Challenge
Trace level determination of rare earth elements and transition metals in complex emission spectra resulting from line rich matrix elements of magnet alloys

Solution
Array ICP-OES with high resolution, high sensitivity and advanced software tools for the interference-free determination of major and trace elements in REE- and Fe-rich materials

Determination of Trace Elements and Main Components in Permanent Magnet Alloys by HR-Array ICP-OES

Introduction

Permanent magnets are employed in a large variety of applications and devices in the fields of clean energy technologies and consumer products. Today, they are utilized as key components in electric generators as part of wind turbines, motors of electric vehicles as well as tools, energy saving lighting, cellphones, hard disk drives and flat panel television devices. Their applications stretch into the fields of medical instrumentation (MRI) and even magnetic toys. Nowadays, neodymium magnets are the strongest type of commercially available magnets with superior performance compared to traditional magnetic compounds such as AlNiCo and ferrite magnets. Additionally, neodymium magnets are cheaper in comparison to other rare earth element (REE) based magnets like samarium-cobalt compounds. Neodymium magnets are predominantly alloys of neodymium, iron and boron in the structure of $Nd_2Fe_{14}B$. Additives like dysprosium, terbium or other REEs are often used to increase the curie temperature, the temperature where a magnetic compound loses its ferromagnetic properties, in order to allow for high temperature applications of this magnet type. The resulting Curie temperature and hence, the magnetic properties at elevated temperatures, strongly depend on the contents and ratios of the REE additives. Neodymium magnets are highly susceptible to corrosion if they are employed in a humid, caustic or acidic environment. Therefore, protective coatings of metals such as nickel or nickel-copper layers need to be applied via an electroplating process, whereas the thickness of the applied layers are a direct measure for the corrosion resistance of the entire magnet assembly.

Since the contents of the main components (neodymium, iron and boron), the additives (dysprosium, terbium, REEs) and the base metals of the protective coating define the magnetic properties and corrosion resistance, and hence the applicability of the magnets, a stringent quality control is required as part of the production process. In this regard, spectroscopic methods such as optical emission spectroscopy with inductively coupled plasma (ICP-OES) represent an ideal tool to analyze main elemental components in the percentage range alongside traces of additives and impurities in the sub mg/kg range.

REEs and transition metals are infamous to produce extremely line-rich spectra with a high risk of spectral interferences on the most prominent analyte lines. High contents of iron, neodymium, dysprosium and terbium produce thousands of highly pronounced emission lines. This complicated spectral situation requires a high-resolution spectrometer in order to resolve severe interferences and allow for the use of sensitive emission lines for the analysis of trace concentrations. Additionally, a high robustness of the plasma system is required to allow for minimal dilution factors of the digested samples. In combination with a high base sensitivity, this allows for optimal analytical performance in the trace and major concentration ranges. In this regard, the high-resolution ICP-OES array, the PlasmaQuant 9100 Elite offers an industry-leading spectral resolution of 2 pm @ 200 nm to resolve even most severe spectral interferences, a highly robust plasma, and torch system to run highly concentrated sample aliquots and a high sensitivity to achieve LODs in the sub mg/kg range in highly demanding sample types such as REE magnets.

Materials and Methods

Sample preparation

Approximately 0.2 g of sample were accurately weighed, transferred into heat-stable 50 mL polypropylene tube and 4 mL of deionized water was added. In the following, 4 mL HNO_3 ($w \geq 65\%$) were successively dropped to that mixture. Subsequent heating (90 °C, 2 h) was performed on a Hot-Block™. Afterwards samples were allowed to cool to room temperature, filled up to 50 mL with deionized water and directly analyzed. The determination of Ce, Fe, Gd, Nd and Pr was carried out in a 100-fold dilution.

Instrument settings

For the measurements an ICP-OES system PlasmaQuant 9100 Elite was used. The instrument was equipped with the standard kit, comprising of a glass concentric nebulizer (1.0 mL/min), a cyclonic spray chamber, a 2.0 mm ID injector tube, PVC tubing and a Teledyne Cetac ASX 560 autosampler.

