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Determination of trace amounts of rare-earth elements in highly pure neodymium oxide by sector field inductively coupled plasma mass spectrometry (ICP-SFMS) and high-performance liquid chromatography (HPLC) techniques

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Abstract

Recently rare-earth elements (REE) have received much attention in fields of geochemistry and industry. Rapid and accurate determinations of them are increasingly required as industrial demands expand. Sector field inductively coupled plasma mass spectrometry (ICP-SFMS) with high-performance liquid chromatography (HPLC) has been applied to the determination of REE. HR ICP-MS was used as an element-selective detector for HPLC in highly pure materials. The separation of REE with HPLC helped to avoid erroneous analytical results due to spectral interferences. Sixteen elements (Sc, Y and 14 lanthanides) were determined selectively with the HPLC/ICP-SFMS system using a concentration gradient methods. The detection limits with the HPLC/ICP-SFMS system were about 0.5–$10 \, \mathrm{pg \, mL}^{-1}$. The percentage recovery ranged from 90% to 100% for different REE. The %RSD of the methods varying between 2.5% and 4.5% for a set of five ($n = 5$) replicates was found for the IPEN's material and for the certificate reference sample. Determination of trace REEs in two highly pure neodymium oxides samples (IPEN and Johnson Matthey Company) were performed. In short, the IPEN's materials which are highly pure ($>99.9\%$) were successfully analyzed without spectral interferences.
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1. Introduction

The neodymium oxide is used for many different high-technology applications such as lasers, optical fibers, super conductors, advanced ceramic material and special metallic alloys. Several analytical techniques have been used for the quantification of rare-earth elements (REE) as impurities in high-purity materials

[1–6]. Stijfhoorn and Zang [7,9] evaluated the spectral interference of RE elements as well in high-purity europium, yttrium and scandium oxide when analyzed by ICP-MS.

The determination via neutron activation analysis has been an analytical technique widely used for the determination of REE [5,6], but even this powerful method has several problems, like costs, low throughput and interelement interference.

The inductively coupled plasma mass spectrometry (ICP-MS) is the most powerful analytical tool in the quantification of these impurities. Zhang et al. [9] made use of the ICP-MS technique for the assay of the RE elements in highly pure europium oxide.

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In general, the ICP-SFMS presents some advantages for element trace analysis, due to high sensitivity, selectivity and low detection limits, when compared with other analytical techniques.

However, in case of the REs there are same problems associated with the matrix, such as the signal suppression, formation of polyatomic ions (MO^+, MOH^+) and double charge ions (M^{2+}), generated in the plasma that interfere in the quantification of the isotopes of interest [10]. Such problems can be overcome by using procedures that allow the separation of the matrix-like ion exchange chromatography, liquid chromatography and solvent extraction [3,5,8].

In this paper, an analytical method was developed for the separation and determination of several RE trace elements in a highly pure neodymium oxide, used as spectrochemical standards, by HPLC and ICP-MS associated techniques.

2. Reagents

RE oxides as standards supplied by SPEX Chemical, Metuchen, N.J. and Johnson Matthey Company (JMC—Batch No. P. 3129B, Ward Hill, USA). Suprapur nitric acid (HNO_3) from Merck Darmstadt, Germany. Sodium hydroxide ($1\,mol\,L^{-1}$), sodium laurylsulfonate and lactic acid of analytical grade were used. Arsenazo III ($50\,\mu g\,mL^{-1}$, with pH 3.8) was acquired from Fluka Co. The standards and sample solutions were prepared with purified water by Milli-Q Water unity (Millipore, $18.2\,M\Omega$) and filtered through a $0.2\,\mu m$ membrane filter. The highly pure neodymium oxide was sample manufactured by IPEN. The solution of neodymium oxide was prepared by dissolving the pure oxide.

3. Sample preparation

Five samples of neodymium oxide (100 mg) were weighed and dissolved with 10 mL 50% (v/v) Suprapur nitric acid heating at 50°C for 30 min. After dissolving, the RE solutions were diluted up to 100 mL by using 1% nitric acid (HNO_3). Therefore, the sample described has a concentration of $1000\,\mu g\,mL^{-1}$. Oxides used as standards went through the same procedure. Then, samples and certified standards solutions were diluted by a factor of 1000.

