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## Methods of chemical analysis of lithium cobalt oxide— Part 1: Determination of cobalt content EDTA titration and potentiometric titration method

钴酸锂化学分析方法

第1部分：钴含量的测定

EDTA滴定法和电位滴定法

*（English Translation）*

GB/T 23367.1—202X

Replace GB/T 23367.1-2009

**National Standards of the People's Republic of China**

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**Foreword**

SAC/TC 243 is in charge of this English translation. In case of any doubt about the contents of English translation, the Chinese original shall be considered authoritatively.

This document is drafted in accordance with the rules given in the GB/T 1.1-2020 "*Directives for Standardization-Part 1:Rules for the Structure and Drafting of Standardizing documents*".

This document replaces GB/T 23367.1-2009 Methods for chemical analysis of lithium cobalt oxide-Part 1:Determination of cobalt content-EDTA titration. In addition to structural adjustment and editorial changes, the following technical deviations have been made with respect to GB/T 23367.1-2009:

a) The lower limit of "determination range for cobalt content" has been changed from "58 percent" to "57 percent" (see chapter 1, 2009 edition, chapter 1);

b) The "normative citation documents" have been added (see Chapter 2);

c) "Terms and Definitions" have been added (see Chapter 3);

d) " EDTA automatic titration method " has been added (see Chapter 4);

e) "Nitric acid (ρ=1.42 g/mL)" has been added (see 4.2.2 and 5.2.2);

f) "Perchloric acid (ρ=1.67 g/mL)" has been added (see 4.2.3 and 5.2.3);

g) The concentration of cobalt standard solution in EDTA titration was changed from "1 mL containing 1.5 mg of cobalt" to "1 mL containing 1.0 mg of cobalt" (see 4.2.4, 3.4 in 2009);

h) Added solution of nitric acid and perchloric acid for some insoluble samples (see 4.5.4.1);

i) The dissolution method of the specimen has been changed from "Add 25 mL hydrochloric acid to dissolve, and heat on the low-temperature electric heating plate until completely dissolved" to "Add 10 mL hydrochloric acid [If the specimen cannot be dissolved by hydrochloric acid, then take another specimen, add 3 mL nitric acid and 3 mL perchloric acid to dissolve], and cover the surface dish. Heat on a low temperature electric plate until completely dissolved. Then the sample liquid is placed at 120 ℃ ~250 ℃ to heat and remove the acid until the volume of solution remains about 1 mL ~2 mL "(see 4.5.4.1, 5.4.1 of the 2009 edition);

j) "Potentiometric titration" has been added (see Chapter 5);

k) The "permissible difference" has been removed (see 7.2 of the 2009 edition);

l) Contents related to "repeatability limits" have been changed (see Table 6.1, Table 7.1, 2009 version);

m) "reproducibility" has been added (see Table 2 in 6.2);

n) "Quality assurance and control" has been removed (see Chapter 8 of the 2009 edition);

o) The "Test Report" has been added (see Chapter 7).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. The issuing body of this document shall not be held responsible for identifying any or all such patent rights.

This document was proposed by China nonferrous metals industry association.

This document was prepared by SAC/TC 243 National Technical Committee on Non ferrous Metals of Standardization.

The previous edition of this document is as follows:

——The first edition was issued in 2009 as GB/T 23367.1-2009. This is the first revised edition.

Methods of chemical analysis of lithium cobalt oxide——

Part 1: Determination of cobalt content

EDTA titration and potentiometric titration method

**1 Scope**

This document specifies the methods for the determination of cobalt content in lithium cobalt oxide.

This document is intended for the determination of cobalt content in lithium cobalt oxide. Determination range: 57.00% ~ 62.00%.

**2 Normative reference document**

The contents of the following referenced documents constitute the essential provisions of this document through normative references in the text. For referenced documents with a date, only the version corresponding to that date applies to this document; for those without a date, only the latest version (including all modification orders) is applicable to this document.

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 17433 Foundation terms for chemical analysis of metallurgical products

3 Terms and definitions

The terms specified in GB/T 17433 apply to this document.

