

Trace amounts of rare earth elements in high purity samarium oxide by sector field inductively coupled plasma mass spectrometry after separation by HPLC

W.R. Pedreira^{b,c,*}, C.A. Queiroz^a, A. Abrão^a, S.M. Rocha^a,
M.E. de Vasconcellos^a, G.R. Boaventura^b, M.M. Pimentel^b

^a Instituto de Pesquisas Energéticas e Nucleares (IPEN/CNEN-SP), 05508-900 São Paulo, SP, Brazil

^b Instituto de Geociências, Universidade de Brasília (UnB), 70910-900 Brasília, DF, Brazil

^c Fundação Jorge Duprat Figueiredo de Segurança e Medicina do Trabalho (FUNDACENTRO), 05409-002 São Paulo, SP, Brazil

Received 26 April 2005; received in revised form 9 August 2005; accepted 17 October 2005

Available online 25 January 2006

Abstract

Today there is an increasing need for high purity rare earth compounds in various fields, the optical, the electronics, the ceramic, the nuclear and geochemistry. Samarium oxide has special uses in glass, phosphors, lasers and thermoelectric devices. Calcium chloride crystals treated with samarium have been employed in lasers, which produce light beams intense enough to burn metal. 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 such as ICP optical emission spectrometry (ICP-OES). 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 (La) pg mL^{-1} to 8 (Gd) pg mL^{-1} . The %R.S.D. of the methods varying between 0.9 and 1.5% 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 samarium oxides samples (IPEN and JMC) was performed. IPEN's material is highly pure (>99.99%) and was successfully analyzed without spectral interference (MO^+ and MOH^+).

© 2006 Published by Elsevier B.V.

Keywords: Rare earth elements; Inductively coupled plasma mass spectrometry; Samarium oxide

1. Introduction

Samarium oxide is used for different technology applications such as lasers, phosphors, magnets, thermoelectric devices production and other purposes. Calcium chloride crystals treated with samarium have been employed in lasers that produce light beams intense enough to burn metal. It can also be used in optical glass manufacturing and in the electronic industry. Quality control of high purity rare earth compounds requires high standards of analytical chemistry in the concentration range down to 10^{-9} g g^{-1} . Several analytical techniques have been used for the quantification of REE as impurities in high purity materials [1–6]. Stijfhoorn et al. [7] and Zhang et al. [9] evaluated the

spectral interference of REEs in high purity europium, yttrium and scandium oxide 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, such as high costs, low throughput and interelement interference.

Inductively coupled plasma mass spectrometry (ICP-MS) is the most powerful analytical tool in the quantification of these impurities [15]. Pedreira et al. [18] used 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, polyatomic ions formation (MO^+ and MOH^+) and doubly charged ions (M^{++}), generated in the

* Corresponding author.

E-mail address: walter.pedreira@fundacentro.gov.br (W.R. Pedreira).

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 [3,5,8,19].

An analytical method was developed for the determination of the rare earth trace elements in a highly pure samarium oxide, used as ICP-MS spectrochemical standards.

2. Experimental

2.1. Reagents

Rare earth oxides standards and SupraPur nitric acid (HNO_3) were obtained from Merck, Darmstadt, Germany Chemical, Metuchen, N.J. and Johnson Matthey Company (JMC, Batch No. P. 3129B, Ward Hill, USA). The highly pure samarium oxide was manufactured by IPEN. The solution of samarium oxide was prepared by dissolving the pure oxide.

2.2. Sample preparation

Five samples of samarium 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 2% nitric acid (HNO_3). Therefore, the sample described has a concentration of 1000 $\mu\text{g mL}^{-1}$. Oxides used as standards went through the same procedure. Then, samples and certified standards solutions were diluted by a factor of 1000.

2.3. Instrumentation

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

3. Results and discussion

The matrix effect was studied by using a 1000 mg L^{-1} of the samarium solution that was submitted to various dilutions (dilution factor 1-, 10-, 100-, 1000- and 10,000-fold), with 2% 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 samarium solution (1000 $\mu\text{g mL}^{-1}$), as can be observed in Fig. 1.

The detection limits were determined according to the International Union of Pure and Applied Chemistry (IUPAC) recom-

Table 1
SF ICP-MS operating conditions

Plasma power	1.250 kW
Cooling gas flow	14 L min^{-1}
Auxiliary gas flow	0.85 L min^{-1}
Nebulizer gas flow	0.91 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	30
Scan mode	E-scan and B-scan

Plasma conditions and mass spectrometer settings.

