese ternary composite hydroxide, lithium nickel cobalt manganese oxide, nickel and cobalt chemical salts and other related materials. Since its chemical composition bears directly on the quality of the product, a set of standard methods for analysing that composition is necessary.

YS/T 1658, Methods for chemical analysis of crude nickel cobalt hydroxide, consists of seven parts: Part 1, determination of the nickel content by the dimethylglyoxime gravimetric method; Part 2, determination of the chromium, phosphorus and manganese contents by inductively coupled plasma atomic emission spectrometry; Part 3, determination of the fluoride ion content by the ion-selective electrode method; Part 4, determination of the copper, aluminium, lithium, zinc, lead and arsenic contents by inductively coupled plasma atomic emission spectrometry; Part 5, determination of the moisture content by the

gravimetric method; Part 6, determination of the hydrochloric-acid-insoluble content by the gravimetric method; and Part 7, determination of the manganese content by potentiometric titration.

The nickel content, being the main element, is the figure that decides the value of the product. The purpose of this part is to standardise the method of testing it and the precision of that method. Because the nickel content is high, and because the dimethylglyoxime gravimetric method is simple to carry out, of high accuracy and the arbitration method in international nickel trading, it is the best method for this kind of sample; and because it differs from the methods used for the other constituents, the determination of nickel warranted a part of its own. This part gives the basis for determining the nickel content of crude nickel cobalt hydroxide scientifically and accurately, which matters for reducing the commercial disputes that testing error causes between buyer and seller and for the development of trade in the product.

1 Scope

This document describes a method for determining the nickel content of crude nickel cobalt hydroxide.

It applies to that determination over the range 5.00 % to 50.00 %.

2 Normative references

The contents of the following documents constitute indispensable provisions of this document through normative reference in the text. For dated references, only the edition corresponding to that date applies. For undated references, the latest edition, including all amendments, applies.

GB/T 6682 Water for analytical laboratory use - Specification and test methods · YS/T 1460-2021 Crude nickel cobalt hydroxide

3 Terms and definitions

No terms and definitions need to be defined for this document.

4 Principle

The test portion is dissolved in hydrochloric acid; the interfering ions are masked with tartaric acid, ammonium acetate and sodium thiosulfate; the nickel is precipitated with dimethylglyoxime in an ammoniacal medium; the precipitate is filtered under suction, washed and dried to constant mass in an oven at 145 degrees Celsius plus or minus 2; and the nickel content is calculated. The nickel remaining in the filtrate is determined by atomic absorption spectrometry and added as a correction.

5 Reagents and materials

Unless otherwise stated, all the reagents used are of analytical grade or better.

Water to GB/T 6682, grade three or better. Hydrochloric acid of density 1.19 g/mL, and hydrochloric acid (1+1). Ammonia solution (1+1). Ethanol (1+4).

Tartaric acid solution at 150 g/L, filtered before use. Ammonium acetate solution at 500 g/L, filtered before use. Sodium thiosulfate solution at 200 g/L, filtered before use and kept in a brown bottle. Dimethylglyoxime in ethanol at 10 g/L, filtered before use and kept in a brown bottle.

6 Instruments and equipment

G4 sintered-glass funnel of 100 mL with a pore size of 4 micrometres to 7 micrometres.

G4 sintered-glass crucible of 30 mL or 40 mL with the same pore size.

7 Sample

The sample is taken and prepared as required by 7.4 of YS/T 1460-2021.

Before analysis the sample is dried for 4 h in an oven at 105 degrees Celsius plus or minus 2, cooled to room temperature in a desiccator and weighed immediately.

8 Test procedure

Test portion: weigh 1.00 g of the sample to the nearest 0.0001 g. Two determinations are carried out in parallel, and a blank test is run alongside the test portion.

Preparation of the test solution: place the test portion in a 250 mL beaker, wet it with a little water, add 20 mL of hydrochloric acid (1+1), cover with a watch glass and heat gently until it has dissolved completely and the volume is about 3 mL to 5 mL; remove and cool to room temperature. Wash the watch glass and the walls of the beaker with water, transfer to a 250 mL volumetric flask, dilute to the mark with water and mix. Filter dry, discard the first runnings and take an aliquot into a 500 mL beaker according to Table 1: 100.00 mL where the nickel mass fraction is 5.00 % to 10.00 %, 50.00 mL where it is above 10.00 % to 20.00 %, and 25.00 mL where it is above 20.00 % to 50.00 %.

Separation of the precipitate where the nickel to cobalt ratio is greater than 1:2: add 10 mL of the tartaric acid solution and 10 mL of the ammonium acetate solution to the test solution and make up to about 250 mL with water. Adjust to about pH 5.0 with ammonia solution, add 5 mL of the sodium thiosulfate solution, stir and let stand for 5 min; this step may be omitted where the sample contains no copper. Adjust to pH 6.0 to 6.5 with ammonia solution and add the dimethylglyoxime solution slowly while stirring - about 4 mL for each

10 mg of nickel and cobalt, plus an excess of 25 mL - then hold in a water bath at 60 degrees Celsius to 70 degrees Celsius and age for 30 min.

Where the nickel to cobalt ratio is not greater than 1:2: proceed as above up to the 30 min ageing, then filter under suction through the G4 funnel, wash the precipitate four or five times with water and keep filtrate A. Rinse the walls of the funnel with about 20 mL of hydrochloric acid of density 1.19 g/mL until all the red precipitate has dissolved and filter under suction, rinse with about 20 mL of hydrochloric acid (1+1) and filter again, then rinse four or five times with water and transfer the solution back to the original beaker. Add 5 mL of the tartaric acid solution and 10 mL of the ammonium acetate solution, make up to about 250 mL with water, adjust to pH 6.0 to 6.5 with ammonia solution and hydrochloric acid (1+1), add the dimethylglyoxime solution slowly while stirring - about 4 mL for each 10 mg of nickel, plus an excess of 25 mL - and age in the water bath at 60 degrees Celsius to 70 degrees Celsius for 30 min.

Filtration, drying and weighing: filter the hot test solution through the G4 sintered-glass crucible, previously brought to constant mass; wash all the precipitate adhering to the beaker and the glass rod into the crucible with ethanol (1+4), wash the precipitate four or five times with water and keep filtrate B. Dry the crucible with its precipitate in an oven at 145 degrees Celsius plus or minus 2 for 2 h, cool to room temperature in a desiccator and weigh, repeating the drying until the mass is constant.

The nickel in filtrate A and in filtrate B is determined and added as a correction according to Annex A.

9 Treatment of the test data

The nickel content, expressed as the mass fraction of nickel, is calculated by formula (1) from the total mass of the crucible and the precipitate after the test and the mass of the crucible itself, the corresponding two masses of the blank test, the total volume of the test solution, the volume of the aliquot taken, the mass of the test portion, the mass fraction of nickel found in the filtrate and the factor 0.2032, which converts nickel dimethylglyoximate to nickel.

The result is given to two decimal places.

10 Precision

Repeatability: for two independent test results obtained under repeatability conditions, the absolute difference shall not exceed the repeatability limit r within the range of mean values of Table 2, and shall exceed it in not more than 5 % of cases; r is obtained by linear interpolation or extrapolation from Table 2. At mass fractions of 5.23 %, 16.20 %, 28.60 % and 46.71 % the repeatability limit is 0.21 %, 0.35 %, 0.42 % and 0.49 % respectively.

Reproducibility: for two independent test results obtained under reproducibility conditions,