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Enabling the recycling of rare earth elements through product design and trend analyses of hard disk drives

Abstract

Hard disk drives consist of a complex mix of various materials. While Aluminum, Copper and Steel are easy to separate, actual recycling processes dilute containing rare earth elements to non-recoverable grades in other material streams. In order to enable future recycling of these materials an in-depth analysis of hard disk drives from Desktop PCs and Notebooks was carried out. Furthermore, possible recycling strategies for rare earth elements were derived and the recycling potential was assessed.

The results show high concentrations of Neodymium (22,9±2,8%), Praseodymium (2,7±2,2%) and Dysprosium (1,4±1,5%) in the magnets. Various types of alloys are applied for different technical or economic reasons. Also a dependency from manufacturing dates was evidenced. Furthermore, Cerium (0,5%) and Neodymium (0,2%) was determined in printed circuit boards.

Test disassemblies of hard disk drives showed a complicated structure and thereby a difficult access to the NdFeB magnets. This applies explicitly for the spindle motor magnets, which hold the main share of applied Dysprosium.

A WEEE collection analysis show an amount of about 12,7t magnets from hard disk drives from PCs in Germany in one year. Put-on-market data predict decreasing shares of hard disk drives from Desktop PCs and significantly increasing amounts of Notebook components in WEEE.

1. Introduction

Due to its content of highly functional and strategically important metals waste electric and electronic equipment (WEEE) has been recently discussed as an upcoming anthropogenic stock for raw material supply. Currently, drivers for WEEE recycling are the legal framework in the EU with specified mass quotas and economic incentives through revenues for bulk material containing main industrial and precious metals [1, 2]. Low recycling rates due to low selling prices and thermodynamic limitations constitute the demand for developing liberation and separation strategies. This applies especially for rare earth elements (REE) [3].

REE is a generic term and describes a group of 17 elements consisting of scandium, yttrium and the lanthanides. These elements have similar chemical and specific physical properties [4]. The diverse physical characteristics are useful only for a few but important application in electric and electronic equipment (EEE). Beside catalysts, glass production and metallurgy in general, the biggest share of REE consumption holds the application in Neodymium iron boron magnets (NdFeB) with 20%, phosphors for lighting products with 7% and alloys for the production of batteries with 9% [5].

Due to the transition to energy efficient EEE products, current and future innovations in the information, telecommunication and entertainment sector are based on the use of REE, resulting in an increasing demand [6].
Security of supply is affected by finite primary resources and also coupled to the political situation of exporting nations. An approach facing these problems is substitution of REE materials to obtain equivalent properties and appropriate electric or electronic components or products. Gutfleisch et al. state that comparable results based on substitution of rare earth elements are not possible with current technical means [7]. Therefore, a circular management has to be implemented. Despite this, no significant recycling of REE materials is applied yet. Rates for a functional recycling are under 1% [3]. Through crushing processes REE are diluted into other output mass flows. These currently used recycling methods lead to a 100% loss of the REE materials [8].

About 13% of the worldwide mining output of Neodymium is used for the manufacturing of permanent magnets [9] of which currently 34% of NdFeB magnets are applied in Personal Computers [10]. In order to enable recycling on a mid term perspective, this publication focuses on NdFeB magnets in hard disk drives from Desktop PCs, but also from Notebooks.

Basis for a successful recycling of specific materials in WEEE is the detailed knowledge of the design and complexity of carrying end-of-life (eol) devices, the concentration in single components and the related freights, which are important for designing recycling processes and calculating economic values. This publication aims at developing approaches for the determination of REE in hard disk drives, particularly in NdFeB magnets through a recycling-oriented product characterization. Generated data and derived trends for the chemical composition can provide relevant data for the adaption of recycling processes enabling the recycling of Nd, Dy and other critical metals. Possible recycling strategies will be shown and the recycling potential of REE in NdFeB magnets in Desktop PCs and Notebooks will be assessed.

2. Background

According to Chancerel et al., the functional application of rare earth elements in hard disk drives is relevant regarding the high contents compared to other EEE types [11].
Hard disk drives consist of a very dense and complex compound structure. Therefore, a liberation of REE carrying components is a difficult process. Since no extensive Design-for-Recycling for new EEE is existent, an easy access for recycling purposes is not possible. For the characterization of REE in hard disk drives and for a 100% recovery of the REE a manual disassembly is a crucial step. Rare earth

materials in hard disk drives are applied in very small amounts in printed circuit boards (PCB) and in NdFeB magnets located in spindle and linear motor (voice-coil actuator) (Fig 1).

Fig 1 Location PCB (l.) and magnets in linear motor and spindle motor (r.)

Depending on required physical properties, NdFeB magnets contain multiple REE and other alloying elements. The base alloy for NdFeB magnets is $Nd_2Fe_{14}B$ [12]. Specific additions of elements are used to adjust the material properties [12, 13]. Cobalt substitutes REE and Fe materials up to over 5% to increase the Curie-temperature, which describes the point at which the magnetic field is offset and permanently destroyed [14, 15]. Dysprosium increases the temperature characteristics of the magnet as the compound has a better stability against demagnetization. This does not mean a significant increase of the Curie-temperature. Moreover, adding Dysprosium decreases the residual induction of the magnet, which leads to lower magnetic field properties [13, 15].
Praseodymium was used to lower production costs as it can substitute Neodymium up to 20-25%. This changed in recent years as quoted trade prices for Praseodymium are even higher by now. [16, 17]

NdFeB magnets in voice-coil actuators are sintered products where powdered material in a mold is heated to temperatures below the melting point. At the same time an external magnetic field is applied. End product is a solid piece with desired dimensions [18]. In this way manufactured magnets have the best results regarding the magnetic properties.

Other manufacturing methods are polymer-bonding and compression-molding, which are used for the production of spindle motor magnets. Compression-molding is similar to sintering processes, but with this method, the powder is heated over the melting point and the material is consolidated with high pressure. Polymer-bonded magnets are made by mixing a special binder to the NdFeB powder. This blend can be pressed to a precise desired shape. With this approach no or only little post-processing is necessary. Magnets produced with this technique are highly suitable for the spindle motor. The typical magnetic properties of these materials are lower compared to sintered magnets [15].
The magnet material, mainly the REE substances are highly oxidizing at contact with air. Because of this, the permanent magnets are coated with a protective layer. This can be thin polymeric coatings, but mainly sacrificial anodes made of Nickel or Tin/Zinc are used. Sacrificial anodes as coatings are not applied for bonded magnets in the spindle motor.

Regarding the recovery of REE in hard disk drives respectively NdFeB magnets, the major problem is the liberation of the NdFeB magnets. All approaches for a successful recycling are based on the processing of already liberated magnet material. Major part of collected hard disk drives is shredded due to data protection reasons and as it is the most economical way of treatment to separate the bulk materials with post shredder technologies. This procedure dilutes minor metals into the main output streams. Magnetic materials will be transferred to the ferromagnetic fraction. This means a complete loss of REE materials. Manual disassembly is one option to face this problem. But still low prices for REE scrap lead to non economical processes. Only social-working companies are able to perform this commissioned work for lower prices.

One additional issue beyond liberation is the availability of recovery and refining options. Currently, most approaches are still in development stage. Largely research studies deal with the recovery of rare earth elements in NdFeB magnets. Table 1 shows a structured overview of given options for the functional respectively elemental recovery of REE based on the input of already liberated, single magnets.

Table 1 Recycling options for NdFeB magnets (based on [4, 19–27])

Methods for re-use or functional recycling of magnet materials are most energy efficient and less technology intensive approaches. Furthermore, no loss of material is expected. As a direct re-use of magnets limits the fields of application and the general application of magnet changes regarding electric mobility and wind power stations, a functional recycling with re-sintering processes is most expedient. Adding 1% of Neodymium to each re-sintering step, new manufactured magnets maintain their physical properties and reach the same magnetic field strengths [20].

With a few exceptions like pyrometallurgical processes or gas phase extraction, the presented methods recover only REE concentrates. To obtain high purity mixed REE materials or single REE for direct application in the production of new electric and electronic goods or components, the concentrates have to be subsequently processed. Adapted from the production of primary resources these processes are mainly hydrometallurgical methods. Therefore, a direct utilization of hydrometallurgical approaches for the recovery of REE in NdFeB magnets of hard disk drives is reasonable. Developed by Elwert et al. and tested under laboratory conditions, a high-purity recovery of other applied materials like Iron and Cobalt is possible [24].

All mentioned approaches are based on the input of liberated NdFeB magnets. Feasible approaches for the treatment of whole hard disk drives filling the gap to apply developed recycling processes have been rarely developed. Most expedient way is the manual dismantling. Another possibility to obtain the complete magnets is presented by Hitachi. This new invention works with a spinning drum-type unit which shakes and swirl the hard disk drives so that the inner connections of the devices come loose. End product of this method are the structural components of the hard disk drives [19]. One problem is here, that the magnets are still connected to the carrying steel plates.
Regarding this, technical approaches for an economic preparation of the hard disk drive are to be developed to apply showed recovery methodologies.

A manual disassembly gives basis information about the structure, connections and helps designing manual or mechanical processes for the liberation of components of interest. Further on, enabling a full circular management for complex end-of-life devices is based on a detailed knowledge about the chemical composition of single components. Chemical analyses are therefore a subsequent and important step for the characterization of end-of-life devices. But conventional driven analytics does not provide set approaches for the characterization of WEEE mass flows yet. As this questioning has been coming up in recent years methodologies for that purpose have to be developed.

3. Materials & Methodologies

Following the recycling-oriented product characterization of WEEE suggested by [28], this study focuses on Personal Computers (UNU Subkey 3021) and on Notebooks (UNU Subkey 3031). This method is a hierarchical and systematic approach for providing information about end-of-life products for designing and optimizing recycling processes to prevent avoidable material mixing and dilution and also for the Design-for-Recycling of new EEE. It is structured in three levels: general information about the equipment (e.g. producer, production year), physical & mechanical properties (e.g. weight, size and connection types) and the chemical analysis of single assemblies and components (e.g. polymer characterization and element analysis). [14, 28]
An in-depth analysis of in total 49 3.5'' HDD from Desktop PCs and 6 2.5'' HDD from Notebooks was conducted to determine the product structure and material composition followed by a semi-quantitative analysis of the casing material, a chemical analysis of the printed circuit boards and the magnet components.

3.1. Recycling oriented product characterization

109 Desktop PCs were disassembled in two German pre-treatment recycling plants in order to obtain the share of 3.5'' hard disk drives. Also 6 Notebooks have been dismantled for comparison reasons. Subsequently, the hard disk drives were investigated in detail.

3.1.1. Manual disassembly of hard disk drives

Manual disassembly is a crucial step for characterizing end-of-life devices in order to get information about the structure and furthermore about opportunities for subsequent recycling strategies and to separate components of interest for chemical analyses. For investigating the REE potential of hard disk drives, NdFeB magnets have to be liberated. The weight of the dismantled components is used in pursuing chemical analyses for an estimation of the overall share of focused materials.

To obtain further information about the disassembled components in the hard disk drives and to characterize the material, an elemental semi-quantitative determination was carried out with an XRF device (Thermo Fisher / Analyticon XL3 air).

3.1.2. Chemical composition of NdFeB magnets

Each material applied in EEE is embedded in a specific matrix related to its functional use. These matrices influence analytical results and the quality of obtained results. The most common approach for facing these matrix effects is to develop calibrations using standard samples with the same matrix as the sample to be measured and known concentrations of the elements which have to be determined [29]. This is explicitly important for solid samples for which the matrix effects are contrastable higher [30]. In order to assess these matrix effects, different methods for the sample preparation and varied solvents for the leaching processes were tested to evaluate the best methodology for the determination of REE in NdFeB magnets. This approach leads to the most accurate results working with an ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrometry) or ICP-MS (Inductively Coupled Plasma - Mass Spectrometry).
Furthermore, first evaluations for the use of X-Ray fluorescence analysis were investigated. Utilizing other measuring principles for the determination of the chemical composition, this technique was intended to obtain a second set of comparable results of REE in NdFeB magnets (cf. Online Resource 1).

