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Rare earth — Analysis by wavelength dispersive x-ray fluorescence spectrometry (WD-XRFS) —

Part 1:
Determination of composition of rare earth magnet scrap using standardless XRF commercial packages

Terres rares — Analyse par fluorescence X à dispersion de longueur d'onde (WD-XRF) —

Partie 1: Détermination de la composition des déchets magnétiques à base de terres rares à l'aide de kits XRF sans étalon vendus dans le commerce

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Contents

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*.

A list of all parts in the ISO 22928 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

Rare earth element (REE) magnets, especially neodymium-based magnets, can be found in numerous different applications.[4] According to some rough estimates, the annual demand of REE magnets was nearly 78 kilotonnes in 2015.[5] Based on those estimates, six major applications (namely wind turbines, hard disk drives, electric vehicles, e-bikes, audio speakers and air conditioners) account for nearly 60 % of the total demand. As components utilizing REE magnets continue to accumulate, the REE repository created by human activity will be crucial to address in the future by recycling.

The commercially used REE magnets can be divided into two main categories: samarium-cobalt (Sm-Co)-based magnets and neodymium-iron-boron (Nd-Fe-B)-based magnets:

- In Sm-Co-based REE magnets, $SmCo_5$ and Sm_2Co_{17} are the two technically important compositions. In the Sm_2Co_{17} magnet, the concentration of Co is sometimes partially replaced by other transition metal elements.
- In Nd-Fe-B magnets, the concentration of Nd is 32 % by mass. A small to considerable amount of other REEs are also sometimes added.

The mass of REE in magnet present in each product varies greatly. Additionally, the concentration of different REE elements within the magnet itself can vary greatly. For example, the incorporation of Dy into Nd-Fe-B magnets can be in the range of < (1 to 10) % mass fraction (10 g/kg). These factors contribute towards challenges in the recycling efficiency of REE magnets.

In the case of magnets derived from end-of-life (EOL) equipment, dismantling is carried out. Apart from REE magnets found inside wind turbines and electronic vehicles, the physical extraction of REE magnets from electronic application scrap is very challenging due to the complexity and small size of the components. This type of scrap is usually shredded. The shredded scrap is then sorted into ferrous and non-ferrous scrap. During the shredding process, the recovery rates of REEs can drop by 90 %.[5] Appropriate guidelines for dismantling the EOL scrap is important for improving the REE recovery. Overall, effective recycling of REE requires information regarding the amount and nature of the REEs present in the magnet scrap.

This document specifies the measurement protocol for assessing the composition of REE magnet scrap. Procedures for dismantling components containing scrap and for cleaning and demagnetizing the scrap are provided. Guidelines for determining the composition of REE magnet scrap using standardless wavelength dispersive X-ray fluorescence (WD-XRF) commercial packages are specified.

This document:

- outlines a procedure for safe handling of the EOL magnet scrap (see Clause 7);
- specifies measurement of the REE content in the EOL magnet scrap (see Clause 8).

Rare earth — Analysis by wavelength dispersive x-ray fluorescence spectrometry (WD-XRFS) —

Part 1:

Determination of composition of rare earth magnet scrap using standardless XRF commercial packages

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 protocol for the application of semi-quantitative standardless wavelength dispersive X-ray fluorescence (WD-XRFS) commercial packages for the assessment of the concentration of rare earth elements (REEs) contained in magnet scrap from end-of-life (EOL) products intended for recycling.

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*

ISO/TS 22451, *Recycling of rare earth elements — Methods for the measurement of rare earth elements in industrial waste and end-of-life products*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 22444-2, ISO 22450, ISO/TS 22451 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
neodymium-iron-boron magnet
Nd-Fe-B magnet
group of permanent magnets based on the $Nd_2Fe_{14}B$ compound

Note 1 to entry: The composition of Nd-Fe-B magnets can vary due to the addition of elements such as Dy or Tb to improve high-temperature properties.

3.2
sintered magnet
type of permanent magnet made by consolidation and thermal treatment to create a dense compact

3.3
bonded magnet
type of magnet synthesized by mixing magnetic powder and binder material such as rubber or plastic to create a dense compact

3.4
recycling
operation by which discarded products are reprocessed into products, product parts, materials or substances whether for the original or other purposes

[SOURCE: IEC/TR 62635:2012, 3.16]

3.5
recycler
organization with the facility to carry out *recycling* (3.4)

3.6
end-of-life scrap
EOL scrap
scrap comprising recyclable materials provided by a collection facility of EOL products

4 Reagents

Use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 Acetone.

