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Chemical analysis methods for non-rare earth impurities of rare earth metals and their oxides—

Part 21: Determination of sulfate content in rare earth oxides—Barium sulfate turbidimetry

*（English Translation）*

稀土金属及其氧化物中非稀土杂质化学分析方法

第21部分：稀土氧化物中硫酸根含量的测定 硫酸钡比浊法

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Foreword

SAC/TC 229 is in charge of this English translation. In case of any doubt about the contents of English translation, the Chinese original shall be considered authoritative.

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 is Part 21 of GB/T 12690 *Chemical analysis methods for non-rare earth impurities of rare earth metals and their oxides*. GB/T 12690 consists of the following 21 parts under the general title:
—*Part 1: Determination of carbon and sulfur contents-High frequency-infrared absorption method*;
—*Part 2: Determination of ignition loss content of rare earth oxides-Gravimetric method;*—*Part 3:* *Determination of water content of rare earth oxides-Gravimetric method;*

—*Part 4:* *Determination of oxygen and nitrogen contents-Impulse-infrared absorption and Impulse-thermal conductivity method;*

—*Part 5:* *Determination of cobalt, manganese, lead, nickel, copper, zinc, aluminum, chromium, magnesium, cadmium, vanadium, and iron contents;*

—*Part 6: Determination of iron content-Kalium thiocyanate, 1,10-Phenanthroline spectrophotometric method;*

—*Part 7:* *Determination of silicon content;*

—*Part 8:* *Determination of sodium content;*

—*Part 9:* *Determination of chlorine content-Silver nitrate turbidimetric method;*

—*Part 10:* *Determination of phosphorus content by molybdenum blue spectrophotometric method;*

—*Part 11:* *Determination of magnesium content-Flame atomic absorption spectrometric method;*

—*Part 12:* *Determination of thorium and uranium contents-Inductively coupled plasma mass spectrum method;*

—*Part 13:* *Determination of molybdenum and tungsten content-Inductively coupled plasma atomic emission spectrographic method and Inductively coupled plasma mass spectrum;*

—*Part 14:* *Determination of titanium content;*

—*Part 15:* *Determination of calcium content;*

—*Part 16:* *Determination of fluorine content-Ion selective electrode analysis;*

—*Part 17:* *Determination of niobium and tantalum contents of rare earth metals;*

—*Part 18:* *Determination of zirconium content;*

—*Part 19:* *Determination of arsenic and mercury contents;*

—*Part 20:* *Determination of trace fluorine and chlorine in rare earth oxides-Ion chromatography method;*—*Part 21: Determination of sulfate content in rare earth oxides-Barium sulfate turbidimetry.*

Attention is drawn to the possibility that some of the elements of this standard 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 and prepared by the National Technical Committee on Rare Earth Standardization (SAC/TC 229).

Introduction

In the field of chemical composition analysis for rare earth products, China has established a comprehensive standard system covering the determination of total rare earth content, non-rare earth impurities, and rare earth impurities. The series standard GB/T 12690 *Chemical Analysis Methods for Non-Rare Earth Impurities of Rare Earth Metals and Their Oxides* is developed based on GB/T 12690.12-GB/T 12690.26—1990 *Chemical Analysis Methods for Rare Earth Metals and Their Oxides*. It incorporates the following standards:

—GB/T 8762.3-1988 Yttrium oxide of phosphor grade-*Determination of acid soluble silicon dioxide -Molybdenum blue photometric method;*

—GB/T 8762.4-1988 Yttrium oxide of phosphor grade-*Determination of iron oxide, lead oxide, nickel oxide and copper oxide contents-Emission Spectrographic method;*

—GB/T 8762.6-1988 Europium oxide of phosphor grade-*Determination of lead oxide, nickel oxide, iron oxide and copper oxide contents-Emission Spectrographic method;*

—GB/T 11074.3-GB/T 11074.7-1989 *Chemical Analysis Methods for Samarium Oxide*.

The integrated series adopts advanced testing methods and comprehensively covers all rare earth metals and oxide matrices. It provides rapid and accurate methods for determining non-rare earth impurities in rare earth metals and oxides, ensuring high operability.

