
**Recycling of rare earth elements —
Methods for the measurement of rare
earth elements in industrial waste and
end-of-life products**

*Recyclage des éléments des terres rares — Méthodes pour le
mesurage des éléments des terres rares dans les déchets industriels et
les produits en fin de vie*

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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 documents 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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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*.

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

With technical advancement, rare earth elements (REEs) are increasingly important due to their importance in a number of applications, including green technologies. However, there are high supply risks arising from the dependence on a single source of extraction. Recycling and systemic management of rare earth elements are key issues for solving the waste and supply risks of REEs.

In order to efficiently recycle and systemically manage rare earth elements, a standard measurement method of REEs in industrial wastes and end-of-life cycled products is needed. Industrial wastes and end-of-life products can be found in solid, solid-liquid mixture and liquid forms. For example, machining waste contains chips and flakes with coolant oils, greases and numerous other forms of aqueous and non-aqueous contaminants. Similarly, waste liquid slurries contain REEs, as in LEDs, and batteries contain numerous acids, bases etc. Furthermore, in order to verify the information provided by the producer about REEs in the waste, standardized measurement procedure is necessary.

There are several scientific methods for quantitatively measure REEs in matters, such as X-ray fluorescence (XRF), inductively coupled plasma mass spectroscopy (ICP-MS), inductively coupled plasma optical emission spectroscopy (ICP-OES) and glow discharge mass spectrometry (GD-MS). However, these different characterization techniques often offer dissimilar measurement results depending on the composition and physical state of the sample under observation. This is another reason to establish standard measurement methods.

This document provides a brief overview and several measurement methods for REEs in industrial wastes and end-of-life products. Sample preparation methods are also provided. The accurate measurement of rare earth content (e.g. in ppm range) is still under active research and is not covered by this document. However, this document does provide measurement methods for identifying the presence and approximate content of rare earth elements.

This document is designed to be used with ISO 22450.

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Recycling of rare earth elements — Methods for the measurement of rare earth elements in industrial waste and end-of-life products

1 Scope

This document provides measurement methods for quantifying rare earth elements (REEs) in industrial wastes and end-of-life products in solid, solid-liquid mixture or liquid forms. It provides an overview of sample preparation and measurement of REEs in industrial waste and end-of-life products.

WARNING — The use of this document can involve hazardous materials, operations and equipment. This document does not 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.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 22444-2, *Rare earth — Vocabulary — Part 2: Metals and their alloys*

ISO 22450, *Recycling of rare earth elements — Requirements for providing information on industrial waste and end-of-life products*

3 Terms, definitions and abbreviated terms

3.1 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 22444-2 and ISO 22450 apply.

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

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <http://www.electropedia.org/>

3.2 Abbreviated terms

REE	rare earth element
TREE	total rare earth element content
ppm	parts per million
XRF	X-ray fluorescence spectrometry
EDXRF	energy dispersive X-ray fluorescence spectrometry

WDXRF	wavelength dispersive X-ray fluorescence spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometry [also referred to as inductively coupled plasma atomic emission spectroscopy (ICP-AES)]

4 Sampling

4.1 Industrial waste

4.1.1 Processing waste

Processing waste can be of solid or liquid type. In the case of solid waste, sampling can be done directly without any special pre-treatment. In the case of liquid waste, it should be ensured that the sample is safe to handle and does not contain any hazardous components. For that purpose, the pH of the waste should be checked and neutralized. After the safety of the liquid waste is established, it should be prepared for analysis. Because processing waste can be of numerous types, a single sampling procedure is not recommended in this document. However, regardless of the sampling procedure used, samples should be taken in such a way that they represent the total package. The samples should be taken from five random points of a package to accurately represent the actual composition.

4.1.2 Scrap

Sampling of scrap containing REE can be directly done without any special pre-treatment. However, demagnetization should precede the sampling stage in the case of magnetic scrap. Due to the large variety of scraps, proposing a sampling procedure for each situation is beyond the scope of this document. However, samples should be taken in such a way that they represent the total package. The samples should be taken from five random points of a package to accurately represent the actual composition.

4.2 End-of-life products

4.2.1 Magnets

For the purpose of measurement, magnets containing end-of-life products should be dismantled and magnets should be identified and separated. The recovered magnets should be demagnetized for further processing. Both XRF and ICP techniques can be used for measurement of REEs inside magnets. If the XRF technique is used, the magnet should be simply used as is for measurement. If the ICP measurement is used, the magnet should be crushed using a hammer mill to obtain a sample for digestion.

4.2.2 NiMH batteries

To prepare NiMH batteries for measurement, manual disassembly of battery components should be carried out. In a NiMH battery, anode metal powder contains the majority of REEs. The anode metal powder should be separated and prepared for analysis. Both XRF and ICP techniques can be used for measurement of REEs inside NiMH batteries.

