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

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Abstract

An analytical method for the determination of traces of rare earth elements (REE) as impurities in high pure lanthanum oxide (La_2O_3) produced in the Instituto de Pesquisas Energéticas e Nucleares (IPEN) and compared with the oxide of commercial lanthanum as a certified reference is discussed in this work. The REE as impurities in the lanthanum oxide were separated from the matrix by a high-performance liquid chromatography (HPLC) technique. The separated individual fractions containing the REE trace impurities were analyzed directly by inductively coupled plasma sector field mass spectrometer (HR ICP–MS) (*Element*, Finnigan MAT). The percentage recovery ranged from 88 to 100 for different rare earth elements. The mean R.S.D. of the method varying between 2 and 5% for a set of five ($n=5$) replicates was found for the IPEN's material and for the certificate reference sample. In short, it can be claimed that both materials are highly pure (>99.9%).

Keywords: Rare earths elements; Inductively coupled plasma mass spectrometry; High-performance liquid chromatography; Lanthanum oxide

1. Introduction

Due to several modern applications in the field of the new materials and with the recent technological progress, more and more high purity rare earth oxides have been demanded. The lanthanum oxide is used in lenses of photographic cameras, battery electrodes, and lighter stones, advanced ceramic material and special metallic alloys.

Several analytical techniques have been used for the quantification of REE as impurities in high purity materials [1–6]. Biswas [7] and Deskalova [8] evaluated the spectral interference of RE elements as well in the emission lines in high purity yttrium and scandium oxide when analyzed by ICP–AES.

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. In general, the inductively coupled plasma mass spectrometry presents some advantages for element trace analysis, due to high sensitivity, selectivity and low detection limits, when compared with other analytical techniques.

However, in the case of the rare earths there are same problems associated with the matrix, such as the signal suppression, formation of polyatomic ions (MO^+, MOH^+) and double charge ions (M^{++}), 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]. In this paper, an analytical method was developed for the separation and determination of several

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rare earth trace elements in a highly pure lanthanum oxide, used as spectrochemical standards, by HPLC and ICP–MS associated techniques.

2. Methods

2.1. Reagents

Rare earth oxides as standards supplied by SPEX Chemical (Metuchen, NJ) and Johnson Matthey (Ward Hill). Suprapur nitric acid from Merck (Darmstadt, Germany). Sodium hydroxide (1 mol l^{-1}), sodium laurylsulphonate and lactic acid were of analytical grade. Arsenazo III (50 μg ml^{-1}, pH 3.8) was acquired from Fluka. The standards and sample solutions were prepared with purified water using a Milli-Q Waters unit (Millipore, 18.2 MΩ) and filtered through a 0.2-μm membrane filter. Lanthanum oxide sample highly pure manufactured by IPEN. The solution of lanthanum oxide was prepared by dissolving their pure oxide.

2.2. Sample preparation

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

2.3. Instrumentation

The liquid chromatograph (HPLC) used in this work was Shimadzu, model LC10Ai (Tokyo, Japan). A Shimadzu module (post-column reagent) was used to transfer the Arsenazo III. For the quantification of the REE elements an inductively coupled plasma (sector field) mass spectrometer, *Element*, from Finnigan MAT (Bremen, Germany) was used.

2.4. Operational parameters

Operating conditions and settings are shown in Tables 1 and 2.

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 laurylsulphonate 0.01 mol l^{-1}, pH 2.9 was used as phase modifier. Both samples and standards were filtered through a 0.2-μm porous membrane. For each determination the injected volume was 100 μl. Lactic acid (0.7 mol l^{-1}) pH 2.9, was ascertained with sodium hydroxide.

Table 1
HPLC Shimadzu operating conditions

Reverse phase	Shim-pack CLC-ODS(M)
Mobile phase	0.7 M lactic acid, pH 2.9
Modifier	0.01 M sodium lauryl sulphonate
Column temperature	50 °C
Sample volume	100 μl
Mobil phase flow	1.0 ml min^{-1}
Colorimetric Reagent	Arsenazo III, 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)

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).

3. Results and discussion

The detection limits were determined according to the International Union of Pure and Applied Chemistry (IUPAC) recommendation (3σ criterion) [16]. Nitric acid (0.14 mol l^{-1}) was used as the blank 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} La solution that was submitted to various dilutions (dilution factor 1-, 10-, 100-, 1000- and 10 000-fold), with 1% Suprapur nitric acid. The multielemental rare earth solution was spiked with a 10 ng ml^{-1} concentration. For most of these isotopes, no expressive signal suppression was observed with 100- and 1000-fold of the original lanthanum solution (1000 μg ml^{-1}), as can be observed in Fig. 1.