4.2 Alkaline cleaning agent, for example an alkali solution containing surfactants and other cleaning medium.

4.3 Bromine.

4.4 Ethanol.

4.5 Binder wax.

5 Apparatus

The usual laboratory apparatus and, in particular, the following shall be used.

5.1 Wavelength dispersive-X ray fluorescent spectrometer (WD-XRFS).

5.2 Furnace, with a capability to heat the sample to 500 °C.

5.3 Demagnetizer.

5.4 Pulverizer.

5.5 Grinder.

5.6 Hydraulic press, with a capability of providing 300 MPa pressure.

5.7 Vacuum desiccator.

5.8 Weighing balance, which can be read to the nearest 0,01 g.

6 Determined elements and concentration ranges

The concentration ranges of samples that can be appropriately analysed by this method are given in Tables 1 and 2, for each type of magnet scrap included in this document.

Standardless XRF analysis should be carried out on all the elements between Na and U. The final report shall only contain the elements in scope that are over 1 % mass fraction (10 g/kg).

Table 1 — Concentration range for Nd-Fe-B magnet scrap major elements

Major elements	Range of concentration % mass fraction (10 g/kg)
Fe	1 to 70,0
Nd	1 to 40,0

Table 2 — Concentration range for Nd-Fe-B magnet scrap minor elements

Minor elements	Range of concentration % mass fraction (10 g/kg)
Pr	1 to 10,0
Dy	1 to 10,0
Tb	1 to 10,0
Gd	1 to 10,0
Ce	1 to 10,0
Ho	1 to 10,0
Ga	1 to 10,0
Co	1 to 10,0
Ni	1 to 10,0
Cu	1 to 10,0
Nb	1 to 10,0
Al	1 to 10,0
Zn	1 to 10,0

7 Handling recyclable magnet resources

7.1 Dismantling EOL scrap

7.1.1 General

REE magnets derived from the EOL scrap are often installed inside complex components and products. It is necessary to dismantle these EOL products to recover the incorporated magnets to reuse or recycle them. Reuse and recycling, important pillars for closing the loop in a circular product economy, require appropriate product information to allow identification, quantification and recovery of REE elements from magnets.

7.1.2 Dismantling of components containing rare earth magnets

The recycler, as defined in ISO 22453, should provide the identification of parts that contain magnets for reuse or recycling that are not readily identifiable and require dismantling.

The following information should be provided along with the measurement results (see 8.5.2):

a) name of supplier, manufacturer or producer and contact details;

b) name of the product;

c) gross mass of the shipment;

d) physical form of the product;

e) method of storage;

f) date of production;

g) country and region;

h) type of magnet;

i) recommended dismantling procedure, e.g. dismantling steps, tools to be used, etc.

7.2 Demagnetization

7.2.1 General

REE magnets and EOL scrap are generally magnetized. To measure the nature and content of REEs in these magnets, the first necessary step is to ensure their demagnetization.

In order to demagnetize the magnets, the magnetically aligned regions of the magnet, which are referred to as “magnetic domains”, shall be randomized to achieve a nominal net zero magnetization state. This process can be achieved in a variety of ways. Two common methods of achieving demagnetization are given in 7.2.2 and 7.2.3.

7.2.2 Heat treatment

A magnet may be thermally demagnetized by heating it above its magnetic transition temperature, or Curie temperature, and cooling it in the presence of a zero magnetic field.

The Curie temperature greatly varies with the type of magnet.

EXAMPLE Nd-Fe-B magnets lose their magnetism beyond a temperature of 400 °C.

7.2.3 Alternating magnetic fields

Another common way of demagnetizing is by subjecting the magnet to a series of alternating applied magnetic fields. This method decreases the remanence of the magnet by randomizing the alignment of the magnetic domains.

7.3 Cleaning magnet scrap

Recovered magnets and magnet scrap shall be cleaned prior to analysis. The magnets are usually attached to a housing component with adhesives. In addition, magnets can also have a protective coating, often comprising a nickel-copper alloy, which should be removed when analysing a bulk sample.

A procedure is provided as follows:

a) The EOL scrap should be initially cleaned with acetone to remove organic impurities, dust and other contaminants.

b) If adhesives are present, the EOL scrap shall be fully immersed and sonicated inside an alkaline cleaning agent. The pH of the cleaning agent can be varied depending upon the nature and quantity of contaminants.

c) In the case of Ni-Cu coatings of Nd-Fe-B magnets may be removed by immersing them in a 1 % volume (10 ml/l) bromine solution in ethanol for 1 h.[6] This process should be carried out inside a chemical fume hood with all the necessary safety precautions.