4 EDTA titration method

**Warning - Personnel using this document should have practical experience of working in a formal laboratories. This document does not address all possible security issues. Users are responsible for taking appropriate safety and health measures for the use of nitric acid and perchloric acid, and ensuring compliance with relevant national regulations.**

4.1 principle

After dissolving the sample in hydrochloric acid or a mixed solution of nitric acid and perchloric acid, the cobalt content is calculated based on the volume of the consumed EDTA standard titration solution in an alkaline buffer solution, with ammonium purpurate as the indicator and EDTA standard titration solution as the titrant.

With EDTA manual titration method, EDTA standard titration solution is titrated directly with the sample solution until the solution changes from orange-yellow to purplish-red.

 With EDTA automatic titration , an automated potentiometric titrator is employed. After inserted a photometric electrode, the sample solution is stirred. Titration to the endpoint is performed with an EDTA standard titration solution according to the titration endpoint identification procedure set by the instrument

4.2 Reagents or materials

The reagents used in this section are all analytical grade or higher purity reagents, and the water used complies with the third grade or higher purity water specified in GB/T 6682.

4.2.1 Hydrochloric acid (1+1).

4.2.2 Nitric acid (ρ=1.42 g/mL).

4.2.3 Perchloric acid (ρ=1.67 g/mL).

4.2.4 Cobalt standard solution: weigh 1.000 0 g of metallic cobalt (mass fraction ≥99.98%) into a 400 mL beaker, add 30 mL of hydrochloric acid (4.2.1), cover the beaker with watch glasses, cool it to room temperature after the metallic cobalt is completely dissolved at low temperature, transfer it to a 1 000 mL volumetric flask with water, dilute it to scale with water, and mix well. 1 mL of this solution contains 1.0 mg of cobalt. Commercially available certified cobalt standard solutions may also be used.

4.2.5 Ammonium purpurate indicator: take 0.4 g ammonium purpurate, add 50 g potassium sulfate, and fully grind in the mortar.

4.2.6 Ammonia-ammonium chloride buffer solution(pH≈10): weigh 54.5g ammonium chloride and dissolve in water, add 350 mL ammonia water, dilute with water to 1 000 mL, mix well.

4.2.7 ethylenediamine tetraacetic acid disodium (C10H14N2O8 Na2•2H2O, EDTA) standard titration solution (about 0.01 mol/L).

4.2.7.1 Preparation: weigh 3.72 g EDTA into 400 mL beaker, add water to slightly heat dissolve, cool to room temperature, transfer to 1 000 mL volumetric bottle, dilute with water to scale, mix well.

4.2.7.2 Calibration of EDTA standard titration solution（Pre use calibration）: Remove 15.00 mL cobalt standard solution (4.2.4) into a glass container, add 50 mL water and approximately 20 mL~25 mL EDTA standard titration solution（3 mL to 5 mL before the end of the reaction process is appropriate）. Then add 10 mL ammonia-ammonium chloride buffer solution (4.2.6), and finally add about 0.1 g ammonium purpurate indicator (4.2.5).

If EDTA manual titration method is selected, the end point is directly titrated with the EDTA standard titration solution until the solution changes from orange yellow to purple red.

If the EDTA automatic titration method is selected, it is necessary to insert photometric electrode on the automatic potentiometric titration instrument, and titrate to the endpoint using the EDTA standard titration solution according to the titration endpoint recognition program set by the instrument under stirring state.

Calculate the concentration of EDTA standard titration solution according to formula (1) :

$$c\_{1}=\frac{ρ\_{Co}×V\_{1}}{58.933×（V\_{2}-V\_{3}）}·······················································(1)$$

In the formula:

$c\_{1}$-- the actual concentration of the EDTA standard titration solution, in moles per liter (mol/L);

$ρ\_{Co}$-- the mass concentration of cobalt standard solution, in milligrams per milliliter (mg/--mL);

$V\_{1}$--transfer the volume of cobalt standard solution, in milliliters (mL);

58.933-- molar mass of cobalt, in grams per mole (g/mol);

$V\_{2}$—the total volume consumed during titration with EDTA standard titration solution, in milliliters (mL);

$V\_{3}$-- the volume of EDTA standard titration solution consumed in the blank test, in milliliters (mL);

Calibrating three parts parallelly, the range of the volume of the EDTA standard titration solution consumed should not exceed 0.05 mL., and the average value should be taken. Keep four significant digits in the calculation result. Numerical rounding shall be carried out in accordance with the provisions of GB/T 8170.