Following the optimized methods for determination of REE in NdFeB magnets described in Online Resource 1, the samples were prepared. Former tests with X-ray and wet-chemical analyses showed roughly the elemental content of the magnets. In further tests with sampling material the dissolving behavior for voice-coil actuator magnets was better with aqua regia and best results were achieved with HNO_3-H_2O for spindle motor magnets. This can be traced back to different production methods for the magnets and the specific dissolubility of REE.
The developed approaches for determination of REE in NdFeB magnets in hard disk drives were applied separately on 35 voice-coil actuator magnets and on 32 spindle motor magnets. The chemical analyses were carried out for a broad range of elements to obtain highest detection rate as possible. Following elements were measured: Metals: Al, Sn; Semi-metals: B; Transition Metals: Co, Cu, Fe, Ni, Zn; Lanthanides: Dy, Gd, Nd, Pr, Sm, and Tb.

The samples of the voice-coil actuator have been crushed and subsequently milled in an agate vibrating tube mill. The acidulation was conducted with 300mg sample material. 6,66ml ultrapure water and 3,33ml HNO_3 (69% Rotipuran Supra, Roth) were added. The vessels were covered and let rest overnight. Subsequently the vessels were locked to perform a microwave-assisted dissolution (1.600W, 20bar, 200°C, 15:00min).

The samples of the spindle motor have been simply crushed without further milling processes. The acidulation was carried out with 300mg sample material and 10ml aqua regia consisting of HNO_3 (69% Rotipuran Supra, Roth) and HCL (37%, Merck) in ratio 1:3. The vessels were let rest for approximately 1h until no gas formation was noticeable any more. Subsequently, the vessels were locked and a microwave-assisted dissolution (1.600Wm 20bar, 200°C, 15:00min) was performed.

For the measurement with ICP-OES a multi-element standard in HNO_3:H_2O (1:2) with stated elements was prepared.

To investigate the change in compositions of applied elements in both magnets, the results of the chemical analyses was put into context to time periods. The chemical composition was split up according to the manufacturing dates of the hard disk drives. This approach was worked out separated for magnets out of the voice-coil motor and the spindle motor in stacked histograms. Through this methods not only time trends but also different blending of magnets can be derived.

3.1.3. Chemical composition of printed circuit boards

Not only the magnets contain rare earth elements. Suspecting small quantities of these elements, also all dismantled printed circuit boards have been investigated as a mixed sample. In total a sample mass of 1450g was prepared in order to determine precious metals: Ag, Au, Pd; base metals: Al, Cu, Fe, Ni, Ti, Zn; rare earth elements: Ce, Nd, Pr, Eu, Tb, Dy, La, Sm, Gd, but also an other critical element: Ta. The chemical analyses were carried out by a third party laboratory as optimized approaches are already applied for printed circuit boards. The concentration of the precious metals Au and Pd was measured with inductively coupled - plasma atomic emission spectrometry (ICP-OES) and additionally for Au, Ag and Pd with a Spark Optical Emission Spectroscopy (Spark-OES). All base and other metals like REE were determined with a laboratory X-Ray fluorescence spectrometer (XRF).

3.2. Recovery potential

Estimation of the recovery potential of REE from hard disk drives in WEEE was conducted in two ways.

<u>WEEE collection</u>

In Germany, WEEE is collected in five separated collection groups. Notebooks and Desktop PCs are classified as group 3 (CG3) “Information and telecommunication equipment, consumer electronics”. For this analysis, Notebooks and Desktop PCs were counted and weighted for the total CG3 input stream of one German pre-treatment facility for one year. The share of hard disk drives relative to Desktop PCs and Notebooks was derived from test disassemblies. Results give information about the share of hard disk drives in collected WEEE in Germany. The recycling potential is calculated with following equations:

Equation 1 Calculation of share eol device in collection group 3 in %

$$Share\ \frac{eol\ device}{CG3}(\%) = \frac{100 * (Number\ eol\ devices\ (units) * avg.\ weight\ eol\ device\ (kg))}{Input\ CG3\ (kg)}$$

Equation 2 Calculation of the recycling potential of REE in collected WEEE in t

$$Reycling\ Potential\ (t) = share\frac{eol\ device}{CG3}(\%) * share\frac{component}{eol\ device}(\%) * share\frac{REE}{component}(\%) * WEEE(t)$$

<u>Recovery potential of put-on-market</u>

Another approach is the analysis of the put-on-market (PoM) data to assess information about the in-stock recovery potential. For this purpose, data of sold Notebooks and Desktop PCs for the last 10 years (CEMIX - Consumer Electronics Markt Index) was analyzed and put into context to information of test disassemblies with following calculation:

Equation 3 Calculation of the recycling potential of REE in put-on-market EEE in t

$$Recycling\ Potential\ (t) = \sum share\frac{component}{eol\ device}(\%) * share\frac{REE}{component}(\%) * PoM\ (units/a)$$

With the obtained data sets and the determined share of particular materials in appointed end-of-life devices, the recovery potential can be calculated.

4. Results

4.1. Structure of Personal Computers

The dismantled Desktop PCs consist of 64% metals, 31% electronic components and 5% plastics (Fig 2). Hard disk drives have with in average 542±68g a share of 3,3% of an average PC with a weight of 12,2kg.

Fig 2 Results for test disassemblies of 109 collected Desktop Computers in two German pre-treatment recycling plants

The results of dismantled Notebooks with an average weight of 3,2kg show a share of 3,6% hard disk drives, which is comparable to Desktop PCs. Absolute weight of HDD from Notebook is 134±26g.

4.2. Structure and composition of hard disk drives

For the disassembly of the main components (casing, printed circuit boards, hard disks, etc.) only form closure connections, mostly screws were found. Structures with REE materials, NdFeB magnets, are mounted with material closures and frictional locking connections. The access to magnets in voice-coil actuators is hindered by the construction as normally two magnets are applied, which are locked to each other by their magnet fields. Furthermore, the magnets are bonded on a carrying steel plate. In order to enable the removal of magnets, the components were heated with a gas burner (<2000°C) to incinerate the organic bonding and to destroy the magnetic field.

Based on different coefficients of thermal expansion of the different assembled materials, the same procedure was used to open the form and frictional locking connections of the spindle motor. Fig 3 shows the procedure for the liberation of NdFeB magnets.

Fig 3 Liberation of NdFeB magnets in voice-coil actuator (top) and spindle motor (bottom)

Additionally to the magnets in voice-coil actuator and spindle motor, a very small, cubic magnet is applied in hard disk drives. As the test disassemblies showed an average weight of under 0,2g per magnet, this component was not considered any further.

4.3. Material composition of hard disk drives

Over 40 dismantled hard disk drives (average mass 544±68g) from Desktop PCs showed following composition: ferrous metals 20±9%; non-ferrous metals 67±13%; printed circuit boards 6±2%, NdFeB magnets 3±1,5% (voice-coil actuator 2,6±1,5%; spindle motor 0,4±0,06%); Plastics 0,8±0,7%; Rest 5,5±1,7%. Rest fraction consists inter alia of different multi-material components like copper coils with Plastics, Aluminum compounds or the read-writing head. The high variety of the weight of the voice-coil actuator magnet is caused by differing numbers of applied magnets in this component. In most cases two magnets are applied. Test disassemblies showed that ca. 18% of investigated hard disk drives have only one magnet in the linear motor. In those cases, the value for weight is cut to the half. Fig 4 shows the statistical evaluation for the results of the manual disassembly.

Fig 4 Heterogeneity of disassembled hard disk drives

The non-ferrous metals represent the biggest share in hard disk drives. With the exception of a few wires and screws, this fraction consist largely of Aluminum. Primarily the cast aluminum casing (210±30g) influence the mass significantly. Measurements with an XRF device for the determination of the alloys showed a mixture of approximately 96-98% Al and the missing 2-4% of Cu and Zn as alloying elements to ensure a high mechanical strength and a high temperature range. Small non-

magnetic steel inlets applied in the casing have a high Chromium and Nickel content (approximately Fe 71-74%, Cr 17-18% and Ni 7-9%).
The storage hard disks contain a pure Aluminum core. The coating consists of several very thin layers to provide the required magnetic storage capabilities and mechanical surface properties. Measurements with the XRF proved the contents of Cr, Co, Ni, Fe, and Zn of the soft magnetic under layers and the magnetic storage layers. Further, the spacer between the single hard disks (5,9±3,7g in total) consist of a high purity Aluminum of the alloy type Al-1000.
Another component made of aluminum is the basis and head of the spindle motor without bearing (26±13g), consisting of 95-99% Al and small amounts of Fe, Cu and Mn.
Two third of the investigated coverings applied to close the body with the aluminum casing consist of brass (~65% Cu, ~35% Zn) with a Ni, eventually Ni-Cu coating (120±60g). The remaining one third (120±25g) is made of steel with high Fe (~70%), Cr (~20%) and Ni (~8%) share but also small amounts of Mn.
The voice-coil magnets are applied on steel plates (46±25g). Mostly these components consist of pure steel (Fe-C) with Nickel coating for corrosion protection.
In both fractions, the ferrous and non-ferrous metals, screws produced with different steel alloy materials, mostly Fe, can be found.

A big share in the miscellaneous fraction usually holds the read-writing head (10±4g) for performing the data reading and writing operations on the hard disks. This component consist of a relatively big copper coil for executing the movement of the head relative to voice-coil motor and hard disks. The basic structure consist of Aluminum with Cu and Ni as alloy and coating materials. The top of the head is based on Fe-Cr-Ni. This unit is connected to a small applied printed circuit board with thin Au and Cu wires.

The comparative disassembly of hard disk drives from Notebooks (~134g average weight) showed slightly higher shares for the magnets with 5,8±0,7% (voice-coil: 4,7±1%; spindle: 1,2±0,4%) and for the PCB with 13,1±0,2%. This is based on the lightweight construction of HDDs in Notebooks. One example for this is the very thin housing material. Owed to this design, less screws were used. Components are more often connected with pressure bonds. This leads to problems in a manual disassembly and can also influence the mechanical treatment.

4.4. Chemical composition of NdFeB magnets

The determined main shares of elements are Fe, Nd, Pr, Dy, Co and Nickel, which is only applied in the voice-coil actuator magnet. Except for Iron (cf. Online Resource 2), Fig 5shows a statistical evaluation of these elements applied in the voice-coil actuator and in the spindle motor.

Fig 5 Comparison of applied critical elements in NdFeB magnets

Notable is the diversification of the results for Co and Dy. This applies especially for the spindle motor magnets. These elements represent the possible admixtures for improving the physical properties of NdFeB magnets. The results show a varying Nd content correlating to percentages of added alloy elements. Therefore, the overall share of REE is nearly constant (cf. Table 2). As there are higher variations in the alloy composition in the spindle motor, the overall share of REE is stronger influenced. This applies especially for the use of high percentages of Dysprosium and Cobalt. Dysprosium with a share up to 12% increase the overall REE content which can go up to measured values of about 38%.

Moreover, the addition of Pr and Co varies. While Pr is applied irregularly to substitute Nd, the addition of Co correlates to the application of Nd. Therefore, higher percentages of Co are connected to lower overall REE contents. This applies explicitly for the voice-coil actuators.