4.2.3 Phosphors

To prepare phosphor for measurement, manual disassembly of its components should be carried out to separate secondary materials such as aluminium caps, electrodes and mercury. REEs containing lamps should be prepared according to the analysis technique. Both XRF and ICP techniques can be used for measurement of REEs inside phosphors. If the XRF technique is used, the phosphor powder should be carefully extracted from the lamp and used for measurement. For ICP measurement, the lamp can be simply broken down.

5 Selection of measurement methods

Any of the given measurement methods can be used for quantification of REE waste with the mutual understanding of the buyer and the waste handler, as defined in ISO 22453.¹⁾ Table 1 summarizes the REEs which can be detected with the measurement techniques described in this document and also give remarks on which technique is suitable for which type of industrial waste or end-of-life product.

Table 1 — Selection of measurement methods

Measurement method	Detection limit	Elements that can be detected	Remarks
XRF	~100 ppm	all elements	due to line overlaps, the accuracy of the measurement can be compromised
ICP-OES	~1 to 100 ppm	all elements	accurate measurement technique
ICP-MS	~1 to 100 ppm	all elements	accurate measurement technique

6 Measurement methods

There are several scientific methods which can be used for quantitatively measure REEs in matter, such as XRF, ICP-OES and ICP-MS. These measurement techniques which are applicable to REE quantification in industrial waste and end-of-life products are described in 6.1 through 6.3 and follow the general steps in Figure 1.

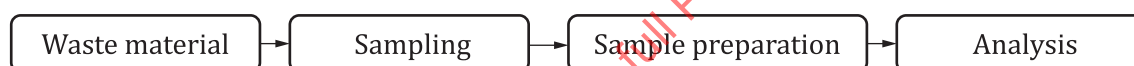


Figure 1 — General steps for measuring of REE content in industrial wastes and end-of-life products

6.1 X-ray fluorescence spectrometry (XRF)

6.1.1 General

XRF is a quantitative method that measures the fluorescent X-rays that are produced when a material is irradiated with X-rays to identify the elements contained in the material. Since it is simple to operate and can measure almost all metallic elements, it is widely used for quantitative analysis of materials. In general, this method can identify the elemental composition at percentage levels. The main advantage of XRF measurement is that it can measure all materials such as metals, ceramics and polymers without any pre-treatment process, even in solution or in powder state. The use of WDXRF, which is more accurate than EDXRF for measuring REEs, is recommended.

6.1.2 Sample preparation

6.1.2.1 General

The samples can be prepared using several procedures. Selecting the right procedure is vital for accurate measurement. Homogeneity of sample is an important factor for XRF and, therefore, the sample should be homogenized before measurement. Non-destructive measurement can be carried out when the waste collected is of homogeneous nature (e.g. end-of-life REE magnets). However, if the waste is in the form of a mixture, measurement is performed after crushing and homogenization.

1) Under preparation. Stage at the time of publication: ISO/FDIS 22453:2021.

6.1.2.2 Pressed pellet sample

For a pelletized specimen, 5 g of powder should be weighed and filled inside a cylindrical die. Afterwards the powder should be pressed using a secondary die inside a press machine. The pellet obtained afterwards should be used for analysis. The obtained pellet should have the structural integrity to withstand the process of measurement without deteriorating. Furthermore, care is needed at the time of applying pressure to avoid cracking due to trapped air. This can be achieved by stepwise application of pressure.

6.1.2.3 Fused beads

For the preparation of fused beads, a mixture between flux (lithium borate ($\text{Li}_2\text{B}_4\text{O}_7$)) and the sample should be prepared. The sample to flux ratio can be between 1:5 and 1:10. Afterwards, the mixture should be placed in an appropriate crucible. The crucible should be heated to 1 200 °C for 30 minutes in a fusion furnace to obtain a melt. Afterwards, the heating should be continued at 1 200 °C for another 30 minutes along with agitation in order to obtain homogeneity. Finally, the crucible should be cooled to obtain fused beads for analysis.

6.1.2.4 Bulk sample

In the case of samples to be tested in bulk form, the surface of the sample should be prepared to remove any roughness on the surface. Grinding should be carried out on an abrasive belt or with grinding paper of 240 grit size. Afterwards, the surface should be cleaned using an appropriate solvent in order to remove any grinding media or foreign substance.

For the measurement of liquid samples, it is recommended to use ICP-OES or ICP-MS because XRF is not commonly used for liquid state measurement.

6.1.3 Calibration

6.1.3.1 General

Calibration is a sensitive process for XRF measurements and should be carried out following the steps in [6.1.3.2](#) through [6.1.3.4](#).

6.1.3.2 Drift correction

Drift correction should be carried out in order to calibrate instrumental drift. A drift monitor containing REE should be used before conducting each analysis.

6.1.3.3 Matrix correction

In order to perform matrix correction, standard binary samples of each minor element with the matrix element should be made. The analysis should be run for each sample. The calibration for each analysis should be made in order to get a total concentration of 100 % for the minor and matrix elements. The results should be updated for further analysis.

