International Standard

ISO 24181-1

First edition
2024-08

Rare earth — Determination of non-rare earth impurities in individual rare earth metals and their oxides — ICP-AES —

Part 1:
Analysis of Al, Ca, Mg, Fe and Si

Terres rares — Détermination des impuretés de terres non rares dans les métaux de terres rares individuels et leurs oxydes — ICP-AES —

Partie 1: Analyse de Al, Ca, Mg, Fe et Si

Reference number
ISO 24181-1:2024(en)

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

Published in Switzerland

Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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).

ISO draws attention to the possibility that the implementation of this document may involve the use of (a) patent(s). ISO takes no position concerning the evidence, validity or applicability of any claimed patent rights in respect thereof. As of the date of publication of this document, ISO had not received notice of (a) patent(s) which may be required to implement this document. However, implementers are cautioned that this may not represent the latest information, which may be obtained from the patent database available at www.iso.org/patents. ISO shall not be held responsible for identifying any or all such patent rights.

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

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

A list of all parts in the ISO 24181 series can be found on the ISO website.

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

Atomic spectroscopy has been recognised as the most common technique for trace elemental determinations. Although atomic absorption spectroscopy is limited to determination of one element at a time, many elements are analysed routinely at the same time by inductively coupled plasma atomic emission spectroscopy (ICP-AES), which utilises the inductively coupled plasma (ICP) as an excitation source for atomic emission spectrometry (AES). Several thousands of these instruments are in routine use throughout the world.

ICP-AES is the most common technique for trace elemental determinations, particularly for the analysis of impurities. This method has been demonstrated to feature a linear response over a wide dynamic range, a low chemical interference/matrix effect, good stability and good reproducibility. It demonstrates a low detection limit and various sample introduction techniques are available for different sample analysis demands.

In rare earth metals and oxides, during processing ores of rare earth elements, Aluminum(Al), calcium(Ca), magnesium(Mg), iron(Fe) and silicon(Si) are contained as impurities. ICP-AES is well-suited for the quantification of non-rare earth impurities in a matrix containing rare earth elements. Additionally, the ICP-AES technique also offers high resolution for rare earth elements as rare earth elements exhibits line-rich emission spectra.

This document provides a guide for chemical analysis of materials for producers, consumers, and traders in the field of rare-earth metals and their oxides. This document is anticipated to reduce discrepancies caused by inconsistencies in the analytical procedures used when working with rare earth metals and their oxides.

Rare earth — Determination of non-rare earth impurities in individual rare earth metals and their oxides — ICP-AES —

Part 1:
Analysis of Al, Ca, Mg, Fe and Si

WARNING — The use of this document can involve hazardous chemicals, 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 to determine the applicability of regulatory limitations before use (e.g. according to ISO 15202-2 and ISO 15202-3).

1 Scope

This document describes procedures for the determination of non-rare earth impurities in individual rare earth metals and their oxides through the use of inductively coupled plasma atomic emission spectroscopy (ICP-AES). Magnesium (Mg), aluminum (Al), silicon (Si), calcium (Ca) and iron (Fe) are included as non-rare earth impurity elements, and the measurement ranges for each impurity element are specified. The applicable measurement range (mass fraction %) of magnesium, aluminum, silicon and calcium is from 0,001 to 0,2, and that of iron is from 0,001 to 0,5. The verified measurement ranges in the interlaboratory tests are described later in this document.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content dictates requirements or specifications 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.

ISO 648, *Laboratory glassware — Single-volume pipettes*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 11885, *Water quality — Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES)*

ISO 22444-1, *Rare earth — Vocabulary — Part 1: Minerals, oxides and other compounds*

ISO 22444-2, *Rare earth — Vocabulary — Part 2: Metals and their alloys*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 22444-1, ISO 22444-2 and the following 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
inductively coupled plasma
ICP
high-temperature (8 000 K to 10 000 K) discharge of energy generated in a ionized gas, usually argon, produced by a radio frequency controlled varying magnetic field, originating from an AC current flowing in a water-cooled copper coil or in an induction coil which surrounds tubes through which the gas flows

3.2
inductively coupled plasma-atomic emission spectroscopy
ICP-AES
type of atomic spectroscopy in which the optical radiation emitted by atoms and ions present in an *inductively coupled plasma* (3.1) is observed and measured

3.3
impurity element
very small amount or trace of element in an otherwise pure substance

3.4
matrix solution
solution of the high purity metal or oxide of an individual rare earth element at a certified concentration(s), suitably prepared known sample which is used for *LOQ* (3.13) confirmations and preparation of *calibration solutions* (3.6)

Note 1 to entry: *Impurity elements* (3.3) in high purity metals or oxides of individual rare earth elements shall be determined prior to analyses, and shall be controlled to less than a mass fraction of 0,001 % or 0,000 1 % depending on the concentration of each impurity element in the high purity rare earth metal or oxide for the preparation of the matrix solution.