GB/T 12690 is structured into 21 parts according to the detection targets, methodologies, and differences in rare earth metal/oxide matrices:

—*Part 1: Determination of carbon and sulfur contents-High frequency-infrared absorption method*;
—*Part 2: Determination of ignition loss of rare earth oxides-Gravimetric method;*—*Part 3:* *Determination of water content of rare earth oxides-Gravimetric method;*

—*Part 4:* *Determination of oxygen and nitrogen contents-Impulse-infrared absorption and Impulse-thermal conductivity method;*

—*Part 5:* *Determination of cobalt, manganese, lead, nickel, copper, zinc, aluminum, chromium, magnesium, cadmium, vanadium, and iron contents;*

—*Part 6: Determination of iron content-Kslium thiocyanate, 1,10-Phenanthroline spectrophotometric method;*

—*Part 7:* *Determination of silicon content;*

—*Part 8:* *Determination of sodium content;*

—*Part 9:* *Determination of chlorine content-Silver nitrate turbidimetric method;*

—*Part 10:* *Determination of phosphorus content by molybdenum blue spectrophotometric method;*

—*Part 11:* *Determination of magnesium content-Flame atomic absorption spectrometric method;*

—*Part 12:* *Determination of thorium and uranium contents-Inductively coupled plasma mass spectrum method;*

—*Part 13:* *Determination of molybdenum and tungsten content-Inductively coupled plasma atomic emission spectrographic method and Inductively coupled plasma mass spectrum;*

—*Part 14:* *Determination of titanium content;*

—*Part 15:* *Determination of calcium content;*

—*Part 16:* *Determination of fluorine content-Ion selective electrode analysis;*

—*Part 17:* *Determination of niobium and tantalum contents of rare earth metals;*

—*Part 18:* *Determination of zirconium content;*

—*Part 19:* *Determination of arsenic and mercury contents;*

—*Part 20:* *Determination of trace fluorine and chlorine in rare earth oxides-Ion chromatography method;*—*Part 21: Determination of sulfate content in rare earth oxides-Barium sulfate turbidimetry.*

These parts address routine detection elements in the production and trade of rare earth metals and oxides. Each part specifies applicable scopes, reagents, equipment, procedures, and precision data validated through multi-laboratory trials, establishing a rigorous standardized foundation for quality inspection.

Currently, sulfate radical limits are critical in the production and trade of many rare earth oxides. While industry laboratories often reference GB/T 16484.12 for testing, its conditions are not fully suitable for rare earth oxides. Therefore, it is necessary to establish a unified, rapid, and accurate standard for sulfate radical determination in rare earth oxides.

This document employs barium sulfate turbidimetry, optimizes experimental conditions through extensive trials, standardizes procedural details, and establishes a robust, user-friendly, and high-accuracy detection method.

Chemical analysis methods for non-rare earth impurities of rare earth metals and their oxides—

Part 21：Determination of sulfate content in rare earth oxides Barium sulfate turbidimetry

1 Scope

This document specifies the method for determination of sulfate content in rare earth oxides using barium sulfate turbidimetry.

This document is applicable to the determination of sulfate content in rare earth oxides, with a measurement range (mass fraction) of ​0.010% to 0.20%.

2 Normative References

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

—GB/T 6379.2 *Accuracy (trueness and precision) of measurement methods and results – Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

—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*

​—JJG 178 *Verification regulation of ultraviolet, visible, near-infrared spectrophotometers*

3 Terms and Definitions

No terms or definitions are listed in this document.

4 Principle

The test portion is dissolved in acid (or separated from rare earth elements via hydroxide precipitation). In dilute hydrochloric acid medium with glycerol stabilizer, sulfate ions react with barium chloride to form barium sulfate suspension. The absorbance is measured at ​400 nm using a spectrophotometer to determine sulfate content.

5 Reagents and Materials

Unless otherwise stated, only reagents confirmed to be of analytical grade or above and secondary water complying with GB/T 6682 are used in the analysis. Certified standard solutions are preferred.
5.1 Hydrogen peroxide [$w$(H₂O₂)≥30%].
5.2 Perchloric acid ($ρ$=1.67 g/mL).
5.3 Nitric acid (1+1).
5.4 Hydrochloric acid (1+1).
5.5 Ammonia solution (1+4).
5.6 Hydrochloric acid (1+9).
5.7 Sodium hydroxide solution (300 g/L).
5.8 *p*-Nitrophenol indicator (1 g/L): Dissolve 0.10 g *p*-nitrophenol in anhydrous ethanol and dilute to 100 mL.
5.9 Glycerol-ethanol solution (1+3).
5.10 Barium chloride solution (250 g/L): Prepare fresh before use and preheat to 60–70℃.
5.11 Sulfate standard stock solution (1 mg/mL): Dissolve 1.4786 g anhydrous sodium sulfate (dried at 105°C to constant mass) in water, dilute to 1000 mL.
5.12 Sulfate standard working solution (100 $μ$g/mL): Dilute 10.00 mL of stock solution (5.11) to 100 mL.
5.13 Sodium matrix solution: Mix 20 mL hydrochloric acid (5.4) with 60 mL sodium hydroxide solution (5.7), dilute to 100 mL.

6 Apparatus

Visible spectrophotometer or UV-Vis spectrophotometer compliant with JJG 178 requirements.