6.1.3.4 Standard calibration using CRM

The measurement of certified reference materials (CRM) should be carried out to generate calibration curves for each element. The reference materials should cover the mass fraction ranges of REEs. Use at least three reference materials for each element. After plotting the results, regression analysis should be done to acquire analytical curve for each element.

6.1.4 Analysis and calculation

After calibration, analysis of the REE waste should be carried out. Samples should be extracted from at least five or more points from a package to obtain reliable value. It should be noted that the preparation

steps of calibration samples and unknown samples should be identical. Three samples for each point should be run; the count rates measured for each element should be measured using an LiF scintillator. The count rates should be used to calculate the mass fraction of each element. The result should be recorded in a form (see example in [Annex A](#)).

6.2 ICP-OES

6.2.1 General

Inductively coupled plasma-optical emission spectrometry (ICP-OES) is a feasible alternative to ICP-MS for REE determination because of its multi-element capacity, adequate sensitivity, wide linear dynamic range, low cost and ease of operation. ICP-OES is an analytical characterization method for measuring the quantity of elements. It could measure the composition of elements in liquid samples which can be formed into plasma. The ICP-OES method is beneficial for the large amount of atoms in the target materials. ICP-OES can detect all 17 REE elements.

6.2.2 Sample preparation

6.2.2.1 When various wastes are collected, it is necessary to homogenize by crushing (this can be omitted if only the same type of waste is present).

6.2.2.2 For the purpose of digestion, 5 to 10 mg of sample should be weighed.

6.2.2.3 Trace metal purity grade solutions of concentrated nitric acid (a mass fraction of 65 %) and hydrochloric acid (a mass fraction of 37 %) should be used for sample dissolution.

6.2.2.4 The dissolution process should be carried out in accordance with ISO 15202-2.

6.2.3.5 The resultant solution should be used for analysis.

WARNING — Concentrated acids are *corrosive* and their vapours are harmful for the body. Care should be taken to avoid any type of contact during use. Appropriate protective equipment should be worn when working with concentrated acids. All the procedures involving acids should be carried out in a fume hood.

6.2.3 Calibration

Calibration should be done according to the manufacturer's recommendations. Blank solution and diluted multi-element stock solution should be used to calibrate the equipment. For the purpose of compensating the spectral background and equipment drift, a known quantity of internal standard should be added to all calibration solutions. Method blank solution should be used to confirm the equipment calibration. The method blank solution should be prepared following the same procedure used for sample digestion.

6.2.4 Analysis and calculation

It is recommended that the standard operating procedures for analysis supplied by the manufacturer of the equipment should be followed. Limits of detection (LOD) should be obtained by considering background equivalent concentrations (BEC) and relative standard deviations (RSD) for 10 measurements of digested blank solutions.

Samples should be extracted from at least five or more points from a package to obtain reliable values. Three samples for each point should be run. Calculation of the concentration of each element should be calculated as follows:

$$w = \frac{C_o \times F_d}{m \times 100}$$

where

w is the mass fraction of the concentration of analyte (%);

C_o is the measured value of the analyte (ppm);

F_d is the dilution factor;

m is the mass of the sample (g).

The result should be recorded in a form (see example in [Annex A](#)).

6.3 ICP-MS

6.3.1 General

ICP-MS is a trace element analyser that uses the inherent mass difference of atoms. From an analytical point of view, ICP-MS is a well-established method for multi-element analysis of elements at trace and ultra-trace levels in particular. The advantage of this method is that it allows more accurate quantitative analysis than ICP-OES and XRF. Those REEs which exist only in miniscule quantities in a material can be measured accurately with ICP-MS. As REEs are used in trace quantities in a number of applications, this method suits the analysis of electronic waste and end-of-life products.

6.3.2 Sample preparation

The sample for ICP-MS should be prepared according to the procedure in [6.2.2](#).

Analytical calibration solutions in the 0,05–5 mg/l range should be prepared by appropriate dilution of a multi-element stock solution of 10 mg/l Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Th, Tm, Y and Yb.

6.3.3 Calibration

The calibration for ICP-MS should be carried out according to the procedure in [6.2.4](#). Calibration should be done according to the manufacturer's recommendations. Blank solution and diluted multi-element stock solution should be used to calibrate the equipment. For the purpose of compensating the spectral background and equipment drift, a known quantity of internal standard should be added to all calibration solutions. Method blank solution should be used to confirm the equipment calibration. The method blank solution should be prepared following the same procedure used for sample digestion.

6.3.4 Analysis and calculation

It is recommended that the standard operating procedures for analysis supplied by the manufacturer of the equipment should be followed. Limits of detection (LOD) should be obtained by considering background equivalent concentrations (BEC) and relative standard deviations (RSD) for 10 measurements of digested blank solutions.