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# Determination of trace amounts of rare earth elements in highly pure praseodymium oxide by double focusing inductively coupled plasma mass spectrometry and high-performance liquid chromatography

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## Abstract

An analytical method for the determination of traces of rare earth elements (REE) as impurities in highly pure praseodymium oxide ($Pr_6O_{11}$) produced at the Instituto de Pesquisas Energéticas e Nucleares (IPEN) and a comparison with commercial praseodymium oxide as a certified reference is reported. REE as impurities in praseodymium oxide were separated from the matrix by high-performance liquid chromatography (HPLC). The separated individual fractions containing REE trace impurities were analyzed directly by inductively coupled plasma sector field mass spectrometry (HR ICP-MS). The percentage recovery ranged from 85 to 100% for different rare earth elements. The mean RSD of the method varied between 3 and 5% for a set of five replicates for the IPEN material and for the certified reference sample. Both materials were found to be highly pure (>99.9%).

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

## 1. Introduction

Due to modern applications in the field of new materials and recent technological progress, more and more high-purity rare earth oxides are being demanded. Praseodymium oxide is used in semiconductor materials, advanced ceramic materials and special metallic alloys.

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

Determination via neutron activation analysis is an analytical technique widely used for the determination of REE [5,6], but even this powerful method has several problems, such as high cost, low throughput and inter-element interference.

Inductively coupled plasma mass spectrometry (ICP-MS) is the most powerful analytical tool for the quantification of impurities. Zhang et al. [9] used ICP-MS for the assay of RE elements in highly pure europium oxide. In general, inductively coupled plasma mass spectrometry presents some advantages for element trace analysis, due to its high sensitivity, selectivity and low detection limits, when compared with other analytical techniques.

However, in the case of rare earths there are problems associated with the matrix, such as signal suppression, the formation of polyatomic ions ($MO^+$, $MOH^+$) and doubly charge ions ($M^{2+}$) generated in the plasma, which interfere in the quantification of the isotopes of interest [10]. Such problems can be overcome by using procedures that allow separation of the matrix, such as ion-exchange chromatography, liquid chromatography and solvent extraction [3,5]. In this paper, an analytical method is reported for the separation and determination of several rare earth trace elements in highly pure praseodymium oxide, used as a spectrochemical standard, by HPLC and ICP-MS-associated techniques.

## 2. Reagents

Rare earth oxides as standards were supplied by SPEX Chemical (Metuchen, NJ, USA) and Johnson Matthey (Ward Hill, USA). Suprapur nitric acid was from Merck

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(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. Standards and sample solutions were prepared with purified water from a Milli-Q Water unit (Millipore, 18.2 MΩ) and filtered through a 0.2 μm membrane filter. Praseodymium oxide of high purity was manufactured by IPEN. Praseodymium oxide solution was prepared by dissolving the pure oxide.

## 3. Sample preparation

Five samples of praseodymium oxide (100 mg) were weighed and dissolved in 10 ml 50% (v/v) Suprapur nitric acid and heated at 50°C for 30 min. After dissolution, the RE solutions were diluted to 100 ml with 1% nitric acid. Therefore, the sample had a concentration of 1000 μg $ml^{-1}$. Oxides used as standards were treated using the same procedure. Samples and certified standard solutions were then diluted by a factor of 1000.

## 4. Instrumentation

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

## 5. Operational parameters

The HPLC and ICP-MS operating conditions 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, reversed-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 M), pH 2.9, was ascertained with sodium hydroxide.

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

Table 1
Shimadzu HPLC operating conditions

| | |
|---|---|
| Reverse phase | Shim-pack CLC-ODS(M) |
| Mobil 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) |

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 |

## 6. Results and discussion

The detection limits were determined according to the International Union of Pure and Applied Chemistry (IUPAC) recommendation (3$\sigma$ criterion) [16]. Nitric acid (0.14 mol $l^{-1}$) was used as the blank solution. The measured values for the RE elements are shown in Table 3.