Table 2 shows the results for all determined elements and the various admixtures in voice-coil actuator and spindle motor magnets and for the total magnet content in hard disk drives.

Table 2 Overview of all determined elements in NdFeB magnets

Other REE like Tb, Gd and Sm were found only in traces below 0,1% for all samples. Due to other manufacturing methods, a special coating for preventing spindle motor magnets from oxidizing is not necessary. Therefore, no Nickel is applied.
Just as a little Cu, Sn and Zn are used in both kind of magnets.

4.5. Time trend in alloy types

The development of blends for the manufacturing of NdFeB magnets changed over time due to economic reasons or higher demands on magnet materials. Chemical compositions related to time periods were assessed with developed stacked histograms separated for the voice-coil and spindle motor magnets.
One example for the detailed results is shown with element Neodymium for the voice-coil magnets in Fig 6. The assessment for all element separated for the voice-coil and the spindle magnet is attached in the Online Resource 3.

Fig 6 Time trend for the application of Praseodymium in voice-coil motor magnets

The chronological trend for voice-coil magnets shows that the admixture of Praseodymium increases until 2005. Like stated before, Praseodymium was used for economical reasons. As the prices raised significantly from 2005-2006 [16] on, the substitution for Neodymium with this material decreased. The same applies for substances with technical benefits like Cobalt. Not only the admixture in each magnet drops in the years 2000 to 2008 from nearly 3% to 1,4-1,6%, also the amount of voice-coil magnets in which this substance is generally applied decreases.
Dysprosium decreases a little bit in the years 2000-2004 before the values nearly recover.
Neodymium hold the biggest share of the REE in the magnets. As it is the most important substance to obtain the typical strong magnetic field it behaves very constant in the distribution in all measured magnets and generally over time. In average it decreases a little bit from 25,5% (1994-2000) to 22,5% (2000-2008). This is traced to a general reduction of the REE overall content in NdFeB magnets: 28,6% (1994-2000) to 26,4% (2000-2008).
As Nickel represents the coating of the voice-coil magnets, the application is very constant over time.

Like for the voice-coil magnets, Dysprosium has a drop in the years 2000-2005 and is again more often applied in spindle motor magnets from the year 2005 and later on. Also the chronological trend for Praseodymium is comparable. In the years 1994-2000 admixtures were under 1% and raised from 2000 on to percentages of 6-7%. The progress of application of Neodymium in spindle motors is similar to the linear motors. Only in the last years 2000-2008, the application of Neodymium decreased to under 20% while Praseodymium and Dysprosium were used for its substitution. Likely results were shown for Cobalt. Nearly all investigated magnets from 1994-2004 have high contents of this substance with about 3%. After 2005, values fall far below 1%.

Different kinds of blending are accounted for the manufacturing of both types of magnets. Depending on market prices and desired physical properties, Neodymium is substituted to a specific level with Dysprosium, Praseodymium or Cobalt. Mainly, Dysprosium and Cobalt are applied together with low concentrations of Praseodymium. In the years from 2000 on, higher concentrations of Praseodymium were determined. In those samples, the Dysprosium content was enhanced while Cobalt content is very low.

4.6. Chemical composition of printed circuit boards

Based on a batch of nearly 50 printed circuit boards the results show the concentrations for a mix of hard disk drives with manufacturing dates in 1994 to 2008.
Due to detection limits of the applied methodologies and as elements are partially not applied not all elements were determined. Table 3 shows the main shares of applied metals in printed circuit boards from hard disk drives in PCs.

Table 3 Chemical composition of applied metals in printed circuit boards from hard disk drives

In addition to small concentration of Ce and Nd as REE, relatively high contents of precious metals like Ag and Au were measured.

4.7. Recovery potential

Assessment of the results for NdFeB magnets in hard disk drives show a wide spread for the recovery potential of applied elements in Desktop PCs and Notebooks. The potential for the REE with a major share is displayed in Table 4 in kg per t of each device and in mg for one HDD and for the whole eol equipment. This data is the basis for the calculation of the collected WEEE potential and for the potential of put-on-market devices.

Table 4 Content and concentration of Nd, Dy, and Pr in end-of-life equipment

Combining the information from the analyses of the printed circuit boards, the NdFeB magnets and the semi-quantitative determination of the remaining material lead to a general overview of applied metals. An average 3.5'' hard disk drive consist of base metals: Al, Fe and Cu; REE: Nd, Pr, Dy, Ce, Sm, Tb and Gd plus precious metals: Ag, Au and Pd. Associated to actual exchange prices for raw materials, Fig 7 shows the distribution of the intrinsic value for one hard disk drive. Prices are referred to solid metals, not oxides, and were taken from London Metal Exchange for base metals (BM), from Metal Bulletin for precious metals (PM) and Metal-Pages for the rare earth elements.

Fig 7 Comparison of material composition and intrinsic value of one 3.5'' HDD (intrinsic value calculation based on prices from London Metal Exchange (BM), Metal Bulletin (PM), Metal-Pages (REE); accessed on 2014-06-14)

<u>WEEE collection</u>

In average about 560.000t/a WEEE was collected for recycling or re-use purposes in the years between 2009 and 2013 in Germany [31]. CG3 holds a share of nearly 50% with 280.000t/a [32].
Over 200 containers of CG-3 input material with in total 1.400t at one German recycling facility have been investigated during the year 2009.

Results show an average mass of 6,5t for one CG3 container with in average 24 Personal Computers. Based on over 400 weighted devices the average mass for a Desktop PC can assumed to be 11,3kg, which leads to 4,2% overall share to collected CG3. In the investigated time frame no relevant amount of Notebooks could be registered. This leads to a total mass of 11.200t collected Desktop PC and subsequently to roughly 400t hard disk drives from Desktop PC collected in one year.

The calculated total share of HDD in German WEEE flow can be assumed to be 0,07% with an equivalent to 12,7t magnets. This leads to a recovery potential of 2.900±300kg Nd, 340±280kg Pr, 180±190kg Dy, 200±170kg Co, 15±18kg Tb and 13±3kg Gd per year. Due to different applied alloy types the values vary widely and influence hereby the quality and economic value of the recycling material.

<u>Recovery potential of put-on-market</u>

Looking on the last ten years nearly 15 million Desktop PCs and over 44 million Notebooks have been sold in Germany on the consumer market [33]. Gathered data for the calculation of the recovery potential is conglomerated in Fig 8.

Fig 8 Put-on-market Desktop PC and Notebook in Germany per year B2C 2004-2013 (sales date from [33]*)*

In recent years the number of sold Notebooks increased rapidly. In opposite, the market for Desktop PCs decreased slightly. Whilst in 2004 the put-on-market amount of Desktop PCs was much higher than for mobile devices, Notebooks constitute the major share of REE, mainly Nd, Pr and Dy, in the sold IT devices by now. This applies even if the sales figures have its peak in 2011 and the market seems to be saturated as the numbers for tablets raised extremely since 2010-2011 due to new technology solutions. Fig 9 shows the put-on-market data of Nd, Pr and Dy for Notebooks and Desktop PCs.

Fig 9 Calculated annual amount of REE put-on-market in Germany Desktop PC vs. Notebook for Nd, Pr and Dy from 2004 to 2013 (sales date from [33]*)*

Cumulating the years 2004-2013 total masses of 125Mg Nd (Desktop PC 54,6Mg; Notebooks 70,5); 14,4Mg Pr (Desktop PC 6,4Mg, Notebooks 8,0Mg); 8,1Mg Dy (Desktop PC 3,3Mg; Notebooks 4,8Mg) were sold with these two electronic devices in Germany.

5. Discussion

The dismantling results differ slightly to other studies. Weng et al. reviewed dismantling tests of Desktop PCs. Here, hard disk drives hold a share of 5,08% [34]. Results of this study show a share of 3,3%.
A direct comparison with dismantling tests of hard disk drives is not possible as generally only magnets from the voice-coil actuator have been investigated. But the results for this magnet type differ in other publications. Schüler et al. state 22g for an average voice-coil actuator magnet [6]. Zepf shows an average of 16,3g and evidenced a time trend [12]. By comparison, this study shows a share of 2,6±1,5% (14g) for the voice-coil actuator and 0,4±0,06% (2,2g) for the spindle motor magnets.

Information about the detailed chemical composition of NdFeB magnets from literature is rarely available. For this type of magnet in general, Du & Graedel summarized the contents as follows: 20% Nd, 5% Pr, 5% Dy and 1% Tb [10, 35, 36]. Zepf determined only two REE: 25% Nd and 5.3% Pr for NdFeB magnets in hard disk drives and 26% Nd and 5% Pr in NdFeB magnets in mobile phones [12]. Compared to the examined chemical analyses for this publication, the results show different concentrations. Nd with a share of 23±2,8% is higher, while Pr (2,7±2,2%) and Dy (1,4±1,5%) have much lower concentrations than expected. Furthermore, Tb is applied only in traces with an average share of under 0,05%. The differentiation between the magnets applied in the voice-coil actuator an in the spindle motor has not yet been utilized in recycling oriented research.

Moreover, printed circuit boards contain small concentrations of REE as well. The determined values for precious metals in this component are roughly double as high as expected. This can be traced back to the analyzed sample with exceptional high concentrations or to the investigated small sample size. Despite that, the precious metals build with the base metals the economic main revenue for recycling efforts with prices from 20€/g for Pd to 30€/g for Au. REE have a far wider spread and generally lower purchase prices with Nd 70€/kg, Pr 120€/kg, Dy 440€/kg. Focusing on the recovery of REE, the spindle motor contains a higher share of valuable materials, e.g. Dy, compared to the voice-coil magnets.

The composition of the NdFeB magnets applied in the voice-coil or in the spindle motor are different and are subjected to alloy changes over time. This have to be considered for calculations of profitability. Also the mass ratio voice-coil magnet (14,3±8,2g per unit) to spindle magnet (2,3±0,3g per unit) with 6:1 must receive attention.

5.1. REE recovery potential

The WEEE collection analyses showed that no relevant amounts of Notebooks were collected in the investigated time frame. Since the commercial sale of Notebooks started ca. 20 years ago, the collection rates are low accordingly to the duration of use. But it has to be stated that a higher collection of Notebooks was expected. The results apply for one recycling facility in Germany. Local variances in the use, disposal and collection may be possible.

The put-on-market data shows, that nearly similar amounts of Desktop PCs and Notebooks were sold in 2004. This is still connected to a higher input of REE material into the in-stock recycling potential by Desktop PCs. The rapidly increasing sales figures of Notebooks predict a change in the use of information technology. In the years 2010 and 2011 the sales figures for Notebooks are five times higher than for Desktop PCs. Although the sales figures drop again from 2012 on, the REE input is dominated by the mobile devices. A possible impact on the recycling potential of REE is given by the use of solid state disks (SSD), which do not contain any magnetic material.

Compared to the sales data of Tablet, this kind of device is going to replace the Notebooks, while the selling of Desktop PC is nearly constant. As this equipment is using flash storage as well, the use of REE in mobile devices will change dramatically.

It is predicted, that end-of-life hard disk drives comprise a dominant part of the Neodymium in-stock material until 2015 and will be the main source for a possible recycling of Neodymium until 2020. The potential recycling supply of this material is very stable in the next decades. In 2030, a availability of still 0,38Gg linked to hard disk drives is estimated [37]. This high values apply also for all other used REE in hard disk drives like Dysprosium, Praseodymium but also Cobalt according to their share in the magnets.

To assess more detailed information about future end-of-life Notebook and Desktop PC mass flows to estimate the recovery potential, more quality data is needed. A specific time frame has to be observed to calculate the returned mass flows, based on a specific life span of each end-of-life device [38]. Reliable data cannot be provided yet.

