

Quantification of trace amounts of rare earth elements in high purity gadolinium oxide by sector field inductively coupled plasma mass spectrometry (ICP-MS)

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Abstract

In recent years, rare earth elements (REEs) have received much attention in the fields of geochemistry and industry. Gadolinium oxide is used for many different high technology applications such as infrared absorbing automotive glass, petroleum cracking catalyst, gadolinium–yttrium garnets, microwave applications, and color TV tube phosphors. It can also be used in optical glass manufacturing and in the electronic industry. Rapid and accurate determinations of the rare earth elements are increasingly required as industrial demands expand. In general, the inductively coupled plasma mass spectrometry (ICP-MS) presents some advantages for trace element analysis, due to high sensitivity and resolution, when compared with other analytical techniques. In this work, sector field inductively coupled plasma mass spectrometry was used. Sixteen elements (Sc, Y, and 14 lanthanides) were determined selectively with the ICP-MS system using a concentration gradient method. The detection limits with the ICP-MS system were about 0.2–8 pg ml⁻¹. The recovery percentage ranged from 95 to 100% for different rare earth elements. The %R.S.D. of the methods varying between 1.5 and 2.5% 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 high pure gadolinium oxides samples (IPEN and JMC) was performed. IPEN's material is highly pure (>99.99%) and was successfully analyzed without spectral interference.

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1. Introduction

Gadolinium oxide is used for many different high technology applications such as infrared absorbing automotive glass, petroleum cracking catalyst, gadolinium–yttrium garnets, used in microwave applications, and color TV tube phosphors. It can also be used in optical glass manufacturing and in the electronic industry. Several analytical techniques have been used for the quantification of rare earth element (REE) as impurities in high purity materials [1–6]. Stijfhoorn et al. [7] and Zang et al. [9] evaluated the spectral interference of REEs in high purity europium, yttrium, and scandium oxide analyzed by inductively coupled plasma mass spectrometry (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, such as high costs, low throughput, and interelement interference.

Inductively coupled plasma mass spectrometry is the most powerful analytical tool in the quantification of these impurities. Pedreira et al. [18] made use of the ICP-MS technique for the assay of the REEs in highly pure praseodymium oxide.

In general, 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 REEs there are some problems associated with the matrix, such as signal suppression, formation of polyatomic ions (MO⁺, MOH⁺) and double charge ions (M⁺⁺), generated in the plasma interfering in the quantification of the isotopes of interest [10]. Such problems can be overcome by using high dilution procedures and separation of the matrix by ion exchange chromatography, liquid chromatography, and solvent extraction [3,5,8].

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In this paper, an analytical method was developed for the determination of the rare earth trace elements in a highly pure gadolinium oxide, used as ICP-MS spectrochemical standards.

2. Reagents

Rare earth oxides standards were obtained from Merck, Darmstadt, Germany Chemical, Metuchen, NJ and Johnson Matthey Company (JMC), batch no. P. 3129B, Ward Hill, USA. Suprapur nitric acid (HNO₃) from Merck. The highly pure gadolinium oxide was manufactured by IPEN. The solution of gadolinium oxide was prepared by dissolving its pure oxide.

3. Sample preparation

Five samples of gadolinium oxide (100 mg) were weighed and dissolved with 10 ml 50% (v/v) suprapur nitric acid at 50 °C for 30 min. After dissolved, the REEs solutions were diluted up to 100 ml with 1% nitric acid (HNO₃). 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 standards solutions were diluted by a factor of 1000.

4. Instrumentation

For the quantification of the REEs an inductively coupled plasma (sector field) mass spectrometer, element, from Finningan MAT (Bremen, Germany) was used (Table 1).

5. 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 val-

Table 2

Detection limits determined by applying the 3σ criterion [15] to the REE on the results of 10 consecutive measurements of a 1% HNO₃ blank solution

Elements	Detection limits (3σ) (pg ml ⁻¹)
Sc	10.3
Y	9.8
La	0.5
Ce	0.8
Pr	4.4
Sm	3.5
Nd	1.6
Tb	3.9
Dy	3.7
Ho	3.8
Er	2.9
Tm	3.3
Yb	4.6
Lu	3.1
Th	0.7
U	0.5

ues for the REEs were measured and are shown in Table 2.

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 the 100- and 1000-fold of the original gadolinium 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 gadolinium oxide aliquot was spiked with the standards. The gadolinium matrix was added to rare earth solution. They were estimated from a separate standard addition experiment. Five independent determinations were made for each REE. The percentage recovery ranged from 90 to 100%, which shows that the method is adequate for analytical applications (see Table 3).

Table 1
ICP-MS operating conditions

Plasma power (W)	1300
Cooling gas flow (l min ⁻¹)	15
Auxiliary gas flow (l min ⁻¹)	0.90
Nebulizer gas flow (l min ⁻¹)	1.20
Nebulizer	Meinhard
Spray chamber	Scott type
Sample orifice, Pt (mm)	1.0
Conical skimmer orifice, Pt (mm)	0.75
Resolution	300
Points per peak	20
Scan mode	E-scan

Plasma conditions and mass spectrometer setting.