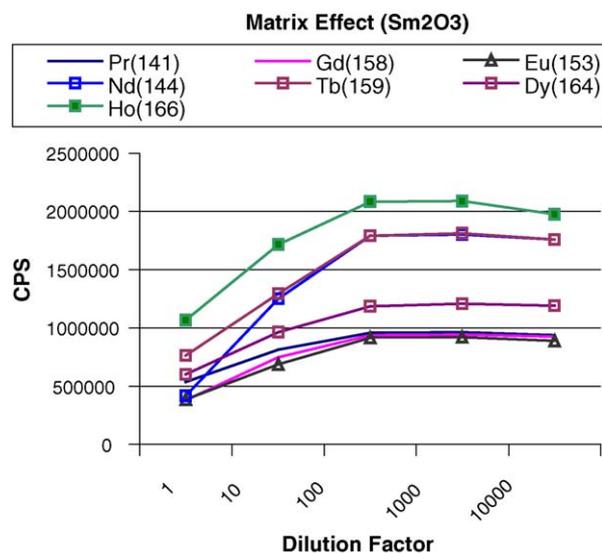


Fig. 1. Matrix effect for the rare earth solution.

mendation (3σ criterion) [16]. Nitric acid (0.14 mol L^{-1}) was used as the blank solution. The values for the REEs were measured and are shown in Table 2.

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 samarium oxide aliquot was spiked with the standards. The samarium matrix was added to rare earth solution. Five independent determinations were made for each REE, they were estimated from a separate standard addition experiment. The recovery percentage ranged from 99 to 102%, which shows that the method is adequate for analytical applications (see Table 3). The results illustrated in Table 3 showed good agreements with data available for Panday et al. [20].

Table 2
Detection limits determined by applying the 3σ criterion [16] to the REE on the results of 10 consecutive measurements of a 2% HNO_3 blank solution

Elements	(pg mL^{-1})
Sc	7.3
Y	9.8
La	0.2
Ce	0.9
Pr	2.4
Gd	8.0
Nd	2.3
Tb	2.4
Dy	2.5
Ho	1.9
Er	3.1
Tm	3.0
Yb	3.6
Lu	2.1
Th	1.2
U	0.7

Table 3
Recovery of rare earth elements, thorium and uranium (%)

	1 ppb	5 ppb	10 ppb	20 ppb
La	99.15	99.35	99.22	99.41
Ce	99.14	99.64	99.17	99.10
Pr	99.98	102.9	99.30	101.1
Gd	102.0	100.8	100.4	99.18
Eu	99.89	101.3	99.83	99.89
Nd	99.79	99.98	100.5	99.10
Ho	99.31	99.58	99.68	100.7
Yb	99.96	100.7	100.1	100.2
Lu	99.22	101.8	99.14	99.01
Th	99.69	99.67	99.10	99.88
U	99.97	100.1	99.85	99.19

4. The quantification

The coupling of liquid chromatography [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 was compared with results obtained using ICP–MS only. The monoisotopic elements Pr, Tb, Ho and Tm, as well as La, could not be analyzed by isotope dilution, but a semi-quantitative 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.

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 samarium oxide manufactured by IPEN are in Table 4. Reproducibility of 3.2% was achieved. In Table 5, the results of the contaminants

Table 4
Impurities determined in samarium oxide produced at IPEN

Elements	Samples ^a	Certificate
Sc	5.23 ± 0.09	5.89 ± 0.03
Y	3.40 ± 0.03	3.37 ± 0.02
La	3.75 ± 0.26	3.79 ± 0.08
Ce	6.88 ± 0.23	7.91 ± 0.12
Pr	5.01 ± 0.15	4.85 ± 0.15
Nd	11.2 ± 0.05	10.9 ± 0.33
Gd	11.7 ± 0.19	12.6 ± 0.41
Eu	7.21 ± 0.38	7.45 ± 0.11
Tb	12.8 ± 0.31	13.9 ± 0.39
Dy	13.9 ± 0.26	14.7 ± 0.66
Ho	7.54 ± 0.37	7.95 ± 0.28
Er	7.12 ± 0.14	6.97 ± 0.39
Tm	1.09 ± 0.06	1.15 ± 0.08
Yb	4.88 ± 0.15	4.86 ± 0.07
Lu	7.7 ± 0.67	7.92 ± 0.31

^a ($\mu\text{g g}^{-1}$) ± σ (standard deviation calculated for $n = 5$).