5.2. Recycling approaches for a successful HDD treatment

Depending on the recycling target, the different alloy types of the spindle motor and voice-coil actuator magnets have to be considered as the depth of liberation processes is influenced hereby.

Direct re-use and re-sintering processes are connected to a precise disassembly of the magnets. These procedures maintain the physical and chemical properties of subsequently produced or re-used magnets. Here, only pure magnets can be processed. A simple and fast liberation of the spindle motor magnets is not possible as the magnets are assembled in a sophisticated compound structure. This applies explicitly for hard disk drives from Notebooks. Therefore, an economic treatment for the spindle motor in this way is not predictable yet. Optimal input is material with same alloying materials. Moreover, contaminations due to coupled magnet coatings like Nickel and/or Copper influence the quality of the re-sintered product and have to be removed.

Also the developed liberation process by Hitachi [19] is optimized only for the separation of the voice-coil magnets. And even this method cannot loose the bonding of magnets to the steel carrier plates. Due to these issues, only a crushing process of hard disk drives seems to be a possible process for an economically feasible and technical successful liberation.

Except for components like the printed circuit boards or the read-writing heads, the structure of hard disk drives consists of only a few metals which are partially covered with other metals for corrosion protection or other technical reasons. Mainly high purity Aluminum, FeC steel but also different alloy types are applied. These materials can be separated mechanically through automated standard processes. For an additional recovery of the magnet material, mechanical liberation, classifying and sorting processes have to be harmonized. As the magnet material consists of a high share of Iron, magnetic separators can pull it with other ferrous materials out of the main material stream. Through

heavy stress in the crusher, the sintered magnets can partially return to their powder condition. This material is still magnetic and stick to separable ferrous fractions [8]. The generated ferrous metals fraction with REE concentration is a feasible basis for further recovery processes.
Removing the printed circuit boards before crushing is also conceivable as high shares of valuable and critical materials are present. Through its exposed location, this component can be disassembled quickly and probably economically feasible.

Subsequent pyro- or hydrometallurgical processes can be used for a recovery of REE concentrates or for the recovery of single REE. Developing and optimizing mechanical processes for adjusting the preparation of input fractions for these metallurgical processes can ensure an economic recovery of valuable materials like precious and base metals as well as critical metals as REE from magnets in the voice-coil and in the spindle motor. Recommended is a subsequently executed hydrometallurgical process including a sequential recovery of Iron, Cobalt and REE.

Basis for further considerations regarding the planning of recycling processes is the possible generated output related to handled masses. For obtaining 1kg of each material, following numbers of hard disk drives have to be processed for Desktop PC: Nd 270, Dy 4600, Pr 2300; Notebook: Nd 530, Dy 7700, Pr 4800. Although the share of REE in hard disk drives in Notebooks is much higher than in Desktop PCs, the total mass is much lower. That leads to more devices to be processed.

6. Conclusion

HDD are characterized by an intrinsic high value of the contained precious metals, aluminum followed by REE. As the disassembly of the PCB is very easy, a prior separation is recommended before utilizing mechanical processes. In particular, the magnets are challenging for their liberation and separation due to the design of HDD.

High variations in alloys used for the voice-coil actuator and for the spindle motor magnet conflict with a direct re-use of the magnets or reutilization of the magnet material for re-sintering processes. Constant output qualities cannot be guaranteed based on mechanical processing. Moreover, the change of alloy compositions over time due to fluctuating raw material prices and higher demands on physical properties aggravates this issue. Therefore, sequential hydro- or pyrometallurgical recovery processes are required. For a successful utilization of refining processes, a development of liberation and separation techniques is crucial.

Mostly, the base alloy mixture of REE in NdFeB magnets is quite similar between magnets from different manufacturers. Since Dysprosium is exclusively applied in the spindle motor magnets with a concentration of up to 10%, the separation of spindle motors should be prioritized due to the prize and criticality of Dysprosium. In terms of liberation the spindle motor magnets are less accessible and, due to the smaller size, promise a smaller yield.

Standardized alloy mixtures for NdFeB magnets, their coatings and alloy types would simplify the recovery of the magnet material for a subsequent use.

In order to maximize the long-term recovery of REE magnets, already put on market laptops and Desktop PCs, there is a need for a selective collection and treatment. While the potential for Desktop PCs will be stable over the next years with approximately 3,6t of REE per annum, the collection and treatment efforts for laptops need to be intensified due to the increasing volume in the return flow in the next years. Nevertheless, when building up the recycling infrastructure one has to take into account the fact that the return volume of REE will show a peak 5-10 years after the peak of 22,5 t of REE put on market in 2010 in Germany.

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Journal of Material Cycles and Waste Management

Online Resource 1

Original article

Enabling the recycling of rare earth elements through product design and trend analyses of hard disk drives

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1. Optimizing laboratory work for determination of REE in NdFeB magnets

In the following, approaches with X-Ray fluorescence and ICP-OES for optimizing the determination of REE in NdFeB magnets are described.

<u>Wet-chemical analysis</u>

Developing standard methodologies for the determination of REE in NdFeB magnets various approaches for the preparation of the samples and conducting the leaching processes were used to obtain comparable results. Each approach was carried out with industrial NdFeB rod magnets (3mm x 6mm) with no or only small differences in their chemical compositions. Beside the chemical composition itself the coating Ni-Cu-Ni is comparable to the material used for NdFeB magnets in hard disk drives. Analogue to possible preparation steps the samples were milled (<0,2mm), roughly crushed, heated and crushed, cut and processed as complete magnet. Following standard leaching procedures for dissolving metallic samples were chosen: HCL (hydrochloric acid), HNO_3 (nitric acid), HNO_3-H_2O_2 (10 nitric acid – 1 hydrogen peroxide), HNO_3-H_2O (1 nitric acid – 2 water) and HNO_3-3HCL (aqua regia) (cf.Fig 1) [1].

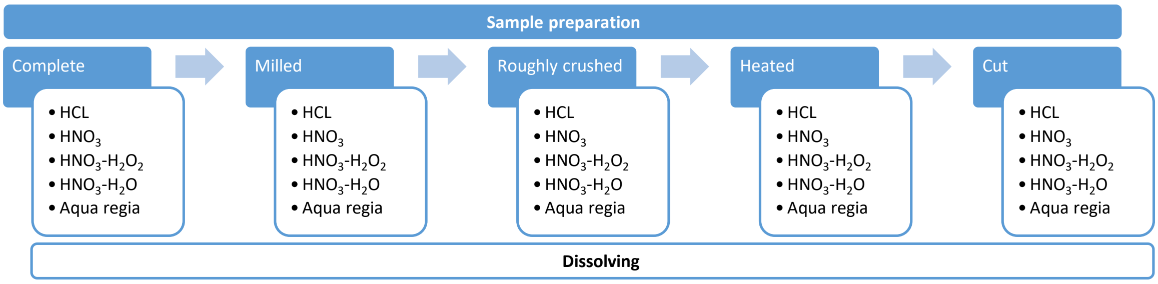

Fig 1 Applied sample preparation approaches

Except for HNO_3-H_2O, for all preparations a microwave-assisted digestion was used (1200W, 20bar, 200°C, 15:00min). For HNO_3-H_2O, two approaches were tested; digestion at room temperature and microwave-assisted digestion (400W, 20bar, 200°C, 15:00min).

For the determination of the chemical composition an ICP-OES was used (Thermo Scientific iCAP 6000 Series). All approaches were executed with a 3-fold determination. Following elements were determined: Silver (Ag), Aluminum (Al), Arsenic (As), Gold (Au), Boron (B), Cerium (Ce), Cobalt (Co), Copper (Cu), Dysprosium (Dy), Europium (Eu), Iron (Fe), Germanium (Ge), Lanthanum (La), Neodymium (Nd), Nickel (Ni), Palladium (Pd), Praseodymium (Pr), Platinum (Pt), Antimony (Sb), Samarium (Sm), Tin (Sn), Tantalum (Ta), Terbium (Tb), Zinc (Zn). Focusing on detected REE, the results for Dy, Nd, Pr, Tb and also B, Fe and Ni were compared. Fig 2 shows results for Nd exemplary for a comparable decision making. For other REE see “2 Results of REE related to different sample preparation methods”.

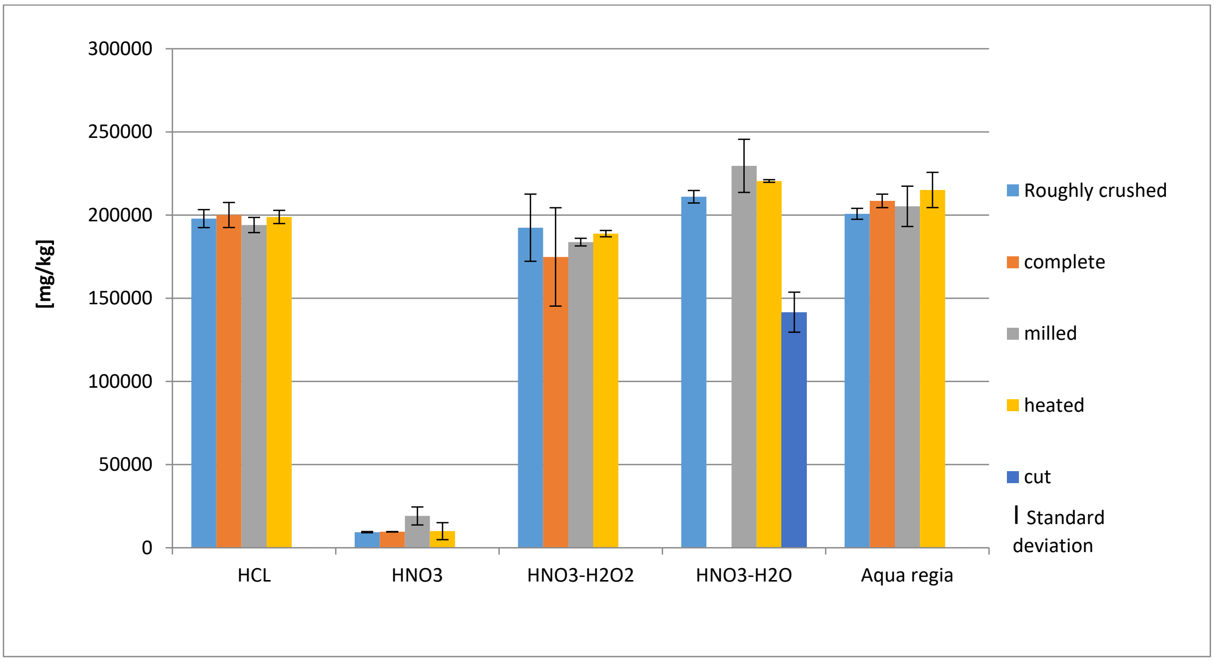

Fig 2 Results of various approaches for determination of Nd in NdFeB magnets

Evaluation of all results shows two possible approaches for the determination of the chemical composition of NdFeB magnets. For the sample preparation milling but also crushing is sufficient and HNO_3-H_2O and aqua regia can be applied for the microwave-assisted digestion step. Approaches with untreated magnets are not feasible as the coating prevents partially the magnets from dissolving.

The tests showed conspicuous interdependences of particular elements. To avoid misinterpretation of analytical results cross-comparisons were carried out to evaluate influences of present elements on elements to be detected. These tests were made for the pairs Ag-Cu, Ce-Nd, Ga-Ce, Ga-Nd, Pt-Co, Zn-Cu and Zn-Ni in a 2-fold determination with the concentrations 10mg/l and 20mg/l for the investigated elements. Significant impacts were measured for Nd-Ce and Ag-Cu. Table 1 shows differences between inserted standards and the result for the chemical analyses.