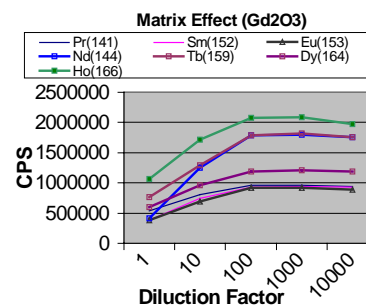


Fig. 1. Matrix effect for the rare earth solution.

Table 3
Recovery of rare earth elements, thorium, and uranium

Elements	1 ppb (%)	5 ppb (%)	10 ppb (%)	20 ppb (%)
La	99.15	96.35	97.22	96.41
Ce	99.14	96.64	98.17	96.10
Pr	97.98	97.98	97.30	97.10
Sm	96.90	99.58	95.94	95.18
Eu	95.89	97.43	97.83	96.89
Nd	98.79	99.98	98.52	99.20
Ho	99.29	96.58	95.68	96.87
Yb	96.96	95.97	95.98	96.36
Lu	96.36	95.48	95.14	96.01
Th	96.69	96.67	96.10	98.88
U	97.97	96.12	95.85	96.19

6. The quantification

Recently, the coupling of liquid chromatograph [13,14] with mass spectrometer technique (HPLC-ICP-MS) has been used for the characterization of radioactive materials and fission products, as well as the REEs [11,12].

This work investigates the use of an HPLC-method for the determination of REE impurities in rare earth oxides based upon the work of Cassidy [17]. The results obtained using the HPLC-method were compared with results obtained using HR ICP-MS only. The monoisotopic 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 of these elements in the mass spectra with the intensities of other REE isotopes with a similar ionization potential and evaporation temperature. A calibration curve ranging from 0.1 to 10 ng ml⁻¹ was constructed for the quantification of the REEs. The quantification of the samples and standards was accomplished with the help of a calibration curve constructed in accordance with certified standards solutions as Merck, in the 0.1–10 ng ml⁻¹ range, presented $r^2 = 0.999$ for the major of the elements analyzed.

The values of REEs found as impurities in the gadolinium oxide manufactured by IPEN are in Table 4. Reproducibility of 4.5% was achieved. In Table 5, are the results of the contaminants found in a certified gadolinium oxide standard (Johnson Matthey Chemical).

The values of the analysis using the procedures described here are in accordance with the procedures with separation of the matrix, except for the isotope ¹⁷⁵Lu, which suffered spectral interference of the ¹⁵⁸GdOH species.

An analytical methodology for the quantification of REE traces as impurities in a highly pure REE oxide by double focusing ICP-MS was used. The results obtained using the HPLC-method were compared with results obtained using HR ICP-MS only.

In any case, the use of the HPLC technique for the separation and concentration of traces of REEs combined with ICP-MS, enabled the determination of low amounts of RE impurities in the high purity REE oxide materials.

Table 4
Impurities determined in gadolinium oxide produced at IPEN

Elements	Samples ^a	Certificate
Sc	4.23 ± 0.09	3.89 ± 0.03
Y	1.40 ± 0.03	2.37 ± 0.02
La	7.75 ± 0.26	4.98 ± 0.08
Ce	6.21 ± 0.23	7.99 ± 0.12
Pr	5.31 ± 0.15	5.85 ± 0.15
Nd	2.45 ± 0.05	11.9 ± 0.33
Sm	7.34 ± 0.19	11.6 ± 0.41
Eu	8.21 ± 0.38	6.45 ± 0.11
Tb	10.3 ± 0.31	14.9 ± 0.39
Dy	6.92 ± 0.26	15.7 ± 0.66
Ho	7.49 ± 0.37	8.85 ± 0.28
Er	6.44 ± 0.14	7.12 ± 0.39
Tm	3.04 ± 0.06	2.15 ± 0.08
Yb	4.53 ± 0.15	3.86 ± 0.07
Lu	15.7 ± 0.67	8.22 ± 0.31

^a (μg g⁻¹) ± σ (standard deviation calculated for $n = 5$).

Table 5
Rare earth impurities analyzed in a certified Johnson Matthey Company gadolinium oxide

Elements	Standard ^a	Certificate
Sc	3.67 ± 0.09	3.89 ± 0.03
Y	2.28 ± 0.06	2.37 ± 0.02
La	5.15 ± 0.17	4.98 ± 0.08
Ce	7.32 ± 0.25	7.99 ± 0.12
Pr	5.38 ± 0.20	5.85 ± 0.15
Nd	12.3 ± 0.46	11.9 ± 0.33
Sm	12.6 ± 0.57	11.6 ± 0.41
Eu	7.15 ± 0.26	6.45 ± 0.11
Tb	15.8 ± 0.57	14.9 ± 0.39
Dy	16.4 ± 0.75	15.7 ± 0.66
Ho	8.76 ± 0.31	8.85 ± 0.28
Er	6.92 ± 0.26	7.12 ± 0.39
Tm	1.94 ± 0.04	2.15 ± 0.08
Yb	4.73 ± 0.11	3.86 ± 0.07
Lu	7.35 ± 0.24	8.22 ± 0.31

^a (μg g⁻¹) ± σ (standard deviation calculated for $n = 5$).

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 highly purity manufactured by IPEN, S. Paulo, Brazil.

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