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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 scraps using standardless XRF commercial packages

ICS: 29.030; 13.030.30; 13.030.50

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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 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).

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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

Rare Earth Element (REE) magnets, especially neodymium-based magnets, can be found in numerous different applications^[1]. According to some rough estimates, the annual demand of REE magnets was nearly 78 kilotons in 2015^[2]. 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, this REE repository created by human activity will be crucial for future 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. The Nd-Fe-B magnets contain around 32% of Nd by mass, while a small to considerable amount of other REEs are also sometimes added. In the case of Sm-Co-based REE magnets, SmCo_5 and $\text{Sm}_2\text{Co}_{17}$ are the two technically important compositions. In the $\text{Sm}_2\text{Co}_{17}$ magnet, the concentration of Co is sometimes partially replaced by other transition metal elements.

The mass of REE 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 %. 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 needs to be carried out. Apart from REE magnets inside wind turbines and electronic vehicles, 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%^[2]. 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.

The purpose of this standard is to specify 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 determination of the composition of REE magnet scrap using Standardless Wavelength Dispersive X-Ray Fluorescence (WD-XRF) commercial packages are specified.

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

Part 1:

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

1 Scope

This document presents a protocol for the application of semi-quantitative Wavelength Dispersive X-Ray Fluorescence Spectrometry (WD-XRFS) commercial packages for assessment of the concentration of rare earth elements (REEs) contained in magnet scrap from End of Life (EOL) products intended for recycling.

The standard can be subdivided into two parts:

1. The first part outlines a procedure for safe handling of the magnet scrap
2. The second part specifies measurement of the REE content in the magnet scrap

WARNING — The use of this document may 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.

The concentration ranges of samples that may be appropriately analyzed by this method are given in [Tables 1](#), for each type of magnet scrap included in the standard.

Table 1 — Concentration range of application for Nd-Fe-B magnet scrap

| Major Elements | Range of Concentration (mass %) |
|----------------|---------------------------------|
| Fe | 1 to 70.0 |
| Nd | 1 to 40.0 |
| Minor Elements | Range of Concentration (mass %) |
| 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 |

NOTE Standardless XRF analysis will be carried out on all the elements between Na and U. The final report will contain the elements in scope that are over 1 mass %.

2 Normative references

The following documents are referred to in the text in such a way that some or all 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*

ISO 22453, *Exchange of information on rare earth elements in industrial wastes and end-of-life cycled 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:

3.1

neodymium iron boron magnet

Nd-Fe-B magnet

A group of permanent magnets based on the $\text{Nd}_2\text{Fe}_{14}\text{B}$ compound

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

3.3

sintered magnet

A type of permanent magnet made by consolidation and thermal treatment to create a dense compact.

Note 1 to entry: Sintered magnets have high anisotropy and maximum magnetism of above 30 MGOe.

Note 2 to entry: Sintered magnets are highly brittle and pyrophoric.

3.4

bonded magnet

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

Note 1 to entry: Bonded magnets usually have higher shape complexity and maximum magnetism of below 10 MGOe.

Note 2 to entry: Bonded magnets are prepared using molding or compression without the use of thermal treatment.

3.5

recycler

An organization with the facility to carry out recycling

3.6 recycling

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

[SOURCE: IEC TR62635:2012, definition 3.16]

3.7 EOL (End-of-Life) scrap

EOL scrap is comprised of recyclable materials provided by a collection facility of end-of-life products.

4 Handling of recyclable magnet resources

4.1 Dismantling of EOL scrap

4.1.1 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.

4.1.2 Requirements for dismantling of components containing rare earth magnets

The handler of the recyclable resources, as defined in ISO 22453, should provide the identification of parts that contain magnets for reuse or recycling that may not be readily identified and for which dismantling is recommended. It is recommended to provide the following information:

- a) manufacturer identification and contact details
- b) website
- c) country of origin
- d) Identification of the magnet type
- e) location, size and/or mass
- f) sketches, drawings, or pictures of the product containing magnet
- g) Recommended dismantling procedure e.g. dismantling steps, tools to be used, etc.

