



Isotopic and chemical analysis of gadolinium oxide nuclear grade



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ABSTRACT

Natural gadolinium oxide is added in nuclear fuels of compact design reactors to control the power mainly on the start of operation, as neutronic poison. Gadolinium has a high neutron absorption cross section (σ_{γ}). All Gd isotopes have significant σ_{γ} , specially 155 and 157 (60,900 and 254,000 b (10^{-24} cm²), respectively). It is important the isotopic and chemistry purity of the nuclear fuels materials to avoid the generation of unwished radioactive elements or extra neutron poisons. Main possible impurities that could be presented are the rest of Rare Earths (REEs) like Eu, Sm, Tb, Yb, and Dy. The objective of the present contribution was to develop methods for the certification of isotopic composition in natural nuclear grade Gd₂O₃ and also to determine the content of REE impurities. Two methodologies were explored for isotopic analysis by Thermal Ionization Mass Spectrometry (TIMS): Total Evaporation (TE) and Conventional Analysis (CA). Results are comparable with both methodologies, although CA uncertainties are better. The analysis of impurities was performed with a Quadrupole Inductively Coupled Plasma Mass Spectrometer (Q-ICPMS). Concentration of different REEs is in agreement with certificate of supplier and nuclear specifications.

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1. Introduction

The effective neutron cross section (σ_{γ}) of a nuclide is the probability that an incident neutron interact with the nucleus, being removed from the neutron flux and absorbed by the nucleus. Nuclides with high σ_{γ} are called neutron absorbers.

Gadolinium is the natural element with higher integrated neutron capture section. For the operation of nuclear reactors, it is also called *neutron poison*. Some elements with these features are deliberately added to the nuclear fuel to control the neutron flux and therefore to vary the reactor's power.

Gadolinium oxide is added as a burnable poison, i.e. as part of the fresh fuel in reactors of compact design, to control the neutron flux and the power.

Natural gadolinium has seven stable isotopes with abundances of: Gd-152: 0.20%, Gd-154: 2.18%, Gd-155: 14.80%, Gd-156: 20.47%, Gd-157: 15.65%, Gd-158: 24.84%, Gd-160: 21.86%, according with IUPAC [1].

The isotopes 155 and 157 have a σ_{γ} of 60,900 and 254,000 b (10^{-24} cm²) respectively [2].

It is important to control the isotopic composition of the raw material as well as its purity, because any unwanted elements entering the reactor core, will be bombarded by neutrons and can generate new radioactive elements or undesirable neutron poisons.

Eugster et al. reported isotopic analysis by thermal ionization mass spectrometry, loading the sample on a single filament and measuring

GdO⁺ ions [3]. Gautier et al. added colloidal carbon as surface and chemical modifier on a single filament, measuring Gd⁺ species [4]. Du-bois et al. employed the total evaporation method and triple filament assembly [5].

Inductively coupled plasma mass spectrometry has been employed to determine impurities in rare earth compounds. Zhang et al. employed internal standards to determine trace amounts in europium oxide (Cd and In for lighter REEs and Tl and Bi for heavier ones) [6], Saha et al. also employed In as internal standard to analyze gadolinium aluminate with a TOF-ICPMS [7]. Pedreira et al. used a high resolution mass spectrometer to determine impurities in gadolinium oxide [8].

2. Experimental

A thermal ionization mass spectrometer (TIMS) was used for the isotopic analysis. The instrument was a Finnigan MAT 262 (Thermo Fischer Scientific, Bremen, Germany), equipped with a turret for 13 samples, a magnetic analyzer and a multi-collector with seven Faraday cups, six of them adjustable and an ion counter for lower signals.

Samples were loaded on zone refined rhenium filaments (Rhenium Alloys, North Ridgeville, OH, USA), previously degassed at 4.5 A during 20 min).

For chemical analysis it was used an inductively coupled plasma mass spectrometer (ICPMS) Nexlon 300 X (Perkin Elmer, Shelton, CT, USA) with concentric nebulizer type Meinhard, cyclonic spray chamber refrigerated at 2 °C (Peltier), nickel sample cones and skimmer, and an aluminum hyperskimmer. A small quadrupole deflects the ion beam

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Table 1
%CV of gadolinium isotopic abundance in the Gd₂O₃ sample.

	% CV-TE	% CV – Red Dull-TE	%CV-CA
Gd-152	0.737	1.494	3.431
Gd-154	0.734	1.699	0.018
Gd-155	1.439	2.565	0.101
Gd-156	1.029	1.731	0.098
Gd-157	2.336	7.456	0.077
Gd-158	0.677	1.361	0.044
Gd-160	0.707	1.680	0.037
Average	1.094	2.569	0.544

90° and a quadrupole analyzer focus ions to an electron multiplier detector.

Analytical reagent grade HNO₃ (Biopack, Buenos Aires, Argentina) was purified in-house prior to use by sub-boiling distillation (Berghof Products, Einingen, Germany).

A multielemental solution of REEs was prepared from single element standard solutions of 1000 mg·L⁻¹, (Chem Lab NV, Zedelgem, Belgium) in 2% v/v HNO₃.

3. Analysis

For isotopic analysis, gadolinium oxide powder was dissolved in HNO₃(c), heated to dryness and re-dissolved in 1 M HNO₃, obtaining a 5.0 mg·mL⁻¹ solution.