Table 1: Instrument settings

Parameter	Specification
Plasma power	1,350 W
Plasma gas flow	14.5 L/min
Auxiliary gas flow	0.5 L/min
Nebulizer gas flow	0.5 L/min
Nebulizer	Concentric, 1.0 mL/min, Borosilicate
Spray chamber	Cyclonic spray chamber, 50 mL, Borosilicate
Outer tube/Inner tube	Quartz/quartz
Injector	Quartz, ID: 2 mm
Pump tubing	PVC (black, black)
Sample pump rate	1.0 mL/min
Delay time	45 s

Table 2: Method parameters

Element	Line [nm]	Plasma view	Integration mode	Read time [s]	Evaluation			
					No. of pixel	Baseline fit, Pixel No.	Polyn. degree	Correction
Al	396.152	radial	peak	3	3	ABC[1]	auto	-
B	249.773	radial	peak	3	3	ABC	auto	-
Ce	413.380	axial	peak	3	3	ABC	auto	-
Cu	324.754	radial	peak	3	3	ABC	auto	-
Dy	353.602	axial	peak	3	3	ABC	auto	CSI[2]
Fe	259.940	radial	peak	3	3	ABC	auto	-
Ga	294.364	axial	peak	3	3	ABC	auto	CSI
Gd	342.247	axial	peak	3	3	ABC	auto	-
La	333.749	axial	peak	3	3	ABC	auto	CSI
Nb	316.340	axial	peak	3	3	ABC	auto	-
Nd	401.225	axial	peak	3	3	ABC	auto	-
Ni	231.604	axial	peak	3	3	ABC	auto	-
Pr	525.973	axial	peak	3	3	ABC	auto	-
Pt	265.945	axial	peak	3	3	ABC	auto	-

1 ... Automated Baseline Correction
2 ... Correction of Spectral Interferences

Calibration

Calibration was performed using matrix-matched standards. Therefore, 8% ((v/v), 4 mL of HNO_3 (w ≥ 65%) to 50 mL deionized water) HNO_3 was spiked with multi-element (Merck IV, 1000 mg/L; Table Mix 2, Sigma Aldrich, 10 mg/L; REE Mix, Sigma Aldrich, 50 mg/L) and single element (Ga, Merck IV, 1000 mg/L) standards to give the respective calibration standards as described below (see Table 3).

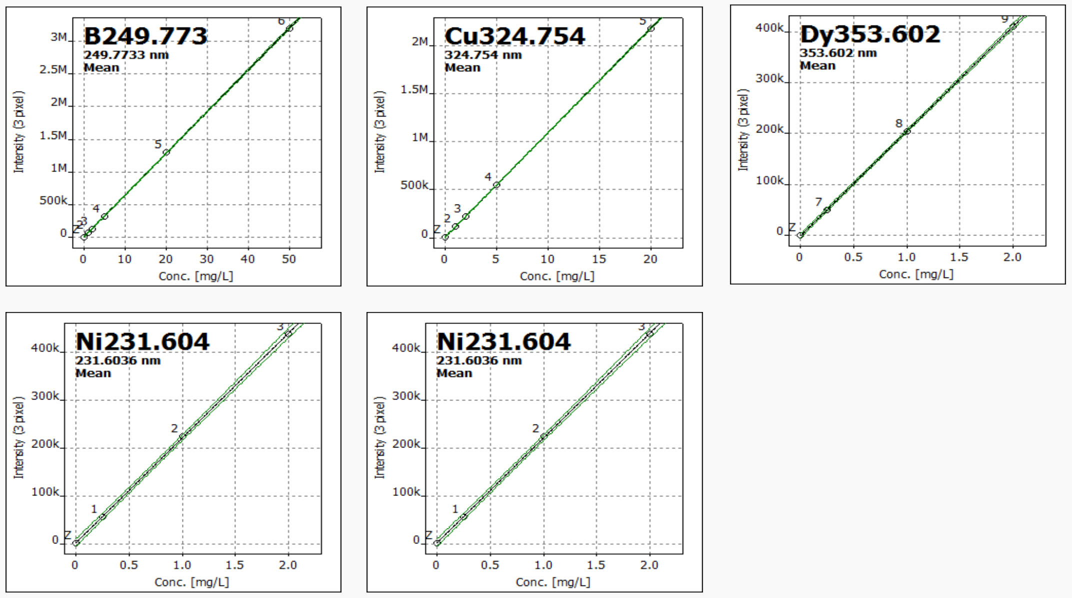

Figure 1: Selection of representative calibration functions for Boron, Copper, Dysprosium, Nickel