4.2 Demagnetization

4.2.1 General

REE magnets and scraps 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, must be randomized to achieve a net zero magnetization state. This process can be achieved in a variety of ways. Two of the recommended ways are given below

4.2.2 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 zero magnetic field.

The Curie temperature greatly varies with the type of magnet. For example, Nd-Fe-B magnets lose their magnetism beyond a temperature of 400 °C

4.2.3 Alternating Magnetic Field

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.

4.3 Guidelines for cleaning magnet scrap

Recovered magnets and magnet scrap must be cleaned prior to analysis. The magnets are usually attached to housing component with adhesives. Further, magnets may also have a protective coating, often comprised of a nickel-copper alloy, which should be removed when analyzing a bulk sample. A procedure is provided as follows:

- a) The scrap should be initially cleaned with acetone to remove organic impurities, dust and other contaminants.
- b) If adhesives are present, the scrap needs to 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) The Ni-Cu coatings of Nd-Fe-B magnets may be removed by immersing them in a 1 volume % bromine solution in ethanol for 60 minutes. This process should be carried out inside a chemical fume hood with all necessary safety precautions.

5 XRF (X-Ray Fluorescence) analysis

5.1 General

X-ray Fluorescence Spectrometry (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.

5.2 Sample Preparation

5.2.1 General

Sample preparation should be conducted according to the sources (categories and condition) of the magnet scrap. In cases where the magnet scrap is very homogeneous, for example coming from one type of product (e.g., wind turbines or magnetic resonance imaging (MRI) equipment), the method for Bulk Sample preparation, described in [5.2.2](#), should be conducted. In cases where the magnetic scrap is inhomogeneous, (e.g., originating from a mixture of different EOL products such as hard disk drives, automobiles, home appliances, industrial motors, etc.), then the method described in [5.2.3](#) should be selected.

5.2.2 Bulk Samples

5.2.2.1 Surface preparation

The surface of bulk solid samples must 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.

5.2.2.2 Sample Storage

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

5.2.3 Powder Samples

5.2.3.1 Binder wax

The preparation of briquettes or tablets from powder to be analyzed may be accomplished using any commercially available wax.

5.2.3.2 Powder particle size

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

5.2.3.3 Weighing and Mixing

A binder to powder ratio of 1:4 by mass is recommended for the preparation of briquettes/tablets. Thoroughly mix the components in a container. In addition, mixing during pulverization is also possible.

5.2.3.4 Pressing

It is recommended that the briquette or tablet be pressed to a minimum of 20 Tonnes (~ 250 MPa). The pressing can be done using collapsible aluminum cups, or rings, or without these devices.

5.2.3.5 Sample Storage

The sample should be stored in a vacuum desiccator.

5.3 Use of the commercial XRF standardless package for analysis

It is recommended to use commercial standardless XRF packages which can calculate the composition taking specific lines overlaps in consideration. This document recommends the use of commercial standardless XRF packages software that are equipped in most modern X-ray spectrometers to perform the elemental analysis of the magnet scrap. Such 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.

5.4 Instrument Setup

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

5.4.1 Measurement conditions

The analytical lines to be used for analysis and suggested conditions of measurement of specific elements are given in Table 2. The expected elements inside the sample to be measured shall be provided to the software.

Table 2 — 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 |
| 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 2](#) are compatible with most of the XRFS systems in the market today (2022).

NOTE 2 All devices are described as generic.

NOTE 3 All operating conditions assume a voltage ranging from 50 to 60 kV, a LiF200/LiF220 crystal, a medium to fine collimator, and a gas proportional / scintillator detector.

5.5 Expression of results

5.5.1 General Comments

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

5.5.2 Reporting of results

5.5.2.1 The result form shall be generated as per the guidelines provided in ISO 22450.

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

5.5.2.3 The detected concentrations shall be normalized to 100 mass %.

5.5.2.4 The normalized concentration shall incorporate 1 mass % of boron

5.5.2.5 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.