A recovery test was done by making measurement of four spiked rare earth standard solutions in the matrix, with 1, 5, 10 and 20 ng ml^{-1}. A lanthanum oxide aliquot was spiked with the standards. They were estimated from a separate standard addition experiment. Five independent

Table 2
ICP–MS operating conditions: plasma conditions and mass spectrometer settings

Plasma power	1300 W
Cooling 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

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

Element	Detection limits (3σ) (pg ml^{-1})
Sc	12.3
Y	11.8
Ce	0.5
Pr	0.8
Nd	2.4
Sm	4.5
Gd	2.6
Tb	2.9
Dy	3.7
Ho	3.8
Er	1.9
Tm	2.3
Yb	3.6
Lu	4.1

determinations were made for each REE. The percentage recovery ranged from 85 to 99%, which shows that the method is adequate for analytical applications (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.

3.1. Quantification

The quantification of the samples and standards was accomplished with the help of a calibration curve constructed in accordance with certified standard solutions as SPEX, in the 0.1–10 ng ml^{-1} range, presented $r^2=0.99$ for the majority of the elements analyzed.

The values of RE traces found as impurities in the lanthanum oxide manufactured by IPEN are in Table 5.

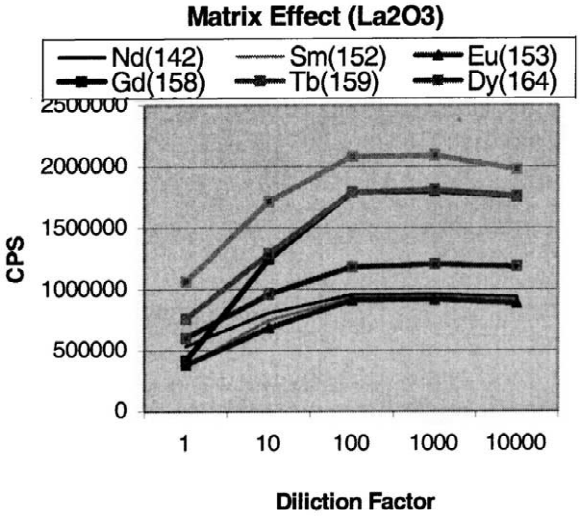

Fig. 1. Matrix effect for the rare earths solution.

Table 4
Recovery (%) of rare earth, thorium and uranium from four spiked rare earth standard solutions in the matrix

Element	Spiked rare earth standard solutions (ng ml^{-1})			
	1	5	10	20
Ce	84.15	86.35	86.22	90.41
Pr	84.14	81.64	89.17	91.10
Nd	86.98	87.98	96.30	97.10
Sm	86.90	89.58	89.94	95.18
Eu	89.89	91.43	97.83	96.89
Gd	87.79	89.98	88.52	99.20
Ho	84.29	91.58	92.68	96.87
Yb	84.96	91.97	92.98	91.36
Lu	85.36	88.48	89.14	92.01
Th	85.69	88.67	91.10	98.88
U	88.97	89.12	85.85	91.19

The figure allowed to conclude that a reproducibility of 5% was achieved.

In Table 6 the results of the contaminants found in a certified lanthanum oxide standard are presented (Johnson Matthey Chemical–JMC).

The values of the analysis by the procedures here described are in accordance with the procedures with separation of the matrix, except for the isotope ^{140}Ce, which suffered the spectral interference of the ^{139}LaH species.

4. Conclusions

In this work an analytical methodology for the quantification of RE trace elements as impurities in a highly pure RE oxide was used. It was applied the separation of the trace elements as impurities from the matrix oxide by using the HPLC technique with a reverse phase column, with sodium lauryl sulphonate as modifier. The impurities were then analyzed by double focusing ICP–MS. The

Table 5
Concentration of impurities determined in lanthanum oxide (IPEN)

Element	Concentration (μg g^{-1})	R.S.D. (%, $n=5$)
Sc	18.2	1.88
Y	20.2	1.98
Ce	6.75	2.31
Pr	26.1	4.69
Nd	3.31	3.84
Sm	18.3	2.61
Eu	17.0	3.67
Gd	19.4	3.78
Tb	16.3	3.98
Dy	16.9	2.75
Ho	17.9	3.96
Er	18.4	3.18
Tm	16.9	2.88
Yb	17.6	2.34
Lu	17.7	3.27

Table 6
Concentration of rare earth impurities analyzed in a certified JMC lanthanum oxide

Element	Concentration ($\mu g\ g^{-1}$)	R.S.D. (%, $n=5$)
Sc	7.32	1.28
Y	11.2	1.68
Ce	6.15	1.31
Pr	17.2	3.39
Nd	3.11	2.74
Sm	17.6	3.51
Eu	16.1	2.67
Gd	12.7	2.78
Tb	16.8	2.58
Dy	15.9	3.55
Ho	8.67	2.56
Er	9.58	2.81
Tm	7.94	3.31
Yb	14.7	1.34
Lu	16.3	4.27

usage of the HPLC technique for the separation and concentration of traces of RE elements conjugated with the ICP–MS, 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.

Further work will be carried out on the characterization of other RE oxides of high purity manufactured by IPEN/CNEN (São Paulo, Brazil).

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