8 X-ray fluorescence analysis

8.1 General

XRFS is a non-destructive technique used to determine the chemical composition of materials. In this technique, an analyte is irradiated with X-rays, resulting in the emission of characteristic fluorescent X-rays that correspond to the elements within the analyte.

8.2 Sample preparation

8.2.1 General

Sample preparation should be conducted according to the sources (categories and condition) of the EOL magnet scrap:

a) in cases where the composition of the EOL magnet scrap is very homogeneous (e.g. coming from one type of product such as wind turbines or magnetic resonance imaging (MRI) equipment), the method for bulk sample preparation, as described in 8.2.2, should be conducted;

b) in cases where the composition of the EOL magnetic scrap is inhomogeneous (e.g. coming from a mixture of different EOL products such as hard disk drives, automobiles, home appliances or industrial motors), the method described in 8.2.3 should be conducted.

8.2.2 Bulk samples

8.2.2.1 Surface preparation

The surface of bulk solid samples shall be flat to ensure accurate analysis using XRF. Grinding the sample surface using a medium with grit size of 600 should be sufficient. Afterwards, the surface should be cleaned using an appropriate solvent in order to remove any grinding media or foreign substance.

NOTE Ground surfaces oxidize immediately.

8.2.2.2 Sample storage

It is good practice to prepare the surface of a sample immediately prior to analysis. However, if the sample cannot be analysed immediately, it should be stored in a vacuum desiccator or in an inert atmosphere glove box.

8.2.3 Powder samples

8.2.3.1 Binder wax

Any commercially available binder wax (4.5) should be mixed with the magnet powders, prior to pressing (compaction). Briquettes or tablets from powder to be analysed may be prepared using the binder wax.

8.2.3.2 Powder particle size

The powder should be pulverized if necessary. To minimize the particle size effect, powder with a size of less than 50 µm should be used. The powder size shall always be under 100 µm.

WARNING — Powder samples of EOL magnet scrap can be pyrophoric as well as pose respiratory hazards. It is the responsibility of the user of this document to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

8.2.3.3 Weighing and mixing

A binder to powder ratio of 1:4 by mass should be used for the preparation of briquettes or tablets. Thoroughly mix the components in a container. Mixing during pulverization can also be used.

8.2.3.4 Pressing

The briquette or tablet should be pressed to a minimum of approximately 250 MPa (20 t). The pressing can be done using collapsible aluminium cups or rings, or without these devices.

8.2.3.5 Sample storage

It is good practice to prepare the surface of a sample immediately prior to analysis. However, if the sample cannot be analysed immediately, it should be stored in a vacuum desiccator or in an inert atmosphere glove box.

8.3 Use of commercial XRF standardless packages for analysis

Commercial standardless XRF packages which can calculate the composition while taking specific line overlaps into consideration shall be used.

Commercial standardless XRF package software that is provided in most modern X-ray spectrometers to perform the elemental analysis of the EOL magnet scrap shall be used.

These XRF packages shall be used, provided that the following qualifications are met:

— all the signals to be used in the quantification of the elements of interest should be calibrated beforehand;

— the software is able to calculate instrument and element sensitivities from the database;

— the software is able to make drift corrections.

8.4 Instrument setup

8.4.1 General

For correct operation of the instrument and software, refer to the manufacturer's recommendations.

8.4.2 Measurement conditions

The analytical lines and conditions that may be used for the measurement of specific elements are given in Table 3. The expected elements inside the sample to be measured shall be provided to the software.

Table 3 — Suggested analytical lines and operating conditions for wavelength dispersive XRF (WDXRF) spectrometers

Element	Lines
Pr	L_β
Nd	L_α
Gd	L_α
Tb	L_α
Dy	L_β
Ce	L_β
Ho	L_β
Ga	L_α
Fe	K_α
Co	K_α

Table 3 *(continued)*

Element	Lines
Ni	K_α
Nb	K_α
Zr	K_α
Cu	K_α
Ti	K_α
Al	K_α
Zn	K_α

NOTE 1 Voltages are variable depending upon the characteristics of the X-ray tube and generator that are used. The values suggested in Table 3 are compatible with most of the XRFS systems currently available in the market today.

