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Rare earth — Determination of rare earth content in individual rare earth metals and their oxides — Titration method

Terres rares — Détermination de la teneur en terres rares dans les métaux des terres rares individuels et leurs oxydes — Méthode de titrage

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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO document should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by Technical Committee ISO/TC 298, *Rare earth*.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Individual rare earth metals and their oxides are both materials containing only one kind of rare earth element. They are refined and separated rare earth products, which are widely used as the feedstock for making downstream products in the rare earth industry. In the products, there exist trace non-rare earth impurities including some carbonates, oxalates and moisture. Some of them (such as Ca, Si, Fe) come from raw materials and others (such as Fe) come from industrial processes of rare earth metal from the electrolytic process.

Rare earth content refers to the mass fraction of all rare earth elements in the material. It is an important chemical composition index to determine the quality of the individual rare earth metals and their oxides. A scientific and standardized method to determine the rare earth content, which is used to price the product in trading, is helpful to reduce variability and to improve the consistency and comparability of interlaboratory results, consequently facilitating the fair trade of rare earth products.

The document aims to supply a classic titration method for the determination of rare earth content for individual rare earth metals and their oxides, which can be adopted by rare earth producers, consumers, traders and other stakeholders.

Rare earth — Determination of rare earth content in individual rare earth metals and their oxides — Titration method

WARNING — The use of this document can involve hazardous materials, operations and equipment. This document does not purport to address any safety problems associated with its use. It is the responsibility of the user of this document to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This document specifies a titration method for the determination of rare earth content in 15 kinds of individual rare earth metals (lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium and yttrium) and their oxides.

The determination ranges for the rare earth content in mass fraction are as follows:

— rare earth metal: 98,0 % (mass fraction) to 99,5 % (mass fraction);

— rare earth oxide: 95,0 % (mass fraction) to 99,5 % (mass fraction).

It does not apply to individual rare earth metals and their oxides when:

a) the relative rare earth purity is less than 99,5 % in mass fraction;

b) the total content of various (non-rare earth) metallic elements is greater than 0,5 % in mass fraction;

c) the content of thorium, scandium or zinc is greater than 0,1 % in mass fraction.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1
rare earth content
total rare earth content
mass fraction of rare earths in the material

Note 1 to entry: For rare earth oxides and other compounds, the fraction is generally provided as a percentage of rare earth oxide, i.e. % REO or % TREO. For metals and alloys, the content is generally provided as a percentage of rare earth metal, i.e. % REM or % TREM.

Note 2 to entry: For rare earth oxides and other compounds, the formula of the rare earth content is RE_2O_3 except for CeO_2, Pr_6O_{11} and Tb_4O_7.

[SOURCE: ISO 22444-1:2020, 3.7, modified — Note 2 to entry added.]

3.2
rare earth content (original basis)
rare earth content (3.1) of a material as contained in the original as-received sample that has not undergone any treatment

3.3
rare earth content (dry basis)
rare earth content (3.1) of a material as contained in the sample subjected to drying in air at 105 °C for 1 h

3.4
rare earth content (ignition basis)
rare earth content (3.1) of a material as contained in the sample subjected to ignition in air at 950 °C for 1 h

3.5
individual rare earth metal
metallic substance containing only one rare earth element, including La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc and Y

Note 1 to entry: It is assumed that the relative purity of an individual rare earth metal is at least 99,5 %.

Note 2 to entry: Pm and Sc are not within the scope of this document.

[SOURCE: ISO 22444-2:2020, 4.2, modified — Note 1 to entry deleted. New Notes 1 and 2 to entry added.]

3.6
individual rare earth oxide
chemical compound containing one rare earth element and the oxygen element

Note 1 to entry: It is assumed that the *relative rare earth purity* (3.7) of an individual rare earth oxide is at least 99,5 %.

3.7
relative rare earth purity
mass fraction of the specified rare earth element or rare earth oxide out of the *rare earth content* (3.1)

Note 1 to entry: It is expressed as a percentage with the basis (REM or REO) stated.

[SOURCE: ISO 22444-1:2020, 3.13]

3.8
permissible tolerance
α
alternative expressions for precision parameters, including r (repeatability limit), R_w (intralaboratory reproducibility limit) and R (interlaboratory reproducibility limit)

Note 1 to entry: Permissible tolerances replace precision parameters only when the precision parameters are independent of the level.