3.5
stock solution
solution of a high purity chemical compound containing *an impurity element* (3.3) at a certified concentration(s) suitably prepared known sample, which is used for the preparation of *calibration solutions* (3.6)

Note 1 to entry: The purity of the chemical compound containing the same single element as *an impurity element* (3.3) for the *stock solution* (3.5) shall be generally controlled to more than a mass fraction of 99,9 %.

3.6
calibration solution
solution prepared with the addition of *matrix solution* (3.4) and any *stock solution* (3.5) for constructing a calibration curve

Note 1 to entry: For the *calibration curve method* (3.12), the *matrix solution* (3.4) prepared without the addition of any stock solution is required as a blank solution. The concentration of the *impurity elements* (3.3) in this blank solution is taken to be zero.

3.7
test sample
solid substance of a rare earth metal or oxide for the determination of an *impurity element* (3.3)

3.8
test portion
quantity of material drawn from the *test sample* (3.7) (or from the laboratory sample if both are the same) and on which the test or observation is actually carried out

[SOURCE: ISO 78-2:1999, 3.3]

3.9
test solution
solution of the weighed *test sample* (3.7) prepared by the *acid digestion method* (3.10)

3.10
acid digestion method
sample preparation method of dissolving *test samples* (3.7) into a solution by adding acids and heating until the complete decomposition of the matrix is achieved

3.11
calibration curve method
method for quantifying *impurity elements* (3.3) in a *test sample* (3.7) using a calibration curve prepared with *calibration solution* (3.6) containing a targeted *impurity element* (3.3) with far lower concentrations of non-targeted elements than that of the targeted *impurity element* (3.3)

3.12
matrix matching
preparation process to fabricate a *calibration solution* (3.6) with the same chemical composition of *test solution* (3.9) for the *calibration curve method* (3.11)

3.13
limit of quantification
LOQ
lowest amount of an analyte that is quantifiable with a given confidence level

Note 1 to entry: The limit of quantification is calculated as ten times the standard deviation of the measurement result of blank, which is the matrix solution prepared without the addition of any stock solutions.

Note 2 to entry: The value of LOQ is used as a threshold value to assure quantitative measurement of an analyte accurately.

4 Principle

The specified measurement ranges for these impurities are shown in Table 1. An instrument capable of the achieving the below ranges is required for this determination. The lower limits of measurement range shall be above the limits of quantification (LOQ) for each impurity element.

Table 1 — Measurement range of impurity elements in rare earth metals and their oxides

Type of impurity elements in rare earth metals and their oxides	Verified measurement range in the interlabotarory test mass fraction %	Applicable measurement range by this determination method mass fraction %
Magnesium (Mg)	0,002 to 0,06	0,001 to 0,2
Aluminium (Al)	0,003 to 0,03	0,001 to 0,2
Silicon (Si)	0,002 to 0,03	0,001 to 0,2
Calcium (Ca)	0,004 to 0,08	0,001 to 0,2
Iron (Fe)	0,003 to 0,03	0,001 to 0,5

NOTE This document provides appropriate sample preparation method and a calculation procedure of the calibration curve for the applicable measurement range shown above.

The concentrations of non-rare earth impurity elements in test samples are quantified by the calibration curve method performed with matrix matching. Test samples of individual rare earth metals and their oxides are prepared by dissolution using the acid digestion method. After the sample preparation, if an insoluble residue occurs, the results obtained by analysing the test solution shall be considered imprecise information. A report shall be required if any insoluble residue occurs. A depiction of the calibration curve method with matrix matching is shown in Figure 1.