4. Instrumentation

The liquid chromatograph (HPLC) used in this work was Shimadzu, model LC10Ai (Tokyo-Japan) (Tables 1 and 2). A Shimadzu module (post-column reagent) was

Table 1
HPLC Shimadzu operating conditions

Reverse phase	Shim-pack CLC-ODS(M)
Mobil phase	0.7 M lactic acid, pH 2.9
Modifier	0.01 M sodium laurylsulfonate
Column temperature	50°C
Sample volume	$100\,\mu L$
Mobil phase flow	$1.0\,mL\,min^{-1}$
Colorimetric Reagent	ArsenazoIII, $50\,mg\,L^{-1}$, pH 3.8
Reagent flow	$0.5\,mL\,min^{-1}$
UV–VIS detector	At 655 nm
Separation column	C_{18} (octadecyl silane)

Table 2
ICP-MS operating conditions. Plasma conditions and mass spectrometer settings

Plasma power	1300 W
Plasma gas flow	$15\,L\,min^{-1}$
Auxiliary gas flow	$0.90\,L\,min^{-1}$
Nebulizer gas flow	$1.10\,L\,min^{-1}$
Nebulizer	Meinhard
Spray chamber	Scott-type
Sample orifice, Pt	1.0 mm
Conical skimmer orifice, Pt	0.75 mm
Resolution	300
Points per peak	20
Scan mode	E-scan

used to transfer the Arsenazo III. For the quantification of the REE elements a ICP (sector field) mass spectrometer, *element*, from Finningan MAT (Bremen, Germany) was used.

5. Operational parameters

The RE minor constituents were separated from the RE matrix by means of liquid chromatography, using the HPLC instrument, reverse phase chromatography mode [13,14]. Sodium laurylsulfonate $0.01\,mol\,L^{-1}$, pH 2.9 was used as phase modifier. Both samples and standards were filtered through a $0.2\,\mu m$ porous membrane. For each determination the injected volume was $100\,\mu L$. Lactic acid ($0.7\,mol\,L^{-1}$) pH 2.9, was ascertained with sodium hydroxide.

The elution time for each trace element eluted from the column was determined by using an UV–VIS detector, working at 655 nm, using Arsenazo III (post-column reagent).

6. Results and discussion

The detection limits were determined according to the International Union of Pure and Applied Chemistry (IUPAC) recommendation (3σ criterion) [16].

Table 3
Detection limits determined by applying the 3σ criterion[15] to the REE on the results of 10 consecutive measurements of a 1% HNO_3 blank solution

Detection Limits (3σ)	
Elements	($ng\,g^{-1}$)
Sc	10.3
Y	9.8
La	0.5
Ce	0.8
Pr	4.4
Sm	3.5
Gd	1.6
Tb	3.9
Dy	3.7
Ho	3.8
Er	2.9
Tm	3.3
Yb	4.6
Lu	3.1

Table 4
Recovery of RE, thorium and uranium

	$1\,pg\,g^{-1}$ (%)	$5\,pg\,g^{-1}$ (%)	$10\,pg\,g^{-1}$ (%)	$20\,pg\,g^{-1}$ (%)
La	89.15	96.35	91.22	90.41
Ce	89.14	91.64	89.17	91.10
Pr	89.98	89.98	96.30	97.10
Sm	86.90	89.58	89.94	95.18
Eu	89.89	91.43	97.83	96.89
Gd	88.79	89.98	88.52	99.20
Ho	89.29	91.58	92.68	96.87
Yb	89.96	91.97	92.98	91.36
Lu	89.36	92.48	89.14	92.01
Th	89.69	89.67	91.10	98.88
U	89.97	89.12	85.85	91.19

5, 10 and $20\,pg\,g^{-1}$. A neodymium oxide aliquot was spiked with the standards. They were estimated from a separate standard addition experiment. Five independent determinations were made for each REE [15]. The percentage recovery ranged from 90 to 100, which shows that the method is adequate for analytical applications (see Table 4).

Recently, the coupling of the liquid chromatograph with mass spectrometer technique (HPLC-ICP-MS) has been used for the characterization of radioactive materials and fission products, as well as the RE [11,12] elements.

7. The quantification

In this work, was investigates the use of an HPLC method for the determination of REE impurities in RE oxides based upon the work of Cassidy [17]. The results obtained using the HPLC method were compared with results obtained by using ICP-SFMS only. The mono-isotopic elements Pr, Tb, Ho and Tm, as well as La, could not be analyzed by isotope dilution, but a semiquantitative measurement could be made by comparing the intensities these elements in the mass spectra with the intensities of other REE isotopes with a similar ionization potential and evaporation temperature.

The quantification of the samples and standards was accomplished with the help of a calibration curve constructed in accordance with certified standards solutions as Spex, in the 0.1–$10\,pg\,g^{-1}$ range, presenting $r^2 = 0.999$ for the major of the elements analyzed.