Table 3: Concentration of calibration standards

Element	Unit	Cal. 0	Std. 1	Std. 2	Std. 3	Std. 4	Std. 5
Al	mg/L	0	1.0	2.0	5.0	20	50
B	mg/L	0	1.0	2.0	5.0	20	50
Ce	mg/L	0	1.0	2.0	5.0	-	-
Cu	mg/L	0	1.0	2.0	5.0	20	-
Dy	mg/L	0	0.25	1.0	2.0	-	-
Fe	mg/L	0	5.0	20	50	-	-
Ga	mg/L	0	0.1	0.2	0.5	-	-
Gd	mg/L	0	0.25	1.0	2.0	-	-
La	mg/L	0	0.25	1.0	2.0	-	-
Nb	mg/L	0	0.1	0.2	0.5	-	-
Nd	mg/L	0	1.0	2.0	5.0	-	-
Ni	mg/L	0	0.25	1.0	2.0	-	-
Pr	mg/L	0	0.25	1.0	2.0	-	-
Pt	mg/L	0	0.1	0.2	0.5	-	-

Results and Discussion

For most of the investigated analytes, spectral interferences could be avoided by the high spectral resolution of the used ICP-OES instrument. Figure 2 shows the examples of neodymium and boron where potentially interfering peaks in close proximity to the analyte peak are sufficiently resolved to perform an accurate quantification.

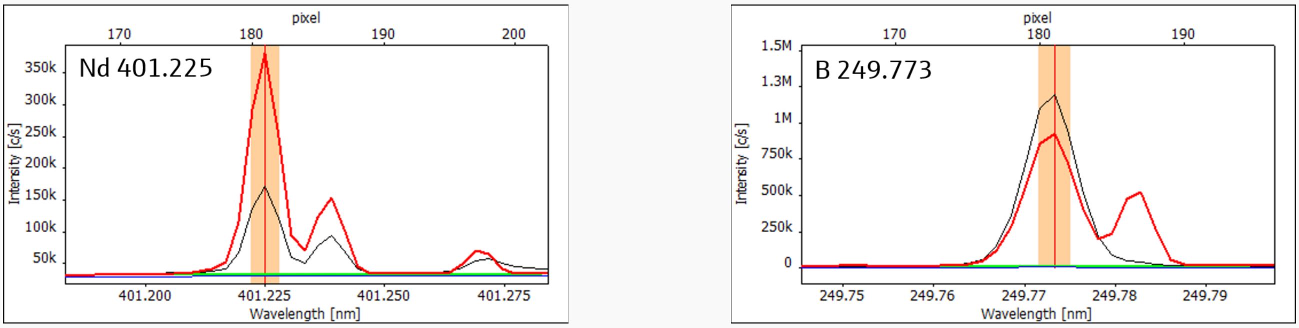

Figure 2: High-resolution spectra of Nd 401.225 (left) and B 249.773 (right) showing sufficient spacing to potentially interfering peaks (red: sample, black: calibration standard, blue: Cal. 0, green: ABC)

Despite of the high resolution of the system, sensitive emission lines of dysprosium, gallium and lanthanum cannot be sufficiently seperated in the complex matrix of neodymium magnets. For these lines, a spectral correction was performed with a spectrum of the clean interferent. The correction spectra were obtained by measuring dilutions of single element standards (e.g. Ce 400 mg/L, Nd 500 mg/L) at the specific analytical line to be corrected. Figure 3 shows the example of the dysprosium line at 253.602 nm. By applying the CSI algorithm of spectral correction, this highly sensitive line becomes accessible for quantification.

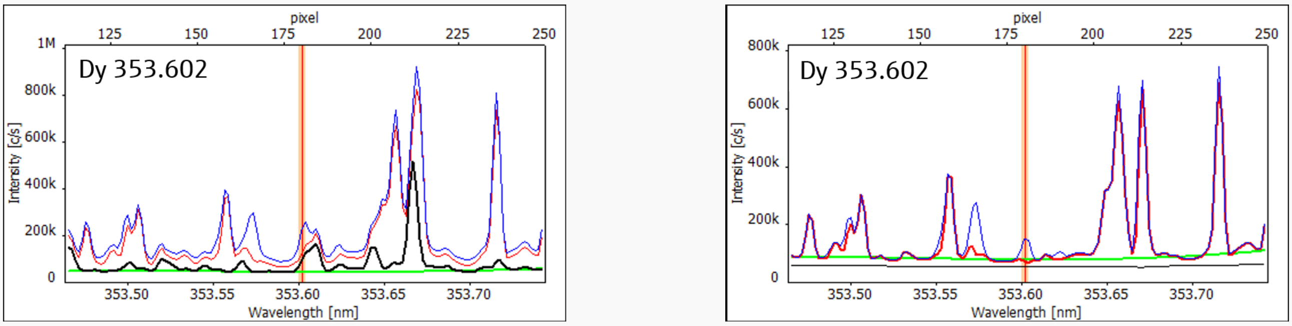

Figure 3: High-resolution spectra of Dy 353.602 as-recorded (left) and CSI corrected (right) showing (red: sample, black: Nd correction spectrum (500mg/L), blue: img/L spike, green: ABC)