7 Sample Preparation

Dry samples at ​105°C for ​1 h, cool in a desiccator until room temperature, and weigh immediately.

8 Test Procedures

8.1 Test portion

Weigh samples according to Table 1. Accurate to 0.0001 g.

Table 1: Test portion mass and aliquot volume

|  |  |  |  |
| --- | --- | --- | --- |
| Sulfate mass fraction (%) | Test portion mass (g) | Total volume (mL) | Aliquot volume (mL) |
| 0.010–0.025 | 2.00 | 50 | 7.50 |
| >0.025–0.10 | 2.00 | 100 | 10.00 |
| >0.10–0.20 | 1.00 | 100 | 10.00 |

8.2 Parallel Test

Weigh ​two test portions (8.1) and perform parallel determinations.

8.3 Blank Test

Carry out a ​reagent blank test alongside the test portion.

8.4 Preparation of Analytical Test Solution

8.4.1 Preparation of Rare Earth-Separated Test Solution

8.4.1.1 The rare earth-separated test solution is applicable to all rare earth oxides.

8.4.1.2 Dissolution of Rare Earth Oxides (excluding cerium oxide):

Place the test portion in a polytetrafluoroethylene beaker, add 20 mL hydrochloric acid (5.4), and dissolve under low-temperature heating until clear. Slowly add 25 mL sodium hydroxide solution (5.7) and mix thoroughly. Cool to room temperature, transfer to a plastic volumetric flask according to Table 1, dilute to the mark with pure water, and mix. Filter the solution dry using quantitative slow-speed filter paper, and collect the filtrate for testing.

8.4.1.3 Dissolution of Cerium Oxide Test Portion:

Place the test portion in a polytetrafluoroethylene beaker, add 20 mL nitric acid (5.3) and 5 mL hydrogen peroxide (5.1), and dissolve under low-temperature heating until clear. Add 5 mL perchloric acid (5.2) and evaporate to near dryness. Add 10 mL hydrochloric acid (5.4) and dissolve under low-temperature heating until clear. Slowly add 25 mL sodium hydroxide solution (5.7) and mix thoroughly. Cool to room temperature, transfer to a plastic volumetric flask according to Table 1, dilute to the mark with pure water and mix. Filter the solution dry using quantitative slow-speed filter paper, and collect the filtrate for testing.

8.4.2 Preparation of Rare Earth-Unseparated Test Solution

8.4.2.1 The rare earth-unseparated test solution is applicable to rare earth oxides excluding cerium oxide, praseodymium oxide, samarium oxide, europium oxide, dysprosium oxide, and holmium oxide.

8.4.2.2 Dissolution of Rare Earth Oxides:

Place the test portion in a beaker, add 20 mL hydrochloric acid (5.4), and dissolve under low-temperature heating until clear. Cool to room temperature, transfer to a volumetric flask according to Table 1, dilute to the mark with pure water and mix.

8.5 Determination

8.5.1 Determination for Rare Earth-Separated Test Solution

Based on the sulfate content range in the test portion, transfer an aliquot of the test solution (8.4.1) as specified in Table 1 into a 25 mL colorimetric tube. Add 1–2 drops of p-nitrophenol indicator (5.8). Adjust the pH using hydrochloric acid (5.4) and ammonia solution (5.5) until the yellow color just disappears. Sequentially add 3 mL hydrochloric acid (5.6) and 4 mL glycerol-ethanol solution (5.9), mixing thoroughly after each addition. Add 5 mL barium chloride solution (5.10), dilute to the mark with water, and mix thoroughly. Let stand for 5 minutes. Transfer the prepared solution into a 3 cm cuvette and measure its absorbance at 400 nm using a spectrophotometer with water as the reference. Subtract the reagent blank absorbance and determine the sulfate content from the calibration curve. Testing should be completed within 20 minutes.

8.5.2 Determination for Rare Earth-Unseparated Test Solution

Based on the sulfate content range in the test portion, transfer an aliquot of the test solution (8.4.2) as specified in Table 1 into two 25 mL colorimetric tubes. Add 1–2 drops of p-nitrophenol indicator (5.8). Adjust the pH using ammonia solution (5.5) and hydrochloric acid (5.6) until the yellow color just disappears, and mix thoroughly. Sequentially add 3 mL hydrochloric acid (5.6) and 4 mL glycerol-ethanol solution (5.9), mixing thoroughly after each addition. One tube is directly diluted to the mark with water, serving as the ​sample blank. The other tube is added with 5 mL barium chloride solution (5.10), diluted to the mark with water, and mixed thoroughly. Let stand for 5 minutes. Transfer the prepared solutions into 3 cm cuvettes and measure their absorbance at 400 nm using a spectrophotometer with water as the reference. ​Subtract both the reagent blank and sample blank absorbances, then determine the sulfate content from the calibration curve. ​Testing should be completed within 20 minutes.