Table 5
Rare earth impurities analyzed in a certified Johnson Matthey Company (JMC) samarium oxide

Elements	Standard ^a	Certificate
Sc	4.99 ± 0.09	5.89 ± 0.03
Y	3.98 ± 0.06	3.37 ± 0.02
La	4.22 ± 0.17	3.79 ± 0.08
Ce	8.44 ± 0.25	7.91 ± 0.12
Pr	4.09 ± 0.20	4.85 ± 0.15
Nd	11.3 ± 0.46	10.9 ± 0.33
Gd	13.6 ± 0.57	12.6 ± 0.41
Eu	8.15 ± 0.26	7.45 ± 0.11
Tb	14.1 ± 0.57	13.9 ± 0.39
Dy	15.4 ± 0.75	14.7 ± 0.66
Ho	8.99 ± 0.31	7.95 ± 0.28
Er	7.12 ± 0.26	6.97 ± 0.39
Tm	0.99 ± 0.04	1.15 ± 0.08
Yb	5.83 ± 0.11	4.86 ± 0.07
Lu	8.01 ± 0.24	7.92 ± 0.31

^a ($\mu\text{g g}^{-1}$) ± σ (standard deviation calculated for $n = 5$).

found in a certified samarium 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 ¹⁶⁹Tm, which suffered spectral interference of the ¹⁵²SmOH species.

5. Conclusions

A new 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 sample was compared with results obtained using certified Johnson Matthey Company.

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.

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 SF 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.

Acknowledgements

IPEN, CNPq, FINATEC and UnB for research grants.

References

- [1] V.K. Panday, J.S. Becker, J.-J. Dietze, Fresenius J. Anal. Chem. 352 (1995) 327–332.
- [2] L.C. Reino, A. Lordello, Publ. IPEN 317 (1990) 3–6.
- [3] B. Li, Y. Zhang, M. Yin, Analyst 122 (1997) 543–548.
- [4] J.M. Hwang, J.S. Shih, Y.C. Yeh, S.C. Wu, Analyst 106 (1981) 869–874.
- [5] K. Yoshida, H. Haraguchi, Anal. Chem. 56 (1984) 2580–2584.

- [6] N. Vansuc, H.B. Desai, R. Parthasarathy, S. Gangadharan, J. Radioanal. Nucl. Chem. Lett. 164 (1992) 321–325.
- [7] D.E. Stijfhoorn, H. Stray, H. Hjelmseth, Spectrochim. Acta 48B (1993) 507–512.
- [8] N. Daskalova, S. Velichkov, N. Krasnobaeva, P. Slavova, Spectrochim. Acta 47 (1992) E1595–E1599.
- [9] S.X. Zhang, S. Murachi, T. Imasaka, M. Watanabe, Anal. Chim. Acta 314 (1995) 193–199.
- [10] Y. Takaku, K. Masuda, T. Takashashi, T. Shimamura, J. Anal. At. Spectrom. 8 (1993) 687–691.
- [11] W. Kerl, J.S. Becker, W. Dannecker, H.-J. Dietze, Fresenius J. Anal. Chem. 362 (1998) 433–438.
- [12] I.G. Alonso, F. Sena, P. Arbore, M. Betti, L. Koch, J. Anal. At. Spectrom. 10 (1995) 381–386.
- [13] N.M.P. Moraes, H.M. Shihomatsu, J. Chromatogr. A 679 (1994) 387–392.
- [14] N.M.P. Moraes, H.M. Shihomatsu, L.B. Zinner, P. Miranda Jr, J. Alloys Compd. 249 (1997) 133–139.
- [15] G.L. Long, J.D. Winefordner, Anal. Chem. 55 (1983) 712A–719A.
- [16] Analytical Methods Committee, Recommendations for the definition, estimation and ISE of the detection limit, Analyst 112 (1987) 199–205.
- [17] R.M. Cassidy, Chem. Geol. 67 (1988) 185–192.
- [18] W.R. Pedreira, A. Abrao, C.A. Queiroz, J. Alloys Compd. 323–324 (2001) 49–52.
- [19] X. Cao, M. Yin, B. Li, Talanta 48 (1999) 517–525.
- [20] V.K. Panday, J.S. Becker, H.-J. Dietze, Fresenius J. Anal. Chem. 334 (1995) 327–334.