Two different analysis methodologies were employed: conventional analysis (CA) and total evaporation (TE). For both of them, double filament assembly was used. Samples were loaded in one of the filament (evaporation filament), which is heated and expels gaseous species that are adsorbed on the surface of the other filament (ionization filament), which is heated at higher temperature. The molecules transfer electrons to the filament and ions are desorbed from the surface. In CA, a determined number of data are collected. In TE, lower quantity of sample is loaded and data are collected until all the samples are consumed, integrating signal of all atomic mass of interest. The advantages of this method arise in the fact that no mass discrimination correction must be applied, due to preferential evaporation of the lighter isotopes from the filament, because the entire sample aliquot is analyzed.

In CA, due to the absence of a certified isotopic reference material of Gd, to calculate the mass discrimination factor due to isotopic fractionation, the ¹⁵⁶Gd/¹⁶⁰Gd ratio was employed as internal standard, considering the value of 0.9364 as “normalized value” [3,4].

In the TE method, the use of reference material for such correction is not required, since it consumes the entire sample and isotopic

Table 2
Isotopic abundance of the sample, by both methods and its comparison with IUPAC representative data for Gd.

Isotope	A% IUPAC	CA	TE
		A%	A%
Gd-152	0.20	0.20 ± 0.01	0.20 ± 0.01
Gd-154	2.18	2.18 ± 0.01	2.18 ± 0.02
Gd-155	14.80	14.81 ± 0.01	14.84 ± 0.21
Gd-156	20.47	20.47 ± 0.02	20.46 ± 0.21
Gd-157	15.65	15.65 ± 0.01	15.65 ± 0.73
Gd-158	24.84	24.83 ± 0.01	24.82 ± 0.17
Gd-160	21.86	21.86 ± 0.01	21.85 ± 0.15

fractionation is compensated by averaging the total number of collected data. Besides that, it has the advantages that it uses much less amount of sample and analysis times are shorter [5]. Anyway, the correction was also held using an internal standard, so the results are subject to comparison by both methods.

For the analysis of impurities in Gd₂O₃, the elements to be determined are mainly other Rare Earths (REEs), Th and U. The accepted values and methodologies of analysis of these elements can be found in ASTM C888 and C889 respectively [9,10]. Analyses are performed by single quadrupole inductively coupled plasma mass spectrometry (Q-ICPMS). Its accuracy and detection limits are adequate for this analysis since the impurities concentrations should be within the range of the few µg·g⁻¹ (ppm) in the solid.

The challenge is to determine low concentrations of impurities in a gadolinium oxide sample, where the matrix effect is important. It is employed in the recovery of internal standard methodology as published by Zhang, et al. [6] and Saha et al. [7]. Other authors employed HR-ICPMS, diluting the matrix previously or through separation by ion chromatography coupled to the spectrometer [8].

Dissolved samples were diluted in 2%v/v HNO₃. Detection limits are from few µg·L⁻¹ to ng·L⁻¹. The ideal working range is between 0.25 and 100 µg·L⁻¹ approximately.

In ICPMS, ionization efficiency is close to 100%, the temperature of the plasma reaches the 6000–8000 K; (while in TIMS is about of 0.01% and the temperature reaches only about 2000 K), therefore ion transmission to the detector is greater; ionization of all the isotopes are instantaneous and measurement times are very short. Isotopic resolution is significantly lower than TIMS.

The optimization of the methodology is very important because this technique may be drawbacks associated with the matrix such as signal suppression, formation of polyatomic ions such as MO⁺ and MOH⁺, in addition, multicharged ions may be produced (M⁺²).

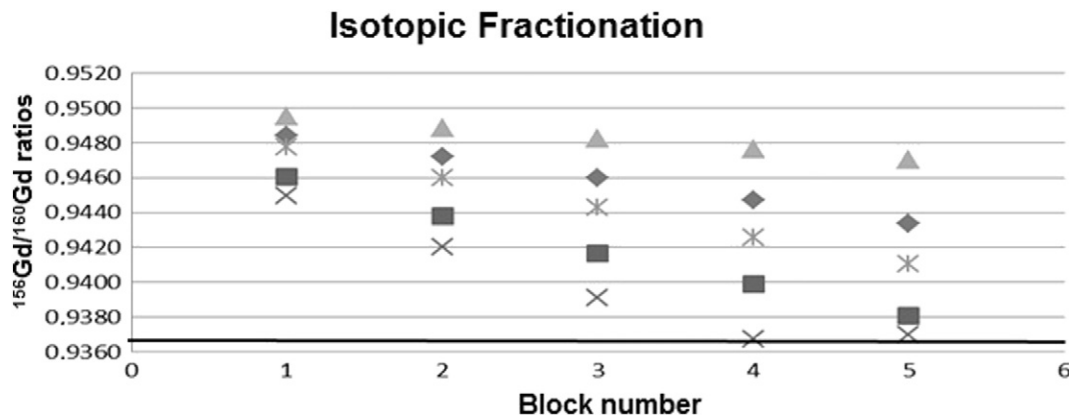


Fig. 1. Isotopic fractionation of ¹⁵⁶Gd/¹⁶⁰Gd ratios and comparison of the average of 5 replicates (dotted lines) with respect to normal value (solid line).

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