

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

Part 20: Determination of minor amounts of fluorine and chlorine in rare earth oxides—Ion chromatography method

稀土金属及其氧化物中非稀土杂质

化学分析方法 第20部分：

稀土氧化物中微量氟、氯的测定

离子色谱法

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**Foreword**

SAC/TC 229 is in charge of this English translation. In case of any doubt about the contents of the 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: Structure and drafting of standards.*

This document is part 20 of GB/T 12690 *Chemical analysis methods for non-rare earth impurities of rare earth metals and their oxides*. The following parts have been released for GB/T 12690:

*—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—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 absorptionspectrometric method;*

*—Part 12: Determination of thorium content—Arsenazo III spectrophotometric method and inductively coupled plasma mass spectrum method;*

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

*—Part 14: Determination of titanium in rare earth metals;*

*—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 minor amounts of fluorine and chlorine in rare earth oxides—Ion chromatography method;*

*—Part 21: Determination of sulfate radical 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 SAC/TC 229 (China Rare Earth Standardization Technical Committee).

**Introduction**

China has established a comprehensive standard system for detecting the chemical composition of rare earth products, including total rare earth, non-rare earth impurities, and rare earth impurities. The series of standards GB/T 12690 *Chemical analysis methods for non-rare earth impurities of rare earth metals and their oxides* is based on the original standard GB/T 12690.12-26—1990 *Chemical analysis methods of rare earth metals and their oxides*. The standards of GB/T 8762.3—1988 *Determination of acid-soluble silicon dioxide in fluorescent grade yttrium oxide—Emission spectrometry*, GB/T 8762.4—1988 *Determination of ferric oxide, lead oxide, nickel oxide and copper oxide in fluorescent grade yttrium oxide—Emission spectrometry*, GB/T 8762.6—1988 *Determination of lead oxide, nickel oxide, ferric oxide and copper oxide in fluorescent grade europium oxide—Emission spectrometry*, GB/T 11074.3-7—1989 *Chemical analysis method of samarium oxide*, etc. have been combined. Finally, a comprehensive analysis standard for non-rare earth impurities in all rare earth metals and their oxides is formed. The integrated series of method standards reference advanced detection methods and basically cover all rare earth metals and their rare earth oxide matrix, providing a fast and accurate method for the determination of non-rare earth impurities in rare earth metals and their oxides, and have good operability.

According to the different detection objects, detection methods, and the differences between rare earth metals and rare earth oxide substrates,the GB/T 12690 consisits of the following twenty-one 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—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 absorptionspectrometric method;*

*—Part 12: Determination of thorium content—Arsenazo III spectrophotometric method and inductively coupled plasma mass spectrum method;*

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

*—Part 14: Determination of titanium in rare earth metals;*

*—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 minor amounts of fluorine and chlorine in rare earth oxides—Ion chromatography method;*

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

The above standard is set up according to the routine detection elements in the production and trade of rare earth metals and their oxides, including one or more detection methods, clarifying the scope of application, the selection of reagent materials and test equipment, standardizing the test steps, and giving precision data through multiple tests and verification by several laboratories, establishing a rigorous and standardized work basis for the verification of quality of rare earth metals and their oxides.

At present, the determination of fluorine content in rare earth metals and their oxides often uses ion selective electrode method, and the determination of chlorine is commonly used in silver nitrate turbidimetric method. However, the detection limits of these two anionic methods are high, which can not meet the requirements of the detection of fluorine and chlorine in the low content of high-purity rare earths. Ion chromatography has the advantages of simplicity, rapidity, good selectivity, low interference, low detection limit, high sensitivity and simultaneous determination of a variety of anions, etc., and has been widely used in the determination of anions, especially fluorine and chlorine, in various products. This document establishes a standardized, easy-to-operate and highly accurate detection standard using ion chromatography.

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

Part 20: Determination of minor amounts of fluorine and chlorine in rare earth oxides—Ion chromatography method

**1　Scope**

This document describes test method for the determination of minor amounts of fluorine and chlorine in rare earth oxides.

This document is applicable to the determination of fluorine and chlorine in rare earth oxides. The determination range (mass fraction) is as follows: fluorine 0.0010%-0.010%; chlorine 0.0010%-0.010%.

**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 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 823　*Ion chromatographs*

**3　Terms and Definitions**

There are no terms or definitions that need to be defined in this document.

**4　Theory**

The sample is decomposed by sulfuric acid, during which the fluorine and chlorine are separated from the sample with water vapor.They are then absorbed by water and determined by ion chromatography. Fluorine and chlorine are qualitatively determined by retention times and quantitatively determined by standard curve method.

**5　Reagents and Materials**

Unless otherwise stated, only reagents confirmed to be superior purity or higher grade and water complying with the Grade I water specified in GB/T 6682 shall be used in the analysis. Certified reference solutions shall be given priority.