Note 2 to entry: Permissible tolerances can be expressed as $\alpha(s_r)$, $\alpha(s_{Rw})$ and $\alpha(s_R)$ and calculated by using the following formula from ISO/TR 21074:2016, 6.6.5:

$$\alpha = 2{,}8 \times \sqrt{\frac{1}{n}\sum_{i=1}^{n} {\beta_i}^2}$$

where

β is the statistical values of s_r, s_{Rw} and s_R for each level;

i is the identifier for each level;

n is the number of levels.

4 Principle

The samples are dissolved in acid solutions. Rare earth ions are titrated and complexed quantitatively at pH 5,5 with a standard EDTA solution and xylenol orange as an indicator after masking coexisting non-rare earth ions such as iron, etc. with sulfosalicylic acid.

5 Reagents

WARNING — Concentrated acids and alkalis are corrosive and their vapours irritate the mucous membranes. Users should consult the safety data sheet and safety labelling for each reagent before using. Care shall be taken to avoid any type of contact during use. Appropriate protective equipment shall be worn when working with concentrated acids and alkalis. All the procedures involving acids and alkalis shall be carried out in a fume hood.

The following reagents and indicators may be used in the titration procedure. Where applicable, instructions are provided for creating solutions. All reagents should be of known analytical grade, and only distilled or demineralized water should be used.

5.1 Ascorbic acid, $C_6H_8O_6$, powder.

5.2 Hydrochloric acid, HCl, $\rho = 1{,}19$ g/ml.

5.3 Nitric acid, HNO_3, $\rho = 1{,}40$ g/ml.

5.4 Ammonia, NH_3, $\rho = 0{,}91$ g/ml.

5.5 Hydrogen peroxide, H_2O_2, 30 % (mass fraction), $\rho = 1{,}11$ g/ml.

5.6 Hydrochloric acid, diluted 1 + 1.

Add 250 ml of hydrochloric acid (5.2) into 250 ml of water and mix.

5.7 Nitric acid, diluted 1 + 1.

Add 250 ml of nitric acid (5.3) into 250 ml of water and mix.

5.8 Ammonia, diluted 1 + 1.

Add 250 ml of ammonia (5.4) into 250 ml of water and mix.

5.9 Sulfosalicylic acid, $C_7H_6O_6S{\cdot}2H_2O$, 100 g/l solution.

Weigh 50 g of sulfosalicylic acid and place into a 500 ml beaker. Add 300 ml of water and stir to dissolve. Make up the volume to 500 ml with water and mix.

5.10 Xylenol orange indicator solution, $C_{31}H_{32}N_2O_{13}S$, 2 g/l.

Weigh 0,2 g of xylenol orange and place into a 150 ml beaker. Add 80 ml of alcohol to dissolve. Make up the volume to 100 ml with alcohol and mix.

5.11 Methyl orange indicator solution, $C_{14}H_{14}N_3SO_3Na$, 2 g/l.

Weigh 0,2 g of methyl orange and place into a 150 ml beaker. Add 80 ml of water and heat at a moderate temperature to dissolve. make up the volume to 100 ml with water and mix.

5.12 Hexamethylene tetramine buffer solution (pH 5,5), $C_6H_{12}N_4$.

Weigh 100 g of hexamethylene tetramine into a 500 ml beaker. Add 300 ml of water and stir to dissolve. Add 35 ml of hydrochloric acid (5.6), make up the volume to 500 ml with water and mix. Check that the pH is 5,5 ± 0,2.

5.13 Zinc standard solution, 1 g/l.

Weigh 0,200 0 g of zinc metal ($w_{Zn} \geq 99{,}99$ %) in a beaker. Add 10 ml of water and then add 10 ml of hydrochloric acid (5.6), and heat gently until completely dissolved. Cool and transfer the solution into a 200 ml volumetric flask. Add 10 ml of hydrochloric acid (5.6), make up the volume with water and mix.

5.14 Disodium ethylenediamine tetra-acetic acid (EDTA) standard titration solution, approximately 0,01 mol/l.

A commercially available product with a certified composition can be used. It does not need be prepared and standardized.

To prepare, weigh approximately 7,5 g of EDTA into a 250 ml beaker. Dissolve with 200 ml of water and transfer into a 2 l volumetric flask. Make up the volume with water and mix.