Table 1 Differences in cross-comparison for Ce-Nd and Ag-Cu

Used standard \ False detection %	Ce4040	Nd4012
Nd 10mg/l	130,4	0,5
Nd 20mg/l	129,7	1,5
Ce 10mg/l	0,0	4,3
Ce 20mg/l	0,6	4,6

Used standard \ False detection %	Ag2246	Cu3247
Cu 10mg/l	-7,7	3,1
Cu 20mg/l	-19,7	-1,4
Ag 10mg/l	-13,5	0,0
Ag 20mg/l	-2,5	0,0

A solution with only added Neodymium shows in chemical analyses detected Cerium with a difference up to 130% to its real value related to the inserted standard. In contrast, present Cerium does not influence the values for the detection of Nd. The same observations apply for the detection of Copper and Gold. These issues lead to an exclusion of Ce and Ag for further determinations.

<u>X-Ray fluorescent analysis</u>

To obtain a second set of results for the chemical composition, X-Ray fluorescence technique (Panalytical PW 2400 x-ray spectrometer) for the analysis of NdFeB magnets was tested. Using XRF analyses for a quantitative determination of the chemical composition of WEEE have not been established yet. Since XRF technique is a comparative measuring method, physical standards with a comparable matrix are needed. For rare earth elements in WEEE no standards are available yet.

Therefore, settings with pre-installed standards which are not optimized for REE in WEEE have to be used. A reliable and quantitative determination is hereby not possible.

Laboratory XRF analysis devices work with different sample preparation methods. Fused tablets and powder pressed tablets are used for best possible results. For the preparation of a powder pressed tablet 1,5g wax (Merck KGaA, Hoechst wax C micropowder) was mixed with 6g sample material. For materials with high differences in density a swirling procedure is used in which the milled sample material is mixed with the wax in air. Even this cannot ensure a homogeneous density of the material. This leads to different results for the same sample. First measuring tests showed that attributing obtained peaks to specific REE is not possible. Furthermore, through the optical properties of the surface accuracy decreases by 10-20%. Due to these issues, no further investigation with powder pressed tablets were made in this case study.
Preparing fused tablets, 0,6g sample material is melted with 3,6g soldering flux (lithium tetraborate:lithium metaborate, 66%:34%; Fluxana, HD Elektronik) at over 1000°C in a platinum crucible. The use of platinum crucibles exclude the determination of platinum group metals, Gold and Silver in the subsequent analysis as these materials are part of the alloy. As the melting process must not exceed higher temperatures than externally applied, the sampling material must not contain sulfides, high metal and/or phosphor contents. Otherwise exothermal reactions may occur and the crucible will be destroyed. To avoid those reactions milled sample material was heated in a muffle furnace to over 1000°C to force oxidation processes. This procedure leads to a loss of material due to annealing loss of volatile substances and in contrast to an increase of the mass due to oxidation processes. Therefore, a quantitative determination of the containing elements is not possible any more. Subsequent analytical results cannot be used for comparison purposes. Carrying out the burning process in a protective atmosphere has not been tested.

Both approaches for a sample preparation, fused tablets and fused tablets, are not suitable for a quantitative determination of REE in WEEE, e. g. NdFeB magnets in hard disk drives. But a qualitative measurement of the chemical composition is possible to adjust the wet-chemical analyses.

2. Results of REE related to different sample preparation methods

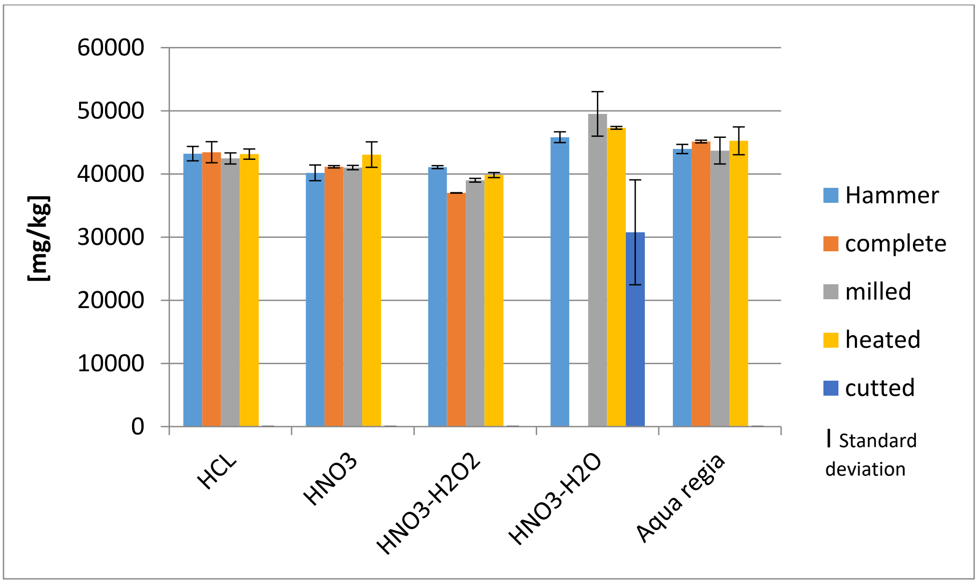

Fig 3 Results of various approaches for determination of Pr in NdFeB magnets

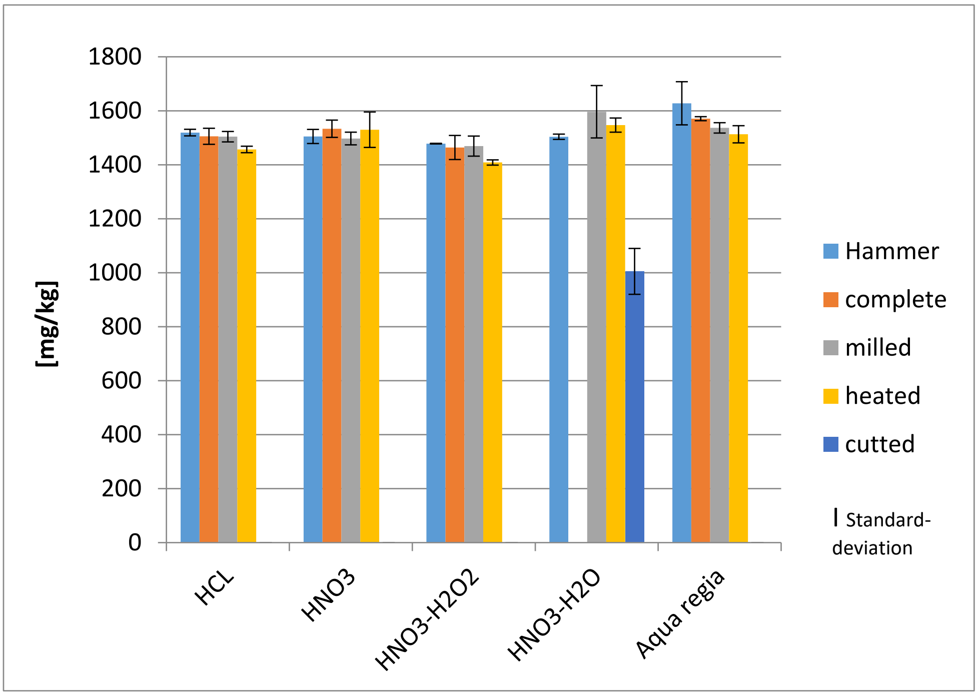

Fig 4 Results of various approaches for determination of Dy in NdFeB magnets

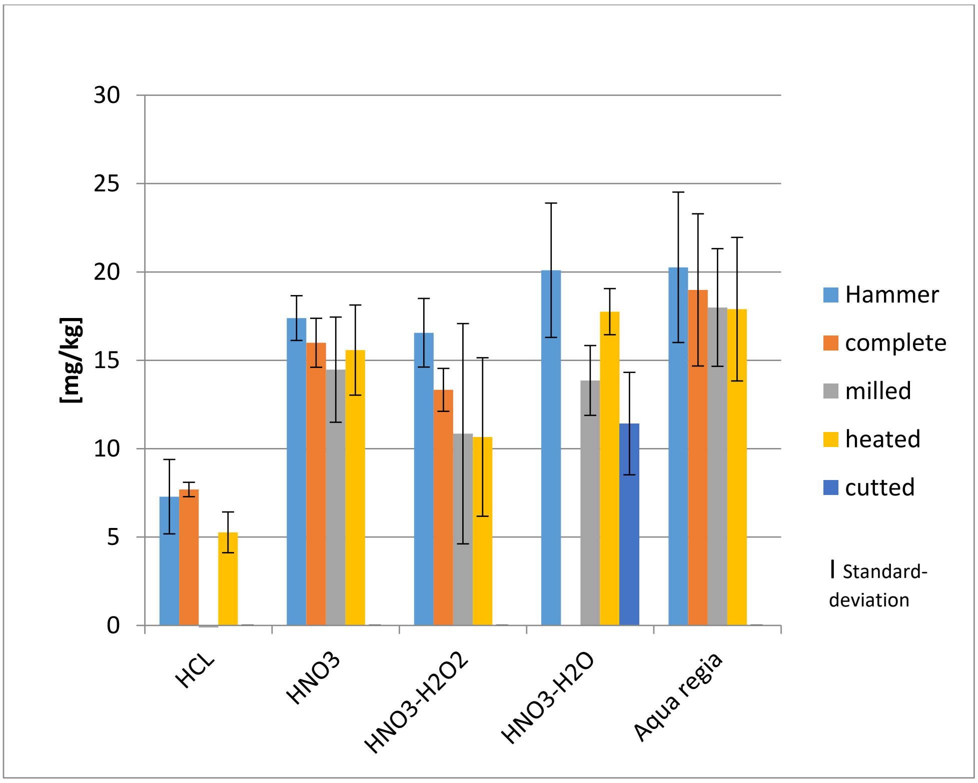

Fig 5 Results of various approaches for determination of Tb in NdFeB magnets

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Journal of Material Cycles and Waste Management

Online Resource 2

Original article

Enabling the recycling of rare earth elements through product design and trend analyses of hard disk drives

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1. Histogram Iron in NdFeB magnets

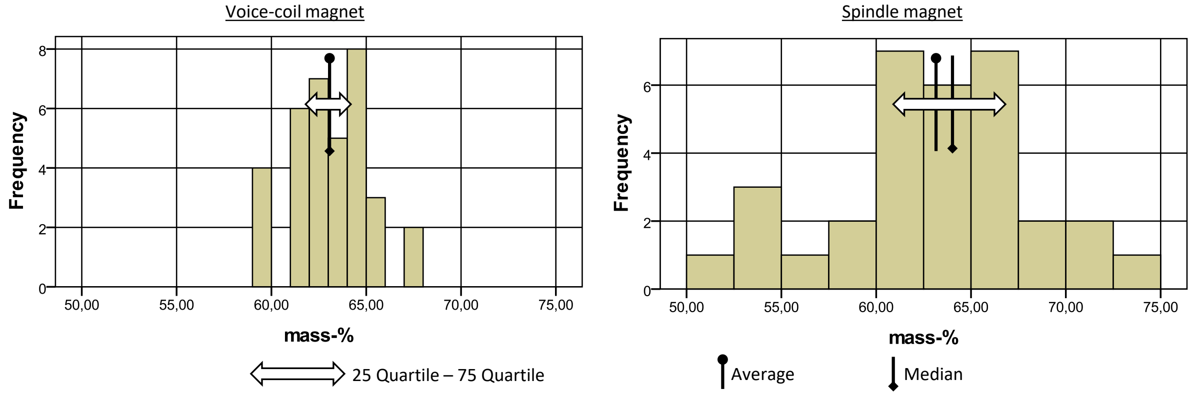

Fig 1 Share of Iron in NdFeB magnets

Journal of Material Cycles and Waste Management

Online Resource 3

Original article

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1. Time trend of alloy types in NdFeB magnets