The matrix effect was studied by using a 1000 mg $l^{-1}$ Pr solution that was submitted to various dilutions (dilution factors 1-, 10-, 100-, 1000- and 10 000-fold) with 1%

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

| | Detection limit (3$\sigma$) (pg $ml^{-1}$) |
|---|---|
| Sc | 12.3 |
| Y | 11.8 |
| La | 0.5 |
| Ce | 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 |

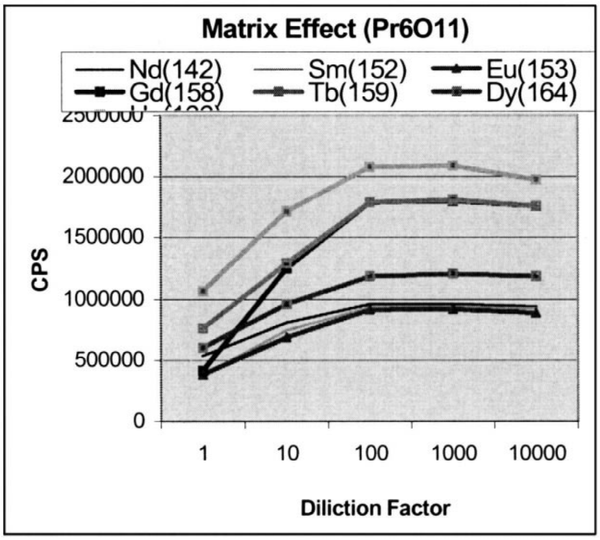

Fig. 1. Matrix effect for rare earth solutions.

Suprapur nitric acid. The multi-elemental rare earth solutions were spiked at a 10 ng ml$^{-1}$ concentration. For most of these isotopes, no signal suppression was observed with the 100- and 1000-fold dilutions of the original praseodymium solution (1000 μg ml$^{-1}$), as can be observed in Fig. 1.

A recovery test was performed by taking measurements of four spiked rare earth standard solutions in the matrix with 1, 5, 10 and 20 ng ml$^{-1}$. A praseodymium oxide aliquot was spiked with the standards. The praseodymium matrix was added to the 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 85 to 99%, which shows that the method is adequate for analytical applications (see Table 4).

Recently, the coupling of liquid chromatography with mass spectrometry (HPLC–ICP-MS) was used for the characterization of radioactive materials and fission products, as well as RE [11,12] elements.

Table 4
Recovery of rare earth, thorium and uranium

| | 1 ppb (%) | 5 ppb (%) | 10 ppb (%) | 20 ppb (%) |
|---|---|---|---|---|
| La | 84.15 | 86.35 | 86.22 | 90.41 |
| Ce | 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 |

## 7. Quantification

Quantification of the samples and standards was accomplished with the help of a calibration curve constructed in accordance with certified standard solutions such as Spex in the 0.1 to 10 ng ml$^{-1}$ range; $r^2 = 0.99$ for the majority of the elements analyzed.

The concentrations of RE traces found as impurities in the praseodymium oxide manufactured by IPEN are shown in Table 5. The data allow us to conclude that a reproducibility of 5% was achieved.

Table 6 shows the results for contaminants found in a certified praseodymium oxide standard (Johnson Matthey Chemical, JMC).

The values obtained using the described procedures are in accordance with those obtained using procedures with separation of the matrix, except for the isotope $^{142}$Nd, which suffered from spectral interference from $^{141}$PrH species.

## 8. Conclusions

In this work an analytical methodology for the quantification of RE trace elements as impurities in a highly pure RE oxide was reported. It was applied to the separation of trace elements as impurities from a matrix oxide using HPLC with a reversed-phase column, with sodium lauryl sulphonate as modifier. The impurities were then analyzed by double focusing ICP-MS. The use of HPLC for the separation and concentration of traces of RE elements

Table 5
Impurities determined in praseodymium oxide (IPEN)[a]

| Element | (μg g$^{-1}$) | RSD (%) |
|---|---|---|
| Sc | 18.2 | 1.88 |
| Y | 20.2 | 1.98 |
| La | 6.75 | 2.31 |
| Ce | 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 |

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

Table 6
Rare earth impurities analyzed in a certified JMC praseodymium oxide[a]

| Element | ($\mu$g g$^{-1}$) | RSD (%) |
|---|---|---|
| Sc | 7.32 | 1.28 |
| Y | 11.2 | 1.68 |
| La | 6.15 | 1.31 |
| Ce | 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 |

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

combined with ICP-MS enabled the determination of small amounts of RE impurities in the high-purity oxide materials. A high sensitivity was obtained through a combination of separation and pre-concentration, using HPLC, in the determination of REE as impurities by HR ICP-MS, giving a profile of the oxide quality.

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

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