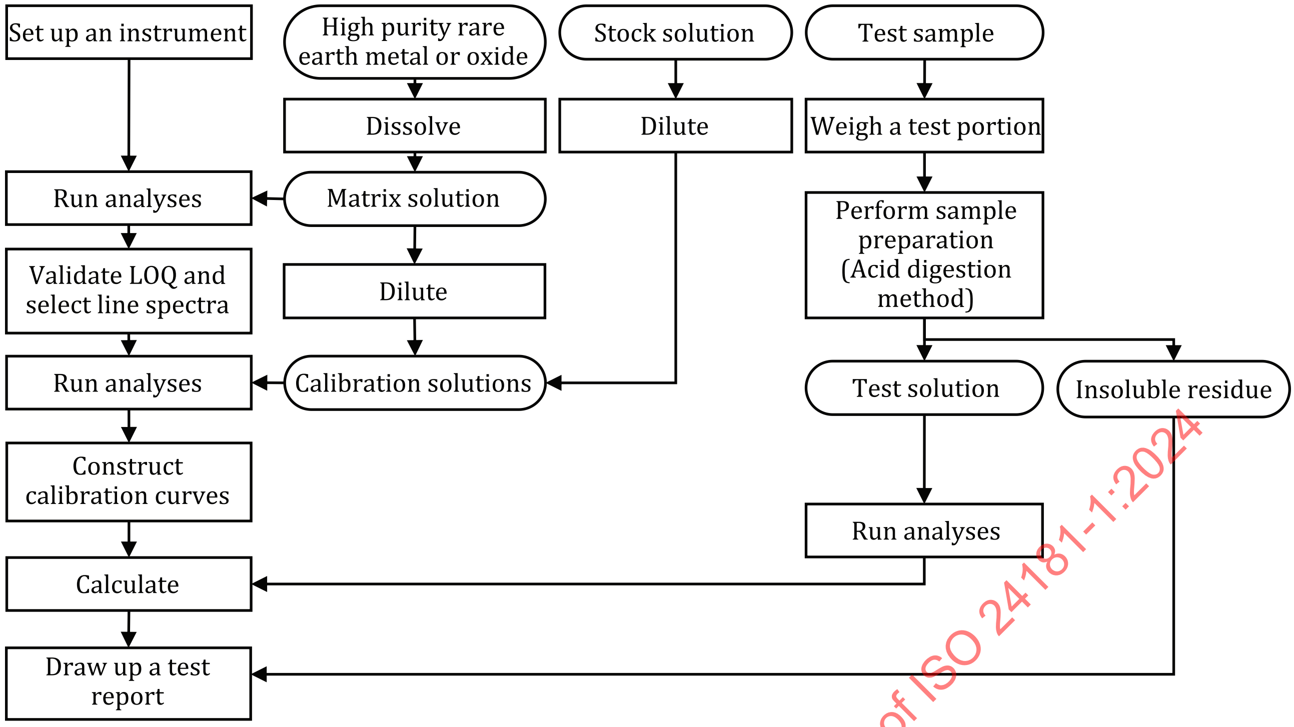

Figure 1 — A flow chart describing the calibration curve method with matrix matching

5 Reagent

During the analysis, unless otherwise stated, use analytical grade reagents and high purity water, in which the concentration of each impurity element is well controlled to less than 0,01 µg/ml. Use high purity water in accordance with ISO 11885 and ISO 3696.

5.1 Nitric acid, HNO_3, appropriate density (e.g. ρ about 1,37 g/ml to 1,41 g/ml).

5.2 Hydrogen peroxide, H_2O_2, ρ about 1,11 g/ml.

6 Apparatus

6.1 Volumetric glassware

All volumetric glassware shall be calibrated in accordance with ISO 648 or ISO 1042, as appropriate.

6.2 Inductively coupled plasma atomic emission spectrometer

6.2.1 General

An instrument shall be optimized in accordance with the manufacturer's instructions.

6.2.2 Line spectra selection

As rare earth elements produce line-rich emission spectra, choice of the specific emission lines for a particular analysis impacts the final determination of the impurity concentration and should be done with care. The main issue for conducting accurate multi-element analyses is that the probability of emission line overlap between spectral lines of different elements is high, creating challenges in elemental concentration determination. Therefore, it is important to select analyte line spectra very carefully according to equipment conditions to minimize potential emission line overlap. The recommended line spectra for analysis are given in Table 2. The wavelengths below 200 nm shown in Table 2 should be detected in a vacuum rather than in the air. The lower limits of the measurement range shall be above the limits of quantification (LOQ) for each impurity element. It shall be confirmed that the LOQs are below the lower limits of the measurement range described in the scope prior to line spectra selection. The lower limits of the measurement range shall be changed and conformed to the LOQs if the LOQs are not below a mass fraction of 0,001 % (10 µg/g).