5.5.2.6 The concentrations will be reported as ranges.

EXAMPLE 1 to 5 mass %, 5 to 10 mass %, 10 to 15 mass %, 15 to 20 mass %, >20 mass %.

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

5.5.2.7 Elements with concentration under 1 mass % shall be omitted from the report.

5.5.2.8 Additional information can be provided as per the specific requirement.

Annex A

Round robin test results

A.1 Precision: Calculation of r , Rw , and R

The precision calculations of the data have been summarized in Table A (1-3). For some of the levels, negative value of variance was estimated due random effects. As per the ISO 5725.2:2019 these values are assumed to be zero. As a result, the value of r is equal to Rw for those levels.

Table A.1 — The r , Rw 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 |
| $S_{(r)}$ (%) | 0.0060 | 0.0044 | 0.0008 | 0.0025 | 0.0012 |
| $S_{(Rw)}$ (%) | 0.0094 | 0.0315 | 0.0055 | 0.0025 | 0.0012 |
| $S_{(R)}$ (%) | 0.5559 | 0.3927 | 0.1078 | 0.0115 | 0.0230 |
| r (%) | 0.0168 | 0.0123 | 0.0024 | 0.0070 | 0.0035 |
| Rw (%) | 0.0263 | 0.0878 | 0.0055 | 0.0070 | 0.0035 |
| R (%) | 1.5554 | 1.0988 | 0.3015 | 0.0363 | 0.0643 |
| $CV(R)$ (%) | 2.31 | 4.99 | 5.83 | 2.87 | 5.94 |

NOTE $s(r)$ repeatability, $s(Rw)$ within-lab reproducibility, $s(R)$ reproducibility,
 r repeatability limit, Rw within-lab reproducibility limit, R reproducibility limit,
 $CV(R)$ coefficient variance.

Table A.2 — The r , Rw 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 |
| $S_{(r)}$ (%) | 0.0609 | 0.0747 | 0.0282 | 0.0019 | 0.0002 |
| $S_{(Rw)}$ (%) | 0.0609 | 0.0747 | 0.0282 | 0.0019 | 0.0002 |
| $S_{(R)}$ (%) | 0.0908 | 0.3301 | 0.1879 | 0.0096 | 0.0426 |
| r (%) | 0.1704 | 0.2090 | 0.0790 | 0.0053 | 0.0006 |
| Rw (%) | 0.1704 | 0.2090 | 0.0790 | 0.0053 | 0.0052 |
| R (%) | 0.3681 | 1.0424 | 0.0061 | 0.0274 | 0.1194 |
| $CV(R)$ (%) | 0.56 | 4.46 | 6.28 | 8.23 | 9.16 |

NOTE $s(r)$ repeatability, $s(Rw)$ within-lab reproducibility, $s(R)$ reproducibility,

r repeatability limit, Rw within-lab reproducibility limit, R reproducibility limit,
 $CV(R)$ coefficient variance.

Table A.3 — The r , Rw and R values for sample NdFeB-3

| Level | Level 3-1 | Level 3-2 | Level 3-3 |
|----------------|------------------|-----------|-----------|
| Sample | NdFeB 3 (Bonded) | | |
| Element | Fe | Nd | Pr |
| Number of data | 6 | 6 | 6 |
| Mean (%) | 68.60 | 28.98 | 0.18 |
| $S_{(r)}$ (%) | 0.0161 | 0.0151 | 0.0002 |
| $S_{(Rw)}$ (%) | 0.0161 | 0.0151 | 0.0004 |
| $S_{(R)}$ (%) | 0.8522 | 0.4737 | 0.0012 |
| r (%) | 0.0450 | 0.0423 | 0.0004 |
| Rw (%) | 0.0450 | 0.0423 | 0.0012 |
| R (%) | 2.4059 | 1.3421 | 0.0035 |
| $CV(R)$ (%) | 3.51 | 4.63 | 0.66 |

NOTE $s(r)$ repeatability, $s(Rw)$ within-lab reproducibility, $s(R)$ reproducibility,
 r repeatability limit, Rw within-lab reproducibility limit, R reproducibility limit,
 $CV(R)$ coefficient variance.

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