5.1　Sodium fluoride, primary standard substance.

5.2　Sodium chloride, primary standard substance.

5.3　Hydrogen peroxide (*w*(H2O2)≥30).

5.4　Sulfuric acid (2+1).

5.5　Eluent: Select the appropriate eluent according to the instruction manual for the separation column .

5.6　Fluorine standard storage solution: Weigh 2.2110 g of sodium fluoride (5.1) that has been dried to constant weight at 105℃ - 110℃. Dissolve it in water and transfer the solution to a 1000 mL volumetric flask. Dilute to the mark with water and mix thoroughly. Transfer to a dry plastic bottle. This solution contains 1 mg of fluorine per 1 mL.

5.7　Chlorine standard storage solution: Weigh 1.6485 g of sodium chloride (5.2) that has been incinerated to constant weight at 500°C - 600°C. Dissolve it in water and transfer the solution to a 1000 mL volumetric flask. Dilute to the mark with water and mix thoroughly. This solution contains 1 mg of chlorine per 1 mL.

5.8　Mixed standard solution of fluorine and chlorine: Accurately remove 2.00 mL each of the fluorine standard storage solution (5.6) and the chlorine standard storage solution (5.7) into a 100 mL volumetric flask. Dilute to the mark with water and mix thoroughly. This solution contains 20 μg of fluorine and 20 μg of chlorine per 1 mL. Store the solution in a plastic bottle.

**6　Apparatuses**

6.1　Ion chromatograph: Equipped with a suppressor, conductivity detector, anion separation column and a guard column. The stability of the instrument complies with the provisions of JJG 823.

6.2　Steam distillation unit, see Figure 1.

Figure 1 Steam distillation unit

1. Heating device
2. Distillation bottle (500 mL)
3. Rubber plugs
4. Safety tube
5. Glass conduit
6. Water stop clamp
7. three-neck round bottom flask (250 mL)
8. Thermometer (300℃)
9. Glass bend nozzle
10. Condensing pipe
11. Receiving bottle (100 mL)

Note: 1-6 can be replaced by other steam generating devices

6.3　Water filter membrane needle filter: 0.45 μm.

6.4　Syringe: 2.5 mL ~ 10 mL。

**7　Samples**

Place the sample in an oven at 105°C for 1 hour, then transfer it to a desiccator to cool to room temperature, and weigh it.

**8　Testing procedures**

8.1　Test portion

Weigh 1.00 g sample (7) accurate to 0.0001 g.

8.2　Parallel test

Carry out two tests in parallel.

8.3　Blank test

Perform a blank test along with the sample.

8.4　Preparation of analytical solution

8.4.1　Measure 200 mL of water into the distillation flask of the steam distillation unit, heat it to boiling, and set it aside(or use another steam generator). Measure 60 mL sulfuric acid (5.4) into a three-necked round-bottom flask, wash the flask with water, and add boiling chips. Connect the distillation unit and turn on the cooling water for the condenser. Heat the solution in the three-necked round-bottom flask to increase its temperature, adjust the power of the heating mantle to control the flow rate of steam, and maintain the temperature at 160°C - 180°C. Place the receiving flask under the condenser to collect the condensate for 30 minutes, then stop heating and discard the collected liquid.

8.4.2　When the sample (8.1) is cerium oxide, measure 20 mL water into a 100 mL receiving flask as the absorption solution and set it aside. After the temperature of the sulfuric acid in the three-necked round-bottom flask drops below 60°C, add the sample to the flask, followed by 2 mL of hydrogen peroxide (5.3). Connect the distillation unit and start the distillation process. Heat the solution in the three-necked round-bottom flask to increase its temperature, adjust the power of the heating mantle to control the flow rate of steam, and maintain the temperature at 160°C - 180°C. After 30 minutes of collecting the condensate in the receiving flask placed under the condenser, remove the receiving flask, transfer the solution to a 100 mL volumetric flask, dilute to the mark with water, and mix thoroughly. The solution is now ready for analysis.

8.4.3　When the sample (8.1) is a rare earth oxide other than cerium oxide, measure 20 mL of water into a 100 mL receiving flask as the absorption solution and set it aside. After the temperature of the sulfuric acid in the three-necked round-bottom flask drops below 60°C, add the sample to the flask and connect the distillation unit to start the distillation process. Heat the solution in the three-necked round-bottom flask to increase its temperature, adjust the power of the heating mantle to control the flow rate of steam, and maintain the temperature at 160°C - 180°C. After 30 minutes of collecting the condensate in the receiving flask placed under the condenser, remove the receiving flask, transfer the solution to a 100 mL volumetric flask, dilute to the mark with water, and mix thoroughly. The solution is now ready for analysis.