Table 2 — Recommended line spectra in the air (nm)

		Types of rare earth metal or oxide							
		La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
Impurity elements	Al	167,020 309,271 396,152	167,020 237,312 257,510	167,020 226,909 266,039 309,271	167,020 226,909 308,215	167,020 237,312 308,215 309,271 394,403 396,153	167,020 237,312 308,215 396,152	167,020 237,312 396,152	167,020 237,312 394,403
	Ca	317,933 393,366 396,847	317,933 396,847 422,673	315,887 393,366 396,847	317,933 393,366	393,366 396,847	393,366 396,847	393,366 396,847	393,366 396,847
	Fe	238,204 239,562 259,940	238,204 239,562 240,488 259,940	234,349 239,562 240,488 259,940	238,204 239,562 259,940	238,204 239,562 240,488 259,940	238,204 240,488 259,940	234,349 239,562 240,488 259,940	238,204 239,562 259,940
	Mg	279,553 280,270	279,553 280,270 285,213	279,553 280,270 285,213	279,553 280,270 285,213	279,553 280,270	279,553 280,270	279,553 280,270	279,553
	Si	212,412 251,611 288,158	212,412 251,611 288,158	212,412 251,611	212,412 251,611 288,158	212,412 251,611	251,611 288,158	212,412 251,611	212,412 251,611 288,158

		Types of rare earth metal or oxide						
		Dy	Ho	Er	Tm	Yb	Lu	Y
Impurity elements	Al	167,020 237,312 257,510 394,403	167,020 237,312 394,403 396,152	167,020 237,312 394,403 396,152	167,020 226,909 394,403 396,152	167,020 226,909 394,403 396,152	167,020 237,312 226,909 394,403 396,152	167,020 237,336 308,215 396,152
	Ca	393,366 422,673	393,366 396,847	393,366 396,847	393,366 396,847	393,366 396,847	393,366 422,673	393,366 396,847 422,673
	Fe	234,349 239,562 259,940	238,204 259,940	238,204 239,562 259,940	238,204 239,562 240,488 259,940	238,204 239,562 259,940	234,349 238,204 259,940	238,204 239,562 240,488 259,940
	Mg	279,553 280,270	279,553 280,270	279,553 280,270	279,553 280,270	279,553 280,270	279,553 280,270	279,553 280,270
	Si	212,412 251,611 288,158	212,412 251,611 288,158	251,611 288,158	212,412 251,611 288,158	212,412 288,158	212,412 251,611 288,158	212,412 251,611 288,158

7 Procedure

7.1 Weighing the test portion

Weigh out a test sample accurately to (1,00 ± 0,001) g of net mass of rare earth element in elemental substance equivalent. The test sample with the known approximate concentration of the impurity elements and dried until a constant mass shall be prepared.

7.2 Sample preparation

In a chemical fume hood, place a weighed test portion (see 7.1) into a 100 ml beaker where 20 ml of water and 5 ml of nitric acid (5.1) shall be added [in the case of cerium oxide, use 5 ml of nitric acid (5.1) and 1 ml of hydrogen peroxide (5.2)]. Heat the beaker and the contents to moderate temperature (353 K to 373 K) until the test sample is completely dissolved [if an insoluble residue occurs from the cerium oxide, do continuous intermittent instillation of hydrogen peroxide (5.2) to promote the dissolution. The dissolving time is sometimes over 30 min]. After dissolution, cool the solution containing the test sample to room temperature and then filter through filter paper. Transfer the filtrate into a volumetric flask, dilute it with water to a volume of 100 ml, and mix well (designated as the test solution 1). When the expected analyte concentration in the test sample is greater than a mass fraction of 0,015 %, transfer 10,00 ml of the test sample solution into a 100 ml volumetric flask, dilute with water to the marked line, and mix well (designated as the test solution 2).

NOTE 1 The cerium oxide calcined at high temperature is not easily dissolved.

NOTE 2 Best practice is to add acid to water where possible.

7.3 Preparation of calibration solutions

Table 3 shows the typical concentrations of the rare earth element (REE) and analyte impurity elements in the calibration solutions prepared for the calibration curve method with matrix matching in the case that the determination range of each impurity element does not exceed a mass fraction of 0,010 % (100 µg/g). When the analyte concentration is quantitatively greater than a mass fraction of 0,010 % (100 µg/g), the concentration of the calibration solutions shown in Table 4 shall be used.

To conduct the matrix matching procedure, the concentration of all the impurity elements in the test sample shall be approximately known. Prepare the calibration solution by the addition of the stock solutions to the matrix solution. For test portions in which the concentration of each impurity element is less than a mass fraction of 0,01 % (100 µg/g), the concentration of each impurity element in the high purity rare earth metal or oxide for the matrix solution shall not exceed a mass fraction of 0,000 1 % (1 µg/g). The concentration of impurity elements in the no. 1 calibration solution (see Table 3 or Table 4), the matrix solution without any stock solutions, should be treated as zero. In the case of cerium oxide, the proportion of used reagents, which are nitric acid (5.1) and hydrogen peroxide (5.2), to the matrix shall be to meet with the condition of sample preparation.