The values of RE traces found as impurities in the neodymium oxide manufactured by IPEN are in Table 5. The figures allowed to conclude that a reproducibility of 4.5% was achieved.

In Table 6 are the results of the contaminants found in a certified neodymium oxide standard (JMC).

The values of the analysis, by the procedures described here, are in accordance with the procedures
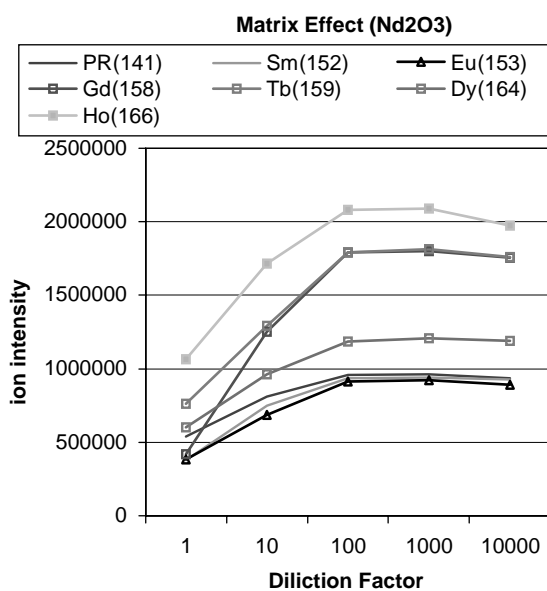

Fig. 1. Matrix effects for the rare-earths solution.

The values for the RE elements were measured and are shown in Table 3.

The matrix effect was studied by using a $1000\,mg\,L^{-1}$ Nd solution that was submitted to various dilutions (dilution factor 1-, 10-, 100-, 1000- and 10,000-fold), with 1% Suprapur nitric acid. The multielemental RE solution were spiked with a $10\,pg\,g^{-1}$ concentration. For most of these isotopes, no expressive signal suppression was observed with the 100- and 1000-fold of the original neodymium solution ($1000\,\mu g\,mL^{-1}$), as can be observed in Fig. 1.

A recovery test was done by making measurements of four-spiked RE standard solutions in the matrix, with 1,

Table 5
Impurities determined in neodymium oxide produced at IPEN

Elements	(μg g^{-1})	RSD%[a]
Sc	4.2	2.24
Y	1.40	2.36
La	7.75	3.31
Ce	6.21	3.69
Pr	5.31	2.84
Sm	12.3	2.61
Eu	11.2	4.67
Gd	10.4	2.78
Tb	15.3	2.98
Dy	6.92	3.75
Ho	7.49	4.96
Er	6.44	2.18
Tm	3.04	1.88
Yb	4.53	3.34
Lu	15.7	4.27

[a] Relative standard deviation(%) for $n = 5$.

Table 6
RE impurities analyzed in a certified Johnson Matthey Company (JMC) neodymium oxide

Elements	(μg g^{-1})	RSD%[a]
Sc	3.67	2.32
Y	2.28	2.68
La	5.15	3.31
Ce	7.32	3.39
Pr	5.38	3.74
Sm	12.6	4.51
Eu	7.15	3.67
Gd	12.3	3.78
Tb	15.8	3.58
Dy	16.4	4.55
Ho	8.76	3.56
Er	6.92	3.81
Tm	1.94	2.31
Yb	4.73	2.34
Lu	7.35	3.27

[a] Relative standard deviation(%) calculated for $n = 5$.

with separation of the matrix, except for the isotope ^{159}Tb, which suffered the spectral interference of the ^{142}NdOH$^+$ species.

8. Conclusions

An analytical methodology for the quantification of rare-earth (RE) trace elements as impurities in a highly pure RE oxide by double focusing inductively coupled plasma mass spectrometry (ICP-MS) was used. It was applied for the separation of the trace elements as impurities from the matrix oxide by using the high-performance liquid chromatrography (HPLC) technique with a reverse phase column, with sodium laurylsulfonate as modifier.

The usage of the HPLC technique for the separation and concentration of traces of RE elements conjugated with the ICP-SFMS, enabled the determination of low amounts of RE impurities in the high-purity oxide materials.

The high sensitivity was obtained through a combination of separation and pre-concentration, by using HPLC, in the determination of the REE as impurities by the HR ICP-MS instrument, giving a profile of the oxide quality.

This work will be continued for the characterization of other RE oxides of high-purity manufactured by IPEN, S. Paulo, Brazil.

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