8.6 Calibration Curve Preparation and Measurement

8.6.1 Calibration Curve for Rare Earth-Separated Analysis

Add sodium-based solution (5.13) equivalent to the aliquot volume of the actual test solution into seven 25 mL colorimetric tubes. Sequentially add 0 mL, 0.25 mL, 0.50 mL, 1.00 mL, 1.50 mL, 2.00 mL, and 2.50 mL of sulfate standard solution (5.12). Add 1–2 drops of p-nitrophenol indicator (5.8). Adjust the pH using hydrochloric acid (5.4) and ammonia solution (5.5) until the yellow color just disappears, and mix thoroughly. Add 3 mL hydrochloric acid (5.6) and 4 mL glycerol-ethanol solution (5.9), mixing thoroughly after each addition. Add 5 mL barium chloride solution (5.10), dilute to the mark with water and mix. Let stand for 5 minutes. Measure the absorbance at 400 nm using a 3 cm cuvette with water as the reference and subtract the absorbance of the zero-point standard. Plot the calibration curve with sulfate content as the x-axis and absorbance as the y-axis. ​The linear correlation coefficient (R²) must be ≥0.999.

8.6.2 Calibration Curve for Rare Earth-Unseparated Analysis

Add 0 mL, 0.25 mL, 0.50 mL, 1.00 mL, 1.50 mL, 2.00 mL, and 2.50 mL of sulfate standard solution (5.12) into seven 25 mL colorimetric tubes. Add 1–2 drops of p-nitrophenol indicator (5.8). Adjust the pH using ammonia solution (5.5) and hydrochloric acid (5.6) until the yellow color just disappears. Add 3 mL hydrochloric acid (5.6) and 4 mL glycerol-ethanol solution (5.9), mixing thoroughly after each addition. Add 5 mL barium chloride solution (5.10), dilute to the mark with water and mix. Let stand for 5 minutes. Measure the absorbance at 400 nm using a 3 cm cuvette with water as the reference and subtract the absorbance of the zero-point standard. Plot the calibration curve with sulfate content as the x-axis and absorbance as the y-axis. ​The linear correlation coefficient (R²) must be ≥0.999.

9. Test Data Processing

The sulfate content, expressed as a mass fraction $w$, is calculated using Formula (1):

$w=\frac{m\_{1}∙V×10^{-6}}{m∙V\_{1}}×100\%$……………………………………（1）

Where:

$m\_{1}$​: Sulfate content obtained from the calibration curve (in ​$μ$g).

$V$: Total volume of the test solution (in ​mL).

$m$: Mass of the test portion (in ​g).

$V\_{1}$​: Aliquot volume of the test solution (in ​mL).

The absolute difference between two parallel determinations should not exceed the repeatability limit (r) specified in Table 2. The average value is reported as the final result. Results are retained to ​two significant figures, and numerical rounding follows the rules of GB/T 8170.

10. Precision

10.1 Precision Raw Data and Statistics

Precision data were derived from a 2023 interlaboratory study involving ​7 laboratories analyzing sulfate content in cerium oxide, praseodymium-neodymium oxide, gadolinium oxide, and yttrium oxide across five concentration levels. Each laboratory performed ​11 independent measurements per level under repeatability conditions. Statistical analysis followed GB/T 6379.2.

10.2 Repeatability

Under repeatability conditions, the absolute difference between two independent test results shall not exceed the repeatability limit (r) listed in Table 2. If exceeded, the probability is ≤5%. The r-values are calculated via linear interpolation or extrapolation.

Table 2: Repeatability Limits (r)

|  |  |
| --- | --- |
| Sulfate Content (%) | Repeatability Limit (r, %) |
| 0.015 | 0.003 |
| 0.017 | 0.003 |
| 0.051 | 0.004 |
| 0.067 | 0.006 |
| 0.16 | 0.02 |
| Note: r=2.8×Sr, where Sr is the repeatability standard deviation. |

10.3 Reproducibility

Under reproducibility conditions, the absolute difference between two independent test results shall not exceed the reproducibility limit (R) listed in Table 3. If exceeded, the probability is ≤5%. The R-values are calculated via linear interpolation or extrapolation.

Table 3: Reproducibility Limits (R)

|  |  |
| --- | --- |
| Sulfate Content (%) | Reproducibility Limit (R, %) |
| 0.015 | 0.004 |
| 0.017 | 0.004 |
| 0.051 | 0.005 |
| 0.067 | 0.009 |
| 0.16 | 0.03 |
| Note: R=2.8×SR, where SR is the reproducibility standard deviation. |