To standardize, transfer 25,00 ml of zinc standard solution (5.13) to a 250 ml Erlenmeyer flask with a calibrated pipette. Add 50 ml of water and a drop (not more than 0,1 ml) of methyl orange indicator solution (5.11). Adjust the acidity with ammonia (5.8) to turn the solution exactly to a yellow colour. Add 5 ml of hexamethylene tetramine buffer solution (5.12) and two drops (not more than 0,2 ml) of xylenol orange indicator (5.10). Titrate the solution with the EDTA standard solution (5.14) just to the point when the colour of the solution changes from red to yellow. Conduct the above standardization process for three portions in parallel. Calculate the concentration of the EDTA standard titration solution (5.14) by using Formula (1) and average the three calculated concentration values until the range of the consumed volumes of EDTA standard titration solution (5.14) is less than 0,10 ml.

The concentration of EDTA standard solution (5.14), c, shall be expressed as an amount-of-substance concentration (mol/l) and is calculated by using Formula (1):

$$c = \frac{\rho \cdot V_1}{V_2 \cdot M_1} \tag{1}$$

where

c is the concentration, in moles per litre, of the EDTA standard titration solution;

ρ is the concentration, in grams per litre, of the zinc standard solution;

V_1 is the volume, in millilitres, of the transferred zinc standard solution;

V_2 is the volume, in millilitres, of the consumed EDTA standard titration solution;

M_1 is the atomic mass of zinc, in grams per mole, of the zinc standard solution.

6 Apparatus

6.1 High temperature furnace (air), with a temperature upper limit ≥ 1 000 °C and a precision of ±10 °C.

6.2 Drying oven, with a precision of ±5 °C.

6.3 pH meter.

6.4 Automatic titrator.

6.5 Analytical balance, accurate to nearest 0,000 01 g (0,01 mg).

7 Sample preparation

7.1 For rare earth metals, the laboratory sample is normally prepared into the form of drillings or fragments after removing the oxidized surface layer by filing. Weigh immediately after sample preparation to minimize oxidization in air.

7.2 For rare earth oxides, keep the sample in its as-received state to determine the rare earth content (original basis).

7.3 For rare earth oxides, approximately 5 g of the sample is put into a shallow weighing vessel of approximately 50 mm diameter and 30 mm height with a cover. Dry the sample in air at 105 °C for 1 h and allow to cool in a desiccator to room temperature to determine the rare earth content (dry basis).

7.4 For rare earth oxides, approximately 3 g of the sample is put into a crucible. Ignite the sample in air at 950 °C for 1 h and allow to cool in a desiccator to room temperature to determine the rare earth content (ignition basis).

8 Procedure

8.1 Test portion

Weigh 0,40 g to 1,00 g of the test sample to the nearest 0,000 1 g.

8.2 Dissolution

8.2.1 Put the test portion (see 8.1) into a beaker. Add 20 ml of water, followed by 10 ml of hydrochloric acid (5.6) or nitric acid (5.7).

10 ml of nitric acid (5.7) and 1 ml of hydrogen peroxide (5.5) shall be used when dissolving the cerium matrix sample.

8.2.2 Heat the solution at a moderate temperature (353 K to 383 K) to avoid a violent chemical reaction until completely dissolved. Evaporate until 1 ml to 2 ml of the solution remains. Add 20 ml of water, followed by 2 ml of hydrochloric acid (5.6), and heat to dissolve the salts.

If an insoluble residue occurs from the cerium oxide, do continuous intermittent instillation of hydrogen peroxide (5.5) to promote the dissolution.

8.2.3 Cool the solution to room temperature. If the mass of the test portion < 0,80 g, transfer the solution into a 100 ml volumetric flask. If the mass of the test portion ≥ 0,80 g, transfer the solution into a 200 ml volumetric flask. Make up the volume with water and mix.

8.3 Titration

8.3.1 Transfer 10,00 ml of the test solution (see 8.2) into a 200 ml to 300 ml Erlenmeyer flask or beaker.

8.3.2 Add 50 ml of water, 0,1 g to 0,2 g of ascorbic acid (5.1) and 2 ml of sulfosalicylic acid (5.9) to the flask or beaker.

8.3.3 Add one drop (not more than 0,1 ml) of methyl orange indicator (5.11). Add ammonia (5.8) by drops just to the point when the colour of the solution changes from red to yellow. Alternatively, adjust the pH value to 5,5 using a pH meter (6.3).

8.3.4 Add 5 ml of the hexamethylene tetramine buffer solution (5.12) and two drops (not more than 0,2 ml) of the xylenol orange indicator (5.10) to the solution.