4.3 Instruments and Equipment

4.3.1 Automatic potentiometric titrator with stirring device.

4.3.2 Photometric electrodes matched with the instrument. The selection of electrodes should follow the manufacturer's instructions.

4.4 Samples

4.4.1 The particle size of the sample should not exceed 100 μ M.

4.4.2 Before sample analysis, it should be dried at 110 ℃± 5 ℃ for 2 hours and cooled to room temperature in a dryer.

4.5 Test steps

4.5.1 Test materials

Weigh 0.10 g of the sample, accurate to 0.000 1 g.

4.5.2 Parallel test

Conduct two independent measurements and take the average value.

4.5.3 Blank test

Make a blank test with the test material.

4.5.4 Measurement

4.5.4.1 Place the test sample (4.5.1) into a 100 mL beaker and add 10 mL of hydrochloric acid (4.2.1). [If the test sample cannot be dissolved by hydrochloric acid (4.2.1), take another test sample and add a mixture of 3 mL of nitric acid (4.2.2) and 3 mL of perchloric acid (4.2.3) for dissolution]. Cover the beaker with a surface dish and heat it on a low-temperature electric plate until completely dissolved. Then place the sample solution under conditions of 120 ℃~ 250 ℃, heat and drive the acid until the remaining volume of the solution is about 1 mL ~ 2 mL. Take beaker off and cool the solution slightly, rinse the watch glasses and the cup wall with water, and heat the beaker at low temperature to dissolve the salts until the solution is clear. After cooling, transfer to a 100 mL volumetric flask, dilute with water to scale, and mix well.

4.5.4.2 Transfer 25.00 mL of the test solution (4.5.4.1) into a glass container, add approximately 50 mL of water and 19 mL ~ 21 mL of EDTA standard titration solution [depending on the cobalt content of lithium cobalt oxide, 3 mL ~ 5 mL before the end of the reaction process is appropriate]. After stirring, add an appropriate amount of ammonia water ammonium chloride buffer solution (4.2.6) and adjust the pH of the test solution to ≈ 10. Finally, add approximately 0.1 g of ammonium purpurate indicator (4.2.5).

If EDTA manual titration method is selected, titrate with EDTA standard titration solution (4.2.7) until the solution changes from orange yellow to purple red, which is the endpoint.

If EDTA automatic titration method is selected, a photometric electrode (4.3.2) needs to be inserted into the automatic potentiometric titrator (4.3.1), stirred, and titrated to the endpoint using EDTA standard titration solution (4.2.7) according to the titration endpoint recognition program set by the instrument.

4.5.5 Experimental data processing

Cobalt content is determined by the mass fraction of cobalt *wCo*, calculated according to formula (2):

$w\_{Co}=\frac{c\_{1}\left( V\_{4}-V\_{5}\right)×10^{-3}×58.933×V\_{6}}{m\_{1}× V\_{7}}$×100%………………………(2)

In the formula:

$c\_{1}$-- the actual concentration of the EDTA standard titration solution, in moles per liter (mol/L);

$V\_{4}$-- the total volume consumed during titration with EDTA standard titration solution, in milliliters (mL)

$V\_{5}$-- the volume of EDTA standard titration solution consumed in the blank test, in milliliters (mL);

58.933-- molar mass of cobalt, in grams per mole (g/mol);

$V\_{6}$-- the constant volume of the sample after dissolution, in milliliters (mL);

$m\_{1}$-- weigh the mass of the test sample, in grams (g);

$V\_{7}$-- divide the volume of the test solution, in milliliters (mL);

The calculation results are expressed to two decimal places, and numerical rounding shall be carried out in accordance with the provisions of GB/T 8170.

5. Potentiometric titration method

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5.1 Principle

After the sample is dissolved in hydrochloric acid （or a mixed solution of nitric acid and perchloric acid）, the standard solution of potassium ferricyanide is added into the mixed solution of ammonium chloride-ammonium citrate-ammonia water to oxidize Co (II) into Co (III). The excess potassium ferrocyanide is titrated back with cobalt standard solution using potentiometric titration until the potential jumps to the endpoint. The cobalt content is calculated based on the volume of consumed potassium ferrocyanide and cobalt standard solution.