If the concentration of each impurity element in the matrix solution is known and the added stock solutions are adjustable, the concentration of each impurity element in the high-purity rare earth metal or oxide shall not be less than a mass fraction of 0,000 1 % (1 µg/g). If the impurity element concentration of a high-purity oxide is less than 10 µg/g and greater than 1 µg/g, the impurity element concentration of the no. 1 calibration solution, which is the mother solution without undiluted solution, shall be treated as an actual value, not zero.

Table 3 — Concentration of the calibration solutions for the test solution 1 (each impurity element < mass fraction of 0,010 %)

No.	REE concentration µg/ml	Analyte concentration µg/ml				
		Al	Ca	Fe	Mg	Si
1	10 000	0	0	0	0	0
2	10 000	0,1	0,1	0,1	0,1	0,1
3	10 000	0,2	0,2	0,2	0,2	0,2
4	10 000	0,5	0,5	0,5	0,5	0,5
5	10 000	1,0	1,0	1,0	1,0	1,0
6	10 000	2,0	2,0	2,0	2,0	2,0

Table 4 — Concentration of the calibration solutions for the test solution 2 (each impurity element ≥ mass fraction of 0,010 %)

No.	REE concentration (µg/ml)	Analyte concentration (µg/ml)				
		Al	Ca	Fe	Mg	Si
1	1 000	0	0	0	0	0
2	1 000	0,05	0,05	0,05	0,05	0
3	1 000	0,1	0,1	0,2	0,1	0,1
4	1 000	0,5	0,5	0,5	0,5	0,5
5	1 000	1,0	1,0	1,0	1,0	1,0
6	1 000	2,0	2,0	5,0	2,0	2,0

7.4 Measurements

7.4.1 Instrument set-up

Set up and operate an ICP-AES instrument in accordance with the manufacturer's operating instructions, and choose an appropriate intensity background correction positions. The suitable analytical spectra lines should be selected depending on each ICP-AES instrument from Table 2.

7.4.2 Measurement of the calibration solution and calibration curve construction

Construct calibration curves for each impurity element using the calibration solutions shown in 7.3.

7.4.3 Measurement of the test solution

In accordance with the instrument calibration procedure, measure the intensity, and calculate the net absolute intensity or intensity ratio of the test solutions which are prepared in an orderly way shown in 7.2.

8 Calculation and expression of results

8.1 Method of calculation

Using the calibration curve constructed in 7.4.2 and the net absolute intensity, or the net intensity ratio of the test solution calculated in 7.4.3, calculate the concentrations of each impurity element in the test solution expressed in micrograms per millilitre.

The mass fraction of each impurity element in a test sample, expressed as a percentage, W_i, is given by Formula (1)

$$W_i = \frac{\rho_i \times V \times 10^{-6}}{m} \times 100 \qquad (1)$$

where

ρ_i is the concentration of each impurity element in the test solution, in µg/ml;

V is the volume of the test solution, in ml;

m is the mass of the test portion, in g.

8.2 Precision

8.2.1 Interlaboratory test

The results of an interlaboratory test are given in Annex A for information.

8.2.2 Statistical analysis

A statistical analysis was done in accordance with ISO 5725-1, ISO 5725-2 and ISO 5725-3. Following outlier tests: Consistency graphical test (Mandel's *k* test and Mandel's *h* test with 95 % confidence level), Intra-laboratory repeatability variance test (Cochran's test), Intra-laboratory repeatability variance test (Grubbs' test), interlaboratory reproducibility variance test (Grubbs' test), are carried out accordance with ISO 5725-3. Outliers are excluded from the statistical analysis, details are shown in Annex A. The evaluation results were used to calculate the values for repeatability r, and intralaboratory reproducibility, R_w, and reproducibility, R, that are shown in Annexes A and B.

9 Test report

The test report shall include the following information:

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

b) the method of the quantification and sample preparation, line spectra and the quality of the reagent used by reference to this document, i.e. ISO 24181-1:2024;

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

d) whether insoluble residues ocurred in the process of sample preparation; if an insoluble residue occured, the test results shall be considered unreliable information;

e) any unusual features noted during the determination;

f) any operation not specified in this document, or any optional operation which can have influenced the results.