8.3.5 Titrate the solution with the EDTA standard titration solution (5.14) just to the point when the colour of the solution changes from red-purple to light yellow. Alternatively, titrate with an automatic titrator (6.4).

9 Calculation and expression of results

9.1 Calculation of results

The rare earth content of the metal sample, w_{REM}, shall be expressed as a percentage by mass fraction and calculated by using Formula (2):

$$w_{\mathrm{REM}} = \frac{M_2 \cdot c \cdot V_3 \cdot V_4}{V_5 \cdot m_1 \times 1\ 000} \times 100 \qquad (2)$$

where

M_2	is the atomic mass, in grams per mole, of the rare earth element contained in the test portion;
c	is the concentration, in moles per litre, of the EDTA standard titration solution;
V_3	is the volume, in millilitres, of the consumed EDTA standard titration solution;
V_4	is the gross volume, in millilitres, of the test solution;
V_5	is the volume, in millilitres, of the transferred test solution;
m_1	is the mass, in grams, of the test portion.

The rare earth content of the oxide sample, w_{REO}, shall be expressed as a percentage by mass fraction and calculated by using Formula (3):

$$w_{\mathrm{REO}} = \frac{M_3 \cdot c \cdot V_6 \cdot V_7}{V_8 \cdot m_2 \cdot x \times 1\ 000} \times 100 \qquad (3)$$

where

M_3 is the atomic mass, in grams per mole, of the rare earth oxide (RE_xO_y) of the test portion;

c is the concentration, in moles per litre, of the EDTA standard titration solution;

V_6 is the volume, in millilitres, of the consumed EDTA standard titration solution;

V_7 is the gross volume, in millilitres, of the test solution;

V_8 is the volume, in millilitres, of the transferred test solution;

m_2 is the mass, in grams, of the test portion;

x is the atomic number of the rare earth element in the molecular formula RE_xO_y.

The rare earth content of the oxide sample shall be given as rare earth content (original basis) or rare earth content (dry basis) or rare earth content (ignited basis) according to the pre-treatment for the test sample. It shall be given together with the formula stated in Note 2 to entry of 3.1.

9.2 Precision

The absolute difference between two independent single test results, obtained using the same method on identical test material in the same laboratory by the same operator using the same equipment within a short interval of time, will not exceed the repeatability permissible tolerance $\alpha(s_r)$ in Table 1 in more than 5 % of cases.

The absolute difference between two independent single test results, obtained using the same method on identical test material in the same laboratory by the same operator using the same equipment, but at a different time (on a different day), will not exceed the intralaboratory reproducibility permissible tolerance $\alpha(s_{Rw})$ in Table 1 in more than 5 % of cases.

The absolute difference between two single test results, obtained using the same method on identical test material in different laboratories by different operators using different equipment, will not exceed the interlaboratory reproducibility permissible tolerance $\alpha(s_R)$ in Table 1 in more than 5 % of cases.

Table 1 — Permissible tolerance α

Values in % (mass fraction)

Sample type	**Determination range**	**Repeatability permissible tolerance** $\alpha(s_r)$	**Intralaboratory reproducibility permissible tolerance** $\alpha(s_{Rw})$	**Interlaboratory reproducibility permissible tolerance** $\alpha(s_R)$
Rare earth metal	98,0 to 99,5	0,45	0,45	0,98
Rare earth oxide	95,0 to 99,5	0,37	0,41	0,81

NOTE The samples for interlaboratory tests cover all the sample types in Table 1, which are different materials and produced by different industrial processes. No satisfactory functional relationship between the values of precision and rare earth content (m) can be established. However, the precision values are similar across some levels from the same sample type. Therefore, the permissible tolerances $\alpha(s_r)$, $\alpha(s_{Rw})$ and $\alpha(s_R)$ are applied in this document instead of the repeatability limit (r) and reproducibility limits (R_w, R) in accordance with ISO/TR 21074:2016.

The details of the samples used and the results obtained in the precision experiment are given in Annex A.

10 Test report

The test report shall contain the following information:

a) all information necessary for the identification of the sample, the laboratory and the date of analysis or of the test report;

b) the method used by reference to this document, i.e. ISO 23597:2023;

c) the results and the units in which they are expressed;

d) any unusual features noted during the determination;

e) any operation not specified in this document, or any optional operation which can influence the results.