<u>Neodymium Voice-coil motor magnet</u>

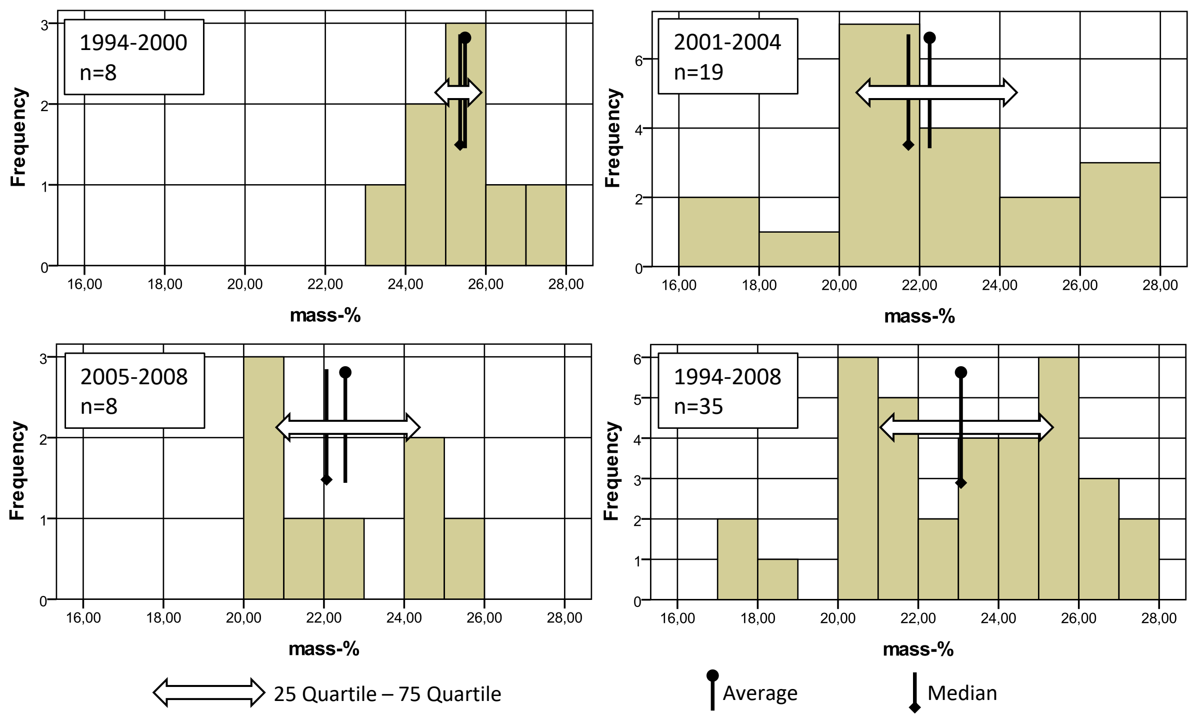

Fig 1 Time trend for Neodymium in voice-coil motor magnets

<u>Neodymium Spindle motor magnet</u>

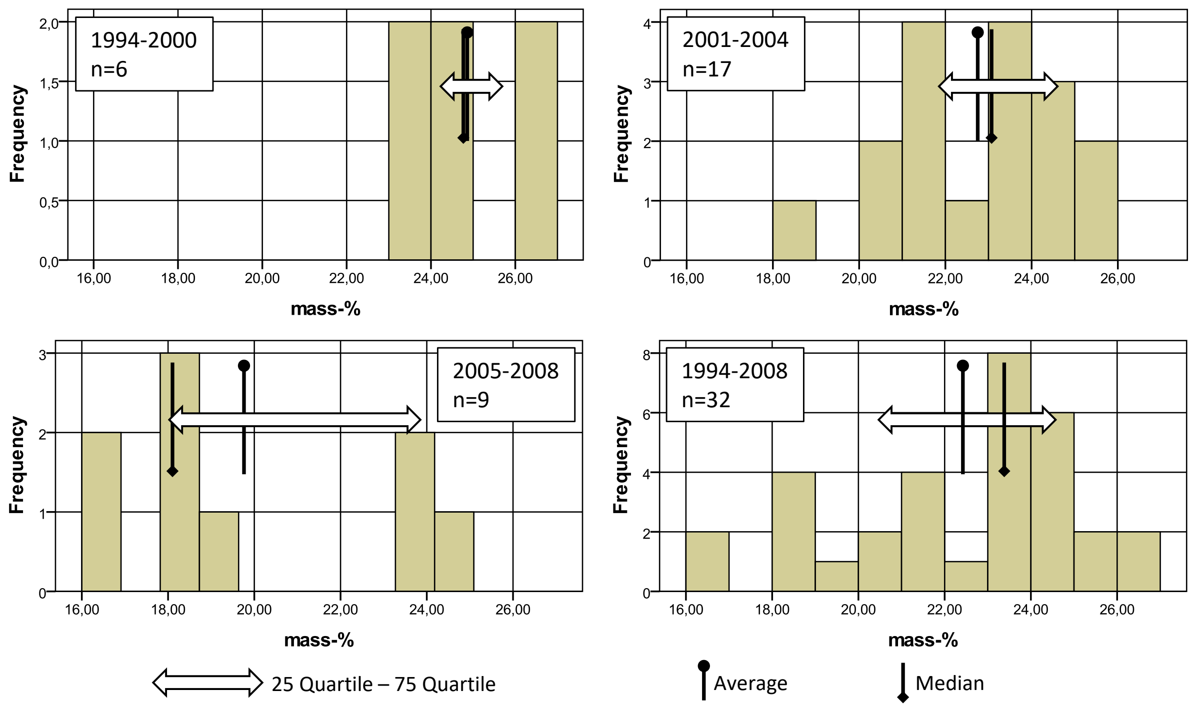

Fig 2 Time trend for Neodymium in spindle motor magnets

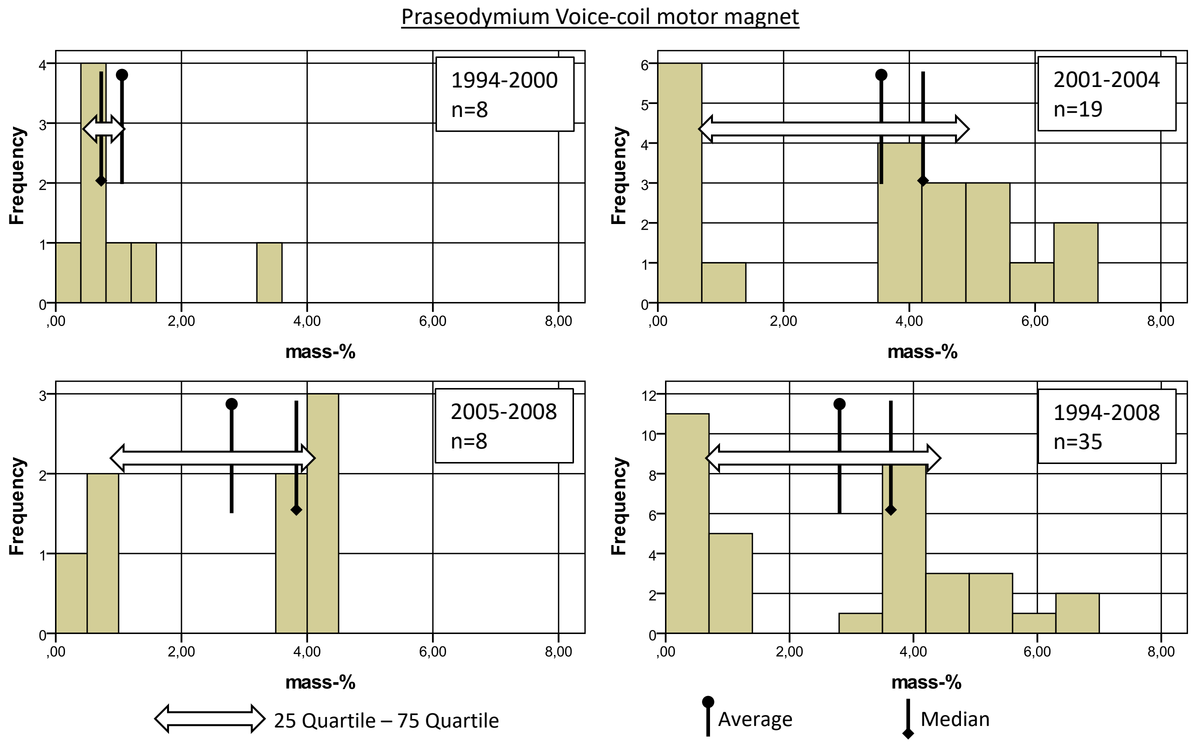

Fig 3 Time trend for Praseodymium in voice-coil motor magnets

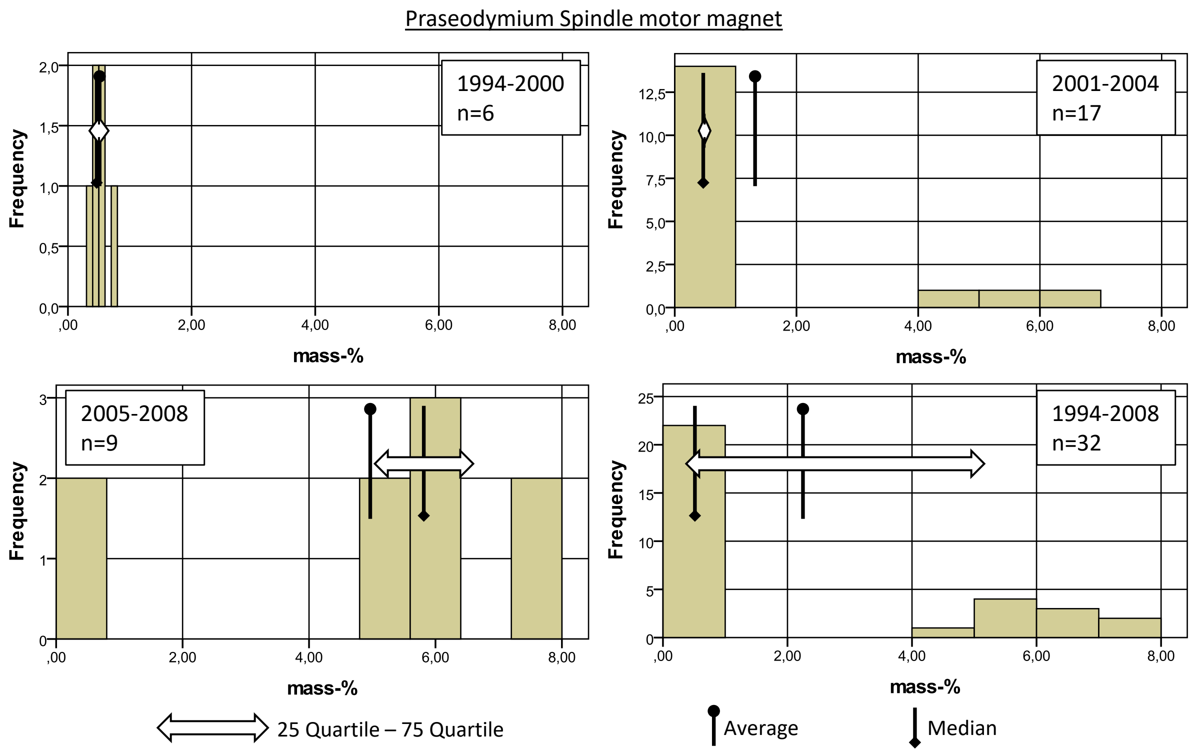

Fig 4 Time trend for Praseodymium in spindle motor magnets