5.2 Reagents or materials

The reagents used in this section are all analytical grade or higher purity reagents, and the water used complies with the third grade or higher purity water specified in GB/T 6682.

5.2.1 Hydrochloric acid (1+1).

5.2.2 Nitric acid (ρ=1.42 g/mL).

5.2.3 Perchloric acid (ρ=1.67 g/mL).

5.2.4 Cobalt standard solution: weigh 3.000 0 g metallic cobalt (mass fraction ≥ 99.98%) into 400 mL beaker, add 30 mL hydrochloric acid (5.2.1), cover beaker with watch glasses, cool it to room temperature after metallic cobalt is completely dissolved at low temperature, transfer it to a 1 000 mL volumetric flask with water, dissolve at low temperature, transfer to 1 000 mL volumetric bottle, dilute with water to scale, and mix well. 1 mL of this solution contains 1.0 mg of cobalt. Commercially available certified cobalt standard solutions may also be used.

5.2.5 Ammonium chloride-ammonium citrate - ammonia water mixed solution (pH ≈10) : weigh 120 g ammonium citrate, 60 g ammonium chloride, add 500 mL water to dissolve, then add ammonia water to 1 000 mL, stir well.

5.2.6 Potassium ferricyanide (K₃[Fe(CN)₆]) standard solution (approximately 0.05 mol/L).

5.2.6.1 Preparation: Weigh 17.4g ~ 17.8g potassium ferricyanide, dissolve it in water to prepare a solution, filter and transfer the solution to 1000 mL brown volumetric bottle, dilute the solution with water to the scale, mix well and store the prepared standard solution away from light.

5.2.6.2 Potassium ferrocyanide standard solution (pre use calibration): Add 25.00 mL potassium ferricyanide standard solution (5.2.6.1) to 250 mL beaker, then add 80 mL ammonium chloride-ammonium citrate - ammonia water mixed solution (5.2.5). On the potentiometric titrator, insert the electrode and titrate with cobalt standard solution (5.2.4) under constant agitation until the potential jumps, which is the endpoint.

The titration coefficient of potassium ferricyanide standard solution equivalent to cobalt standard solution is calculated according to formula (3) :

$$K=\frac{V\_{8}}{V\_{9}}··················································································(3)$$

In the formula:

$K$-- titration coefficient, the volume of cobalt standard solution consumed per unit volume of potassium ferricyanide standard solution;

$V\_{8}$-- the volume of cobalt standard solution consumed during titration, in milliliters (mL);

$V\_{9}$-- The volume of potassium ferricyanide standard solution added to the system, in milliliters (mL).

Parallel calibration of three parts, the range of the cobalt standard titration solution volume consumed should not exceed 0.05 mL., and the average value should be taken. The calculation result is retained to four decimal places. Numerical rounding shall be carried out in accordance with the provisions of GB/T 8170.

5.3 Instruments and Equipment

5.3.1 Automatic potentiometric titrator with stirring device.

5.3.2 Photometric electrodes matched with the instrument. The selection of electrodes should follow the manufacturer's instructions.

5.4 Samples

5.4.1 The particle size of the sample should not exceed 100 μ M.

5.4.2 Before sample analysis, it should be dried at 110 ℃± 5 ℃ for 2 hours and cooled to room temperature in a dryer.

5.5 Test steps

5.5.1 Test materials

Weigh 1.00 g of the sample（5.4）, accurate to 0.000 1 g.

5.5.2 Parallel test

Conduct two independent measurements and take the average value.

5.5.3 Measurement

5.5.3.1 Place the test sample (5.5.1) in a 100 mL beaker, moisten with a small amount of water, and slowly add 20 mL of hydrochloric acid (5.2.1). If the test sample cannot be dissolved by hydrochloric acid (5.2.1), take another test substance and add a mixed solution of 5 mL nitric acid (5.2.2) and 5 mL perchloric acid (5.2.3) for dissolution. Cover the surface dish, heat at low temperature until the sample is completely dissolved, and cool to room temperature. Then place the sample solution under conditions of 120 ℃~ 250 ℃, heat and drive the acid until the remaining volume of the solution is about 1 mL ~ 2 mL. Take it off and cool it slightly, rinse the watch glasses and the cup wall with water, and heat it at low temperature to dissolve the salts until the solution is clear. After cooling, transfer it into a 250 mL volumetric flask, dilute with water to scale, and shake well.