8.5　Preparation of a series of standard solutions

Accurately transfer 0 mL, 0.25 mL, 0.50 mL, 1.00 mL, 2.50 mL, and 5.00 mL of the mixed standard solution of fluorine and chlorine (5.8) into six 100 mL volumetric flasks, respectively. Dilute each flask to the mark with water and mix thoroughly. These solutions are ready for analysis. The mass concentrations of this series of standard solutions, see Table 1.

Table 1 Concentrations of a series of standard solutions

Unit: ug/mL

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Standard solution number | 1 | 2 | 3 | 4 | 5 | 6 |
| Concentration of fluoride ions | 0 | 0.050 | 0.10 | 0.20 | 0.50 | 1.00 |
| Concentration of chloride ions | 0 | 0.050 | 0.10 | 0.20 | 0.50 | 1.00 |

8.6　Drawing of Standard Curves

After the ion chromatograph has stabilized, use the syringe (6.4) to draw the series of standard solutions (8.5) and connect it to the filter (6.3). Inject and measure the solutions in ascending order of concentration. Plot the standard curve with the mass concentration of fluorine and chlorine (μg/mL) as the x-axis and peak area or peak height as the y-axis. The correlation coefficient of the standard curve for each element should be above 0.995. Otherwise, re-standardization should be performed or the standard solution should be re-prepared for standardization.

8.7　Determination

Connect the syringe (6.4), which has drawn the blank test solution (8.3) or the analytical test solution (8.4), to the filter (6.3), and then inject it into the ion chromatograph. Elute the chromatographic column with the eluent (5.5) and record the chromatogram. Qualitative determination of fluorine and chlorine is performed based on the retention time of the peaks, and quantitative determination of fluorine and chlorine is carried out using the standard curve method.

9**Test data processing**

The content of fluorine or chlorine is calculated as a mass fraction w(i) using the formula (1):

$w\left(i\right)=\frac{\left(C\_{1}−C\_{0}\right)×V×10^{−6}}{m}×100\%$…………………(1)

Where:

*C*1 isthe mass concentration of fluorine or chlorine in the test solution, expressed in micrograms per milliliter (μg/mL);

*C*0 is the mass concentration of fluorine or chlorine in the blank solution, expressed in micrograms per milliliter (μg/mL);

*V* is the volume of analytical solution, expressed in milliliter (mL);

*m* is sample quality, expressed in gram (g).

The absolute difference between the results of two parallel determinations should not exceed the corresponding repeatability limit given in Table 2. The average value is taken as the result of the determination with two significant figures retained. The rounding of numerical values is carried out according to the provisions of GB/T 8170.

1. **Precision**

10.1　Precision raw data and statistics

The precision data are based on the collaborative trial statistics and calculations from six laboratories in June 2023, using six different levels of samples, including cerium oxide, gadolinium oxide, lutetium oxide, two spiked synthetic samples of lutetium oxide, and one spiked synthetic sample of gadolinium oxide. Each laboratory independently determined the content of fluorine and chlorine in cerium oxide, gadolinium oxide, lutetium oxide, and the spiked synthetic samples of lutetium oxide and gadolinium oxide under repeatability conditions, with 11 determinations for each level. The experimental data were statistically analyzed according to GB/T 6379.2.

10.2　Repeatability

Under repeatability conditions, the absolute difference between two independent test results should not exceed the repeatability limit (r), and the occurrence of exceeding the repeatability limit (r) should not exceed 5% . The repeatability limit (r) is determined using linear interpolation or extrapolation based on the data in Table 2.

Table 2 Repeatability Limits (*r*)

|  |  |  |
| --- | --- | --- |
| Element | mass fraction % | repeatability limit (*r*)% |
| Fluorine | 0.0013 | 0.0003 |
| 0.0048 | 0.0005 |
| 0.010 | 0.001 |
| Chlorine | 0.0011 | 0.0003 |
| 0.0021 | 0.0005 |
| 0.0055 | 0.0006 |
| 0.0069 | 0.0006 |
| 0.0096 | 0.0007 |
| **Note:** The repeatability limit (r) is 2.8×Sr, where Sr is the standard deviation of repeatability. |

10.3　Reproducibility

Under reproducibility conditions, the absolute difference between two independent test results should not exceed the reproducibility limit (R), and the occurrence of exceeding the reproducibility limit (R) should not exceed 5%. The reproducibility limit (R) is determined by linear interpolation or extrapolation based on the data in Table 3.

Table 3 Reproducibility limit (*R*)

|  |  |  |
| --- | --- | --- |
| Element | mass fraction % | reproducibility limit (*R*)% |
| Fluorine | 0.0013 | 0.0003 |
| 0.0048 | 0.0014 |
| 0.010 | 0.002 |
| Chlorine | 0.0011 | 0.0004 |
| 0.0021 | 0.0006 |
| 0.0055 | 0.0010 |
| 0.0069 | 0.0006 |
| 0.0096 | 0.0014 |
| **Note:** The reproducibility limit (R) is 2.8×SR, where SR is the standard deviation of reproducibility. |