Dysprosium Voice-coil motor magnet

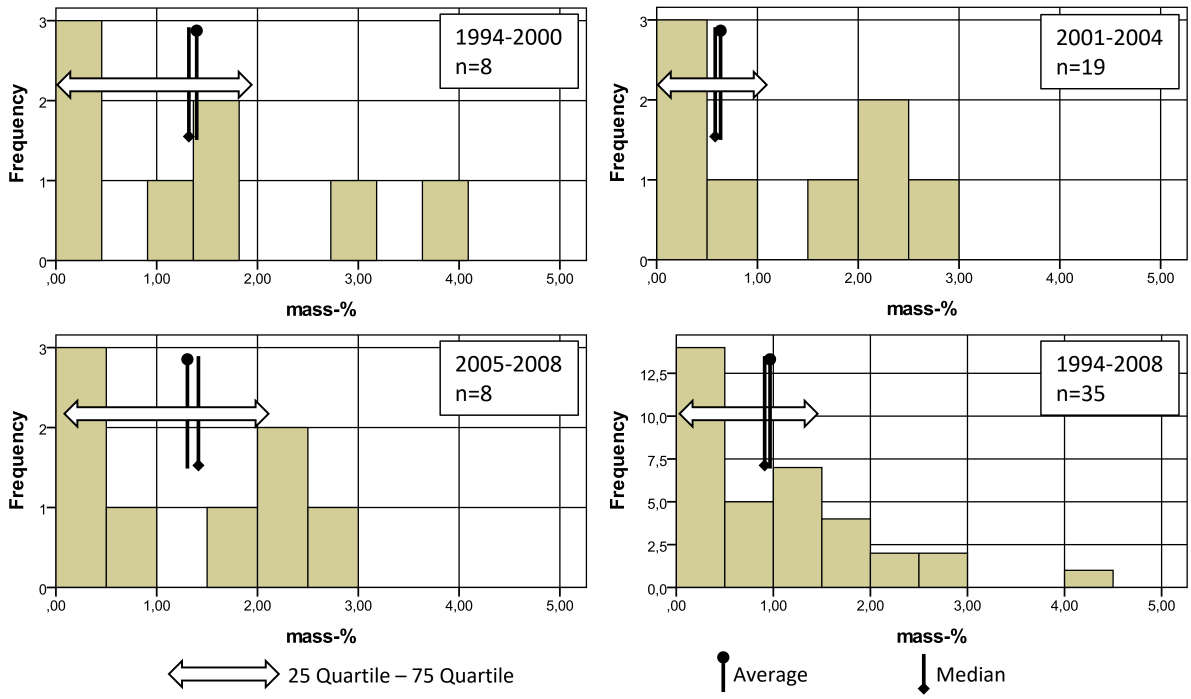

Fig 5 Time trend for Dysprosium in voice-coil motor magnets

Dysprosium Spindle motor magnet

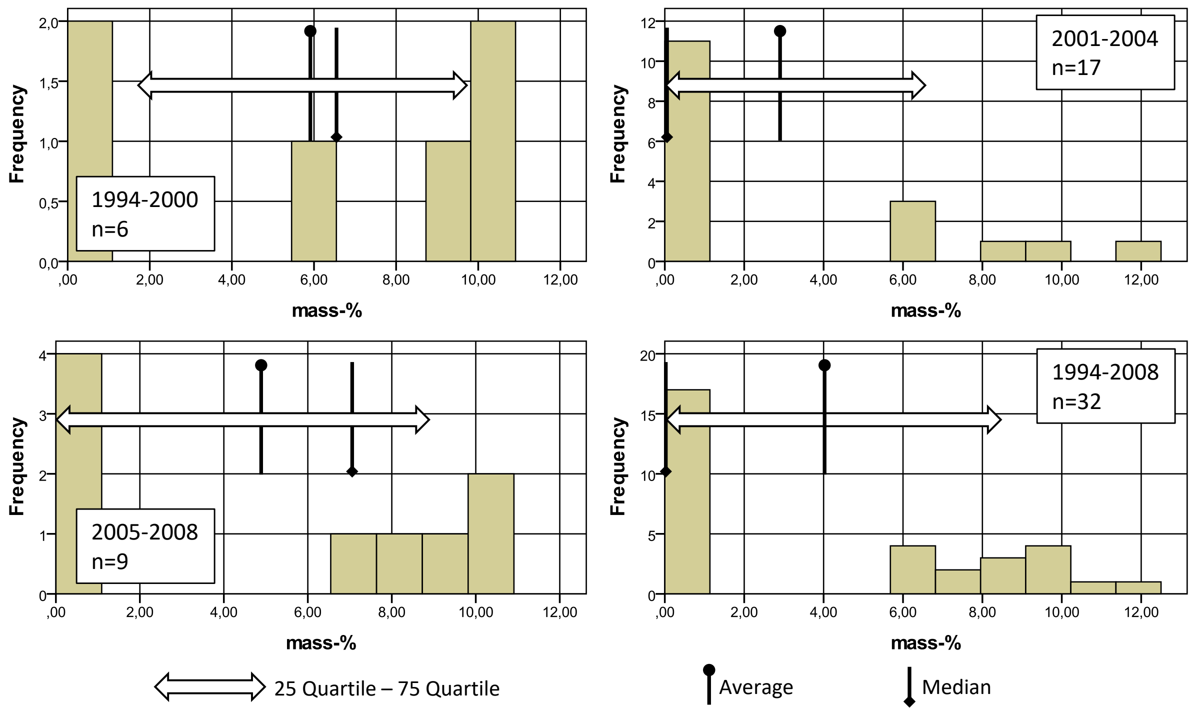

Fig 6 Time trend for Dysprosium in spindle motor magnets

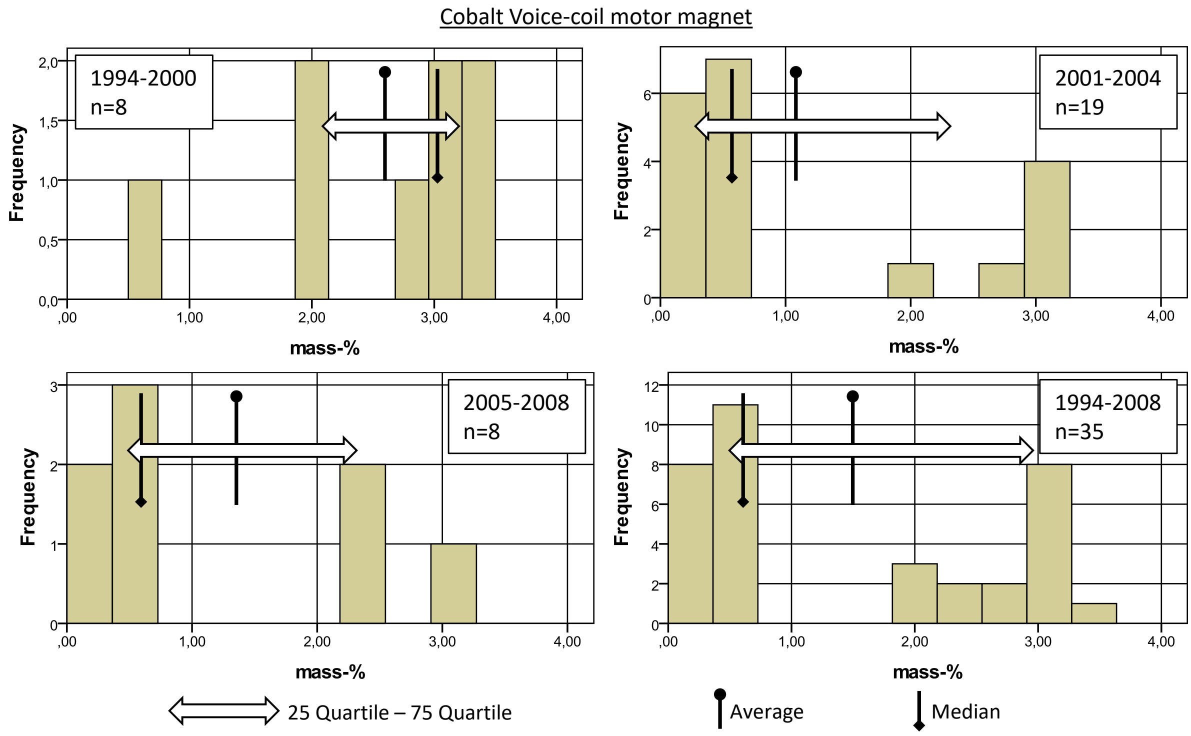

Fig 7 Time trend for Cobalt in voice-coil motor magnets

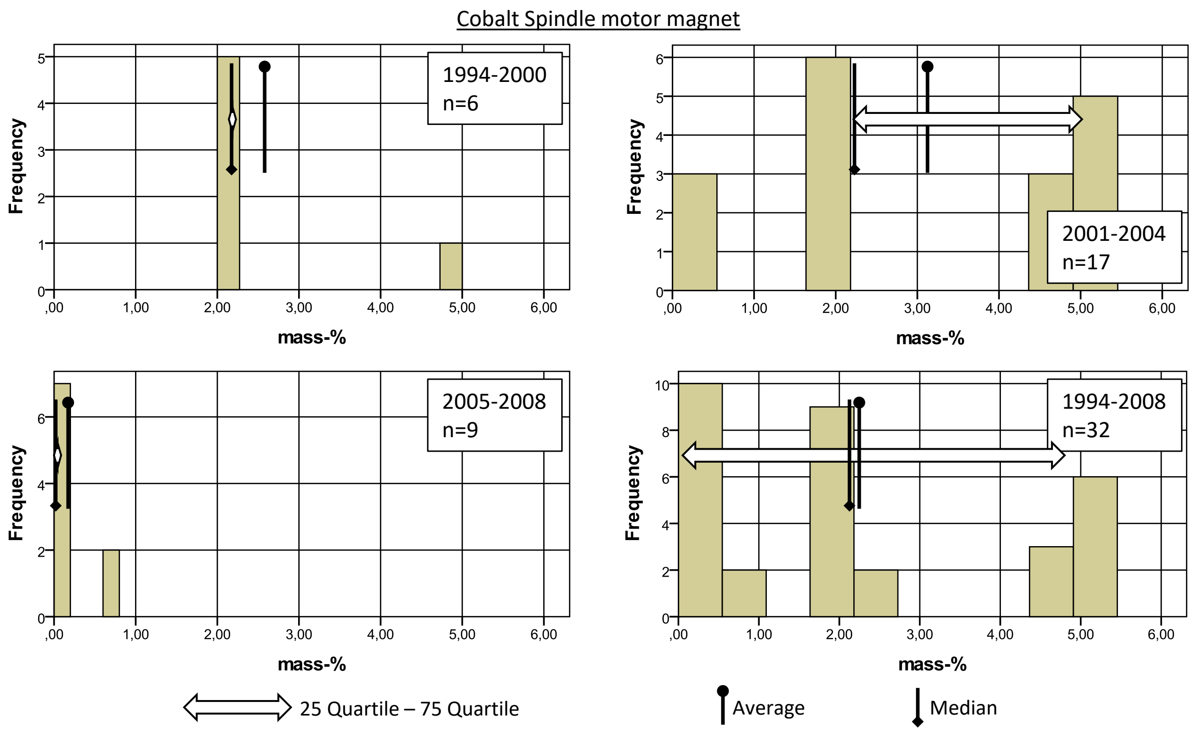

Fig 8 Time trend for Cobalt in spindle motor magnets