5.5.3.2 Accurately add 21 mL ~ 26mL potassium ferricyanide standard solution (5.2.6) into 250 mL beaker [depending on the cobalt content of lithium cobalt oxide, it is appropriate to overdose 2 mL ~ 5mL potassium ferricyanide standard solution during the reaction process]. Then add 80 mL ammonium chloride-ammonium citrate - ammonia water mixed solution (5.2.5), and transfer 25.00 mL test solution (5.5.3.1) while stirring. On the potentiometric titrator, insert an electrode and titrate with cobalt standard solution (5.2.4) in a stirred state until the potential jumps, which is the endpoint.

5.5.4 Experimental data processing

Cobalt content is determined by the mass fraction of cobalt ω(Co), the value is expressed as %, calculated according to formula (4):

$w\_{Co}=\frac{ρ\_{Co}\left(KV\_{10}- V\_{11}\right)V\_{12}×10^{-3}}{m\_{2}× V\_{13}}$×100………………………………………(4)

In the formula:

*ρ*$(Co)$ --The mass concentration of cobalt standard solution, in milligrams per milliliter (mg/mL);

*K*- titration coefficientthe, volume ratio of the standard solution of potassium ferricyanide per unit volume to the standard solution of cobalt consumed;

$V\_{10}$-- the volume of potassium ferricyanide standard solution added in the system, in milliliters (mL);

$V\_{11}$-- the volume of cobalt standard solution consumed by back titration, in milliliters (mL);

$V\_{12}$-- the total volume of the solution used in the process of constant volume, in milliliters (mL);

$m\_{2}$-- weigh the mass of the test sample, in grams (g);

$V\_{13}$-- divide the volume of the test solution, in milliliters (mL);

The calculation results are expressed to two decimal places, and numerical rounding shall be carried out in accordance with the provisions of GB/T 8170.

6 Precision

6.1 Repeatability

The absolute difference between the two independent test results obtained under repeatability conditions does not exceed the repeatability limit (r), as shown in Table 1. The situation where the repeatability limit (r) is exceeded does not exceed 5%. The repeatability limit (r) is obtained by linear interpolation or extension method according to the data in Table 1.

Table 1 Repeatability limits

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| EDTA automatic titration method | $w\_{Co}$/% | 58.78 | 59.40 | 59.86 |
| *r*/% | 0.22 | 0.23 | 0.24 |
| EDTA manual titration method | $w\_{Co}$/% | 58.55 | 59.19 | 59.66 |
| *r*/% | 0.19 | 0.17 | 0.15 |
| Potentiometric titration | $w\_{Co}$/% | 58.78 | 59.40 | 59.86 |
| *r*/% | 0.22 | 0.23 | 0.24 |

6.2 Reproducibility

For the measured values of the two independent test results obtained under the reproducibility condition, within the mean value range given in Table 2, the absolute difference between the two test results shall not exceed the reproducibility limit (R), and the cases exceeding the reproducibility limit (R) shall not exceed 5%. The reproducibility limit (R) shall be obtained by linear interpolation or epitaxy method according to the data in Table 2.

Table 2 Reproducibility limits

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| EDTA automatic titration method | $w\_{Co}$/% | 58.80 | 59.31 | 59.79 |
| *R*/% | 0.27 | 0.41 | 0.41 |
| EDTA manual titration method | $w\_{Co}$/% | 58.78 | 59.40 | 59.86 |
| *R*/% | 0.31 | 0.30 | 0.34 |
| Potentiometric titration | $w\_{Co}$/% | 58.55 | 59.19 | 59.66 |
| *R*/% | 0.66 | 0.36 | 0.34 |

7 Test report

The test report should include the following aspects:

-- Test subjects;

-- The number of this document;

- The method used;

-- Test results;

-- Observed anomalies;

-- Test date;

--Other differences from the steps specified in this document or requirements not specified in this document.