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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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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, ρ = 1,19 g/ml.

5.3 Nitric acid, HNO_3, ρ = 1,40 g/ml.

5.4 Ammonia, NH_3, ρ = 0,91 g/ml.

5.5 Hydrogen peroxide, H_2O_2, 30 % (mass fraction), ρ = 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} ≥ 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.