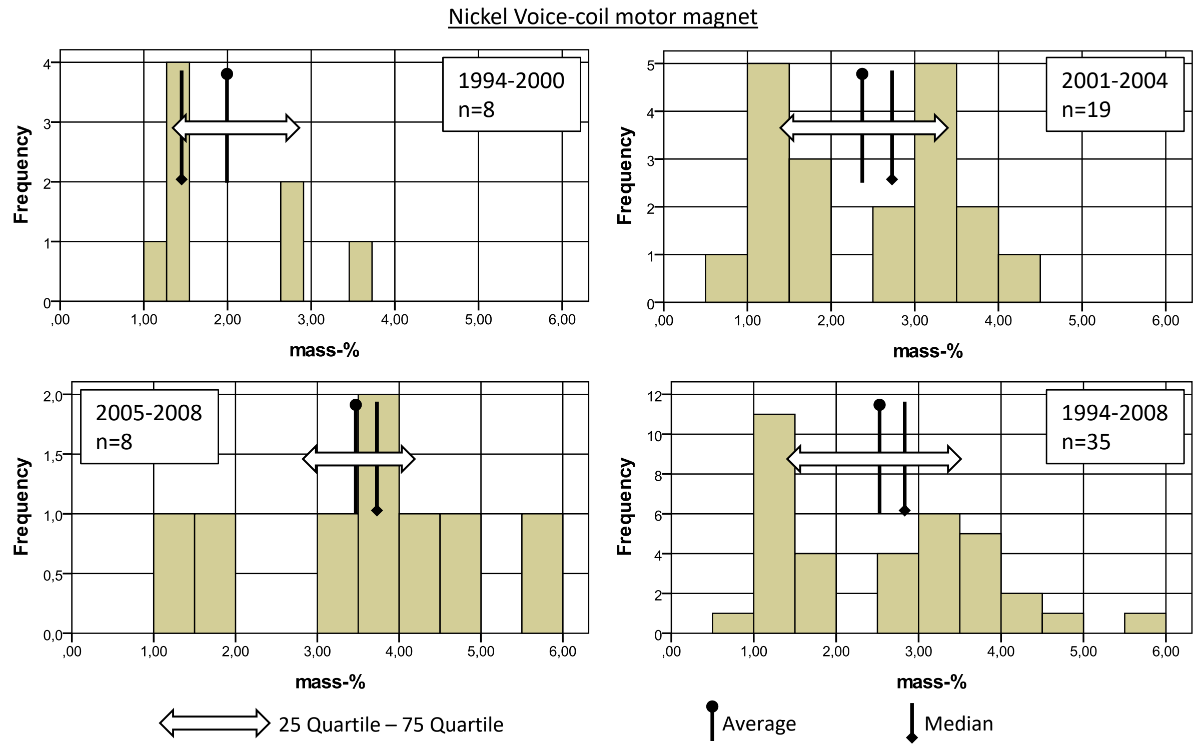

Fig 9 Time trend for Nickel in voice-coil motor magnets

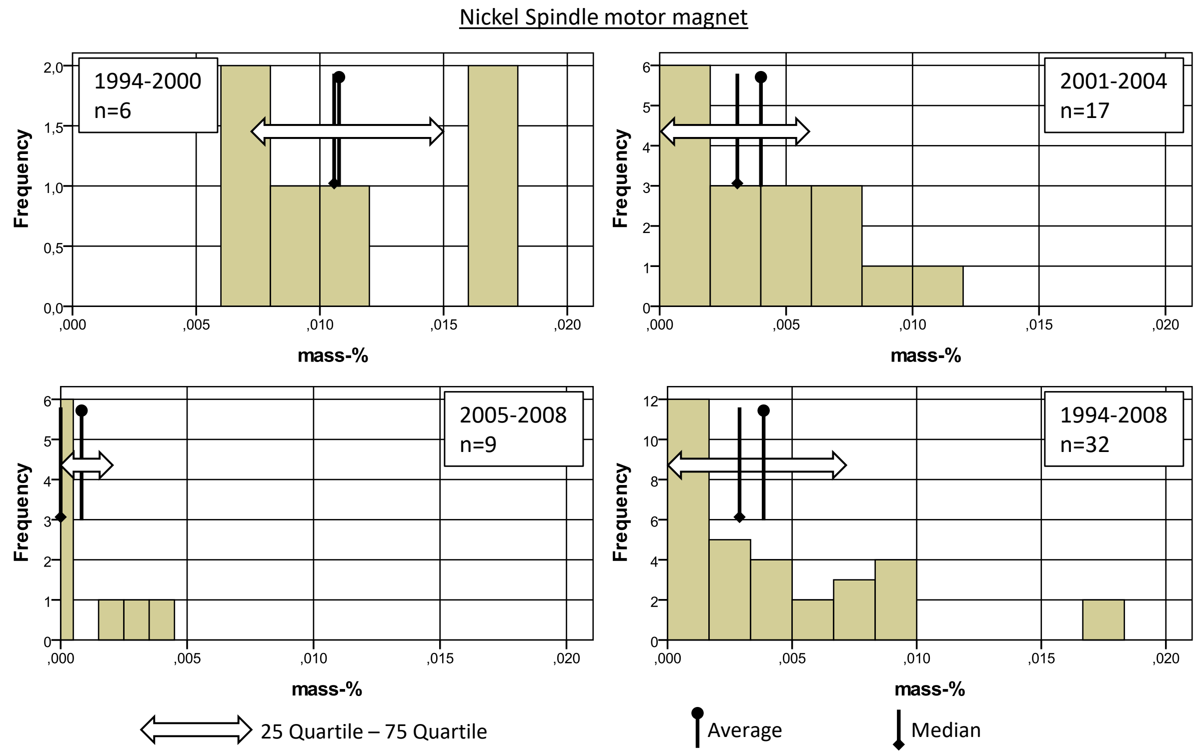

Fig 10 Time trend for Nickel in spindle motor magnets

Iron Voice-coil motor magnet

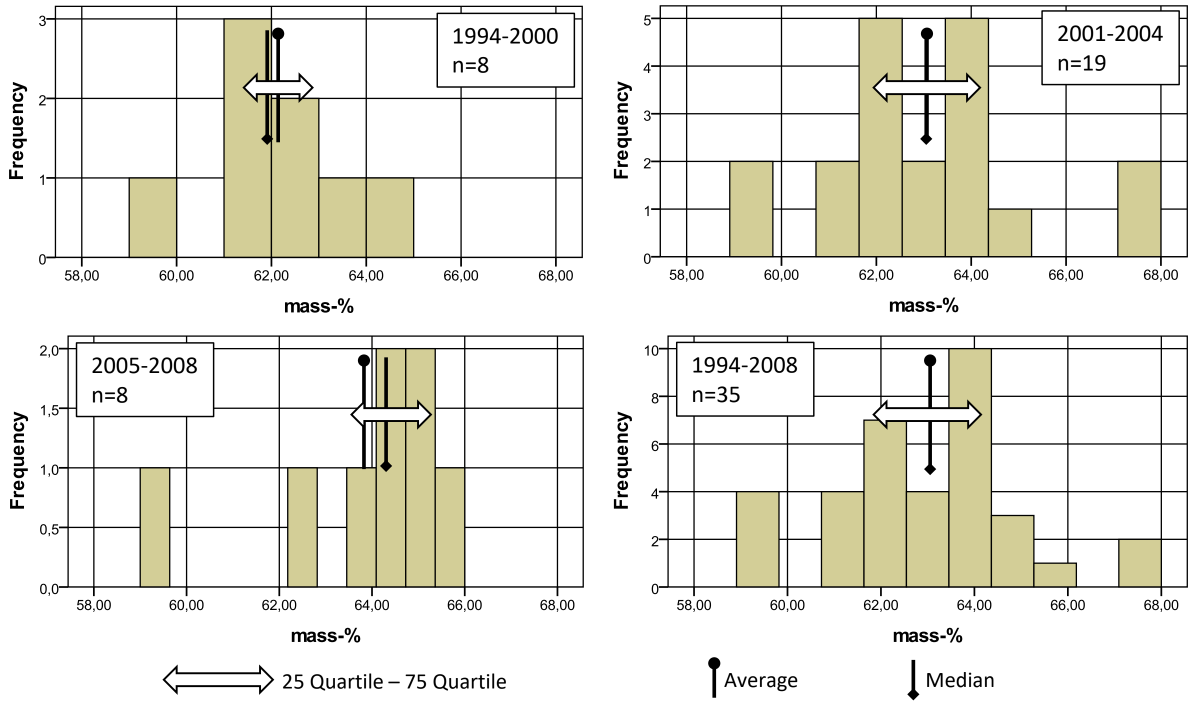

Fig 11 Time trend for Iron in voice-coil motor magnets

Iron Spindle motor magnet

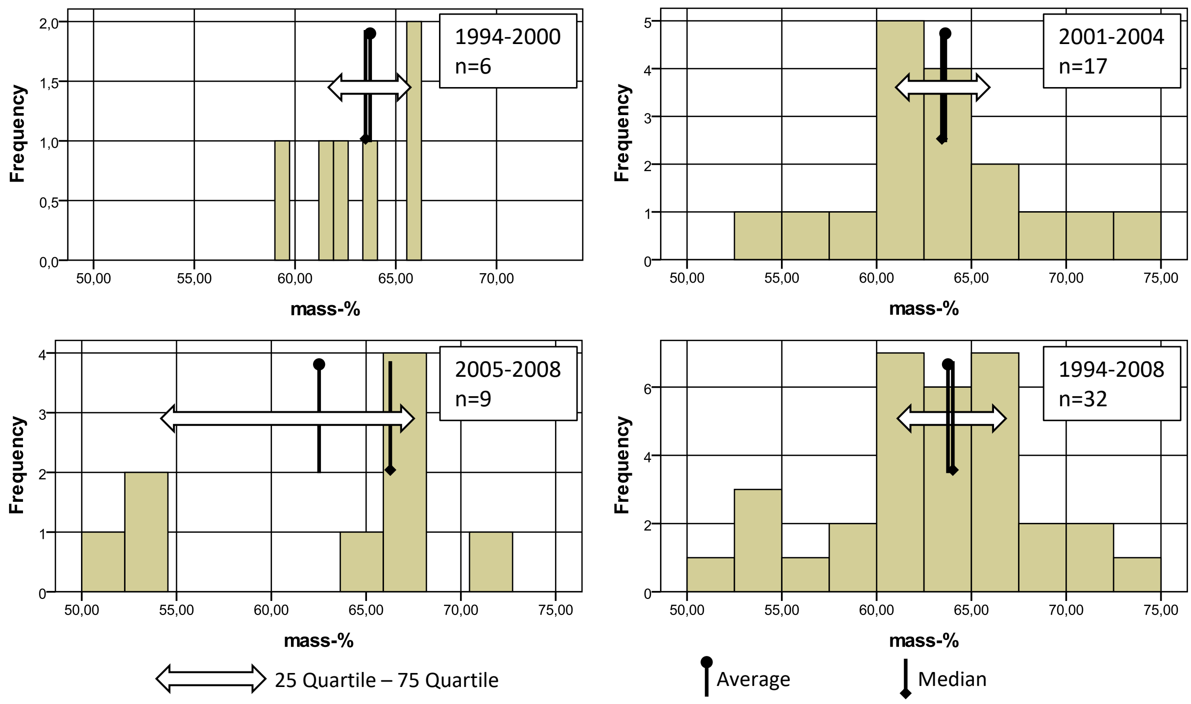

Fig 12 Time trend for Iron in spindle motor magnets