NOTE 2 All operating conditions assume a voltage ranging from 50 kV to 60 kV, a LiF200/LiF220 crystal, a medium to fine collimator and a gas proportional/scintillator detector.

NOTE 3 All devices are described as generic.

8.5 Expression of results

8.5.1 General comments

The conversion of intensities to concentrations can be done with most of the commercial software packages accompanying the XRF instruments.

8.5.2 Reporting of results

8.5.2.1 The result form shall be generated in accordance with ISO 22450.

8.5.2.2 The concentrations shall be reported as mass percentages of each element.

8.5.2.3 The detected concentrations shall be normalized to 100 % mass fraction (10 g/kg).

8.5.2.4 The normalized concentration shall incorporate 1 % mass fraction (10 g/kg) of boron.

8.5.2.5 The type of magnet (sintered magnet or bonded magnet) shall be reported along with the results. For bonded magnets, the appropriate amount of binder content shall be incorporated in the normalized concentration.

8.5.2.6 The concentrations should be reported as ranges.

EXAMPLE (1 to 5) % mass fraction (10 g/kg), (5 to 10) % mass fraction (10 g/kg), (10 to 15) % mass fraction (10 g/kg), (15 to 20) % mass fraction (10 g/kg), > 20 % mass fraction (10 g/kg).

NOTE Additional details can be provided upon agreement between the concerned parties.

8.5.2.7 Elements with a concentration under 1 % mass fraction (10 g/kg) shall be omitted from the report.

8.5.2.8 Additional information can be provided in accordance with the specific requirement.

Annex A
(informative)

Interlaboratory test results

A.1 Precision — Calculation of r, R_w and R

The precision calculations of the data are summarized in Tables A.1 to A.3. For some of the levels, negative value of variance was estimated due random effects. In accordance with ISO 5725-2:2019, these values are assumed to be zero. As a result, the value of r is equal to R_w for those levels.

Table A.1 — r, R_w and R values for sample NdFeB-1

Levels		**Level 1-1**	**Level 1-2**	**Level 1-3**	**Level 1-4**	**Level 1-5**
Sample		**NdFeB 1 (sintered)**				
Element		**Fe**	**Nd**	**Pr**	**Tb**	**Dy**
Number of data		6	5	6	5	4
Mean	%	67,40	21,98	5,17	1,59	1,08
s_r	%	0,006 0	0,004 4	0,000 8	0,002 5	0,001 2
s_{Rw}	%	0,009 4	0,031 5	0,005 5	0,002 5	0,001 2
s_R	%	0,555 9	0,392 7	0,107 8	0,011 5	0,023 0
r	%	0,016 8	0,012 3	0,002 4	0,007 0	0,003 5
R_w	%	0,026 3	0,087 8	0,005 5	0,007 0	0,003 5
R	%	1,555 4	1,098 8	0,301 5	0,036 3	0,064 3
$C_{V,r}$	%	2,31	4,99	5,83	2,87	5,94

Key

s_r repeatability, s_{Rw} intralaboratory reproducibility, s_R reproducibility, r repeatability limit, R_w intralaboratory reproducibility limit, R reproducibility limit, $C_{V,r}$ coefficient of variation, reproducibility

Table A.2 — r, R_w and R values for sample NdFeB-2

Level		**Level 2-1**	**Level 2-2**	**Level 2-3**	**Level 2-4**	**Level 2-5**
Sample		**NdFeB 2 (sintered)**				
Element		**Fe**	**Nd**	**Pr**	**Tb**	**Dy**
Number of data		6	6	5	5	4
Mean	%	66,03	23,38	5,67	0,33	1,30
s_r	%	0,060 9	0,074 7	0,028 2	0,001 9	0,000 2
s_{Rw}	%	0,060 9	0,074 7	0,028 2	0,001 9	0,000 2
s_R	%	0,090 8	0,330 1	0,187 9	0,009 6	0,042 6
r	%	0,170 4	0,209 0	0,079 0	0,005 3	0,000 6
R_w	%	0,170 4	0,209 0	0,079 0	0,005 3	0,005 2
R	%	0,368 1	1,042 4	0,006 1	0,027 4	0,119 4
$C_{V,r}$	%	0,56	4,46	6,28	8,23	9,16

Key

s_r repeatability, s_{Rw} intralaboratory reproducibility, s_R reproducibility, r repeatability limit, R_w intralaboratory reproducibility limit, R reproducibility limit, $C_{V,r}$ coefficient of variation, reproducibility