The investigated samples were prepared and measured in duplicate in order to verify the repeatability of the applied method. The precision of the individual measurements is below 1.5% RSD whereas the precision of the duplicate measurement is below 3% RSD. All results are shown in Table 4. The detectability of low to sub µg/L concentrations in the measurement solutions translate into method limits of detection in the sub mg/kg range for all investigated elements. The accuracy of the method was verified by recovery measurements of 1 mg/L spikes in the measurement solutions. As shown in Table 5, all investigated elements show recovery values of 95% to 110%.

Table 4: Results of Nd magnet sample

Element	**Mass fraction 1**	**RSD^{+}**	**Mass fraction 2**	**RSD**	**LOD$_{inst}$***	**LOD$_{meth}$#**
	[mg/kg]	**[%]**	**[mg/kg]**	**[mg/kg]**	**[µg/L]**	**[mg/kg]**
Al	8,603	0.8	8,236	0.1	3.57	0.89
B	9,739	1.0	9,428	0.5	1.53	0.38
Ce	102,900	1.2	99,490	0.9	1.09	0.27
Cu	1,473	0.2	1403	1.3	1.45	0.36
Dy	< LOD	n.a.	< LOD	n.a.	0.97	0.24
Fe	669,000	0.6	660,600	0.6	1.36	0.34
Ga	< LOD	n.a.	< LOD	n.a.	3.41	0.85
Gd	37,600	0.3	36,410	0.2	0.28	0.07
La	< LOD	n.a.	< LOD	n.a.	0.10	0.03
Nb	< LOD	n.a.	< LOD	n.a.	0.41	0.10
Nd	129,900	1.5	125,300	1.3	0.77	0.19
Ni	201	0.8	202	0.2	0.44	0.11
Pr	40,470	0.7	40,070	0.6	1.95	0.49
Pt	< LOD	n.a.	< LOD	n.a.	2.37	0.59

LOD - limit of detection
* Instrumental limit of detection determined in 8% (v/v) HNO_3
# Method limit of detection refers to 0.2 g sample in 50 mL
+ Relative standard deviation obtained from 3 replicate measurements

Table 5: Method-specific spike 1 (mg/L) recovery rates for exemplary elements in undiluted sample matrix

Element	Line [nm]	Recovery rate [%]
Cu	324.754	97
Dy	353.602	102
Ga	294.364	110
La	333.749	95
Ni	231.604	98

Summary

It is well known that neodymium and iron produce line-rich spectra with high baseline noise. Additionally, the sample matrix of Nd-magnets exhibits considerable concentrations of other REEs (e.g., Ce) and transition metals resulting in highly complex spectra with a high risk of spectral interferences for most of the considered analytical lines. Usually matrix matching is recommended for the calibration to overcome these issues. For this purpose, standards or reference materials of high purity are needed for all elements to be determined. Since the availability of such materials is often limited, the analysis of Nd-magnets is quite challenging.

One possibility to overcome the application issues is to use high resolution instruments which possess the capability of separating spectral interferences from the desired analytical line. The here presented results clearly demonstrate the enormous application advantages originating from the high resolution (2 pm @ 200 nm) of the PlasmaQuant 9100 Elite system. Its high sensitivity and the possibility to use most sensitive emission lines without spectral interferences allows for highly precise and accurate results and low limits of detection in the sub mg/kg range for all investigated analytes. Additionally, the automated baseline correction (ABC) software tool reduces data handling efforts and reduces the complexity of data analysis.

Another possibility to handle materials infamous for their wealth of emission lines and complex interferences is to use software tools enabling the correction of spectral interferences (CSI). With the aid of the CSI-software tool it was possible to subtract one or more unsmoothed correction spectra from interfering elements. This results in more accurate data for the trace element analysis.

In summary, the PlasmaQuant 9100 Elite is the ideal instrument for the quality control of permanent magnet alloys such as Nd-magnets. With its high resolution, high sensitivity and advanced software tools, the determination of major and trace elements can be easily performed in REE- and Fe-rich materials.

Figure 4: PlasmaQuant 9100 Elite

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