



# Determination of trace rare earth elements in gadolinium aluminate by inductively coupled plasma time of flight mass spectrometry



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## ABSTRACT

An analytical methodology was developed for the precise quantification of ten trace rare earth elements (REEs), namely, La, Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho, and Tm, in gadolinium aluminate (GdAlO<sub>3</sub>) employing an ultrasonic nebulizer (USN)-desolvating device based inductively coupled plasma mass spectrometry (ICP-MS). A microwave digestion procedure was optimized for digesting 100 mg of the refractory oxide using a mixture of sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and water (H<sub>2</sub>O) with 1400 W power, 10 min ramp and 60 min hold time. An USN-desolvating sample introduction system was employed to enhance analyte sensitivities by minimizing their oxide ion formation in the plasma. Studies on the effect of various matrix concentrations on the analyte intensities revealed that precise quantification of the analytes was possible with matrix level of 250 mg L<sup>-1</sup>. The possibility of using indium as an internal standard was explored and applied to correct for matrix effect and variation in analyte sensitivity under plasma operating conditions. Individual oxide ion formation yields were determined in matrix matched solution and employed for correcting polyatomic interferences of light REE (LREE) oxide ions on the intensities of middle and heavy rare earth elements (MREEs and HREEs). Recoveries of ≥90% were achieved for the analytes employing standard addition technique. Three real samples were analyzed for traces of REEs by the proposed method and cross validated for Eu and Nd by isotope dilution mass spectrometry (IDMS). The results show no significant difference in the values at 95% confidence level. The expanded uncertainty (coverage factor 1σ) in the determination of trace REEs in the samples were found to be between 3 and 8%. The instrument detection limits (IDLs) and the method detection limits (MDLs) for the ten REEs lie in the ranges 1–5 ng L<sup>-1</sup> and 7–64 μg kg<sup>-1</sup> respectively.

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## 1. Introduction

Gadolinium (Gd) and boron (B) are well known thermal neutron absorbers. These elements in the form of stoichiometric compounds are employed as burnable poison in nuclear reactors, as their negative reactivity decreases with time. The microscopic thermal neutron absorption cross section ( $\sigma_a$ ) of <sup>10</sup>B is 3840 b whereas the same for <sup>155</sup>Gd and <sup>157</sup>Gd are 61,000 and 254,000 b respectively. The total natural abundance of the two nuclides of Gd is higher than that of <sup>10</sup>B in boron. The use of B in reactor as neutron absorber requires enrichment of <sup>10</sup>B isotope and hence Gd offers a better choice when used as burnable poison. Gadolinium nitrate solution is being used as secondary shut down system in Pressurized Heavy Water Reactors (PHWRs) [1]. Gadolinium aluminate (GdAlO<sub>3</sub>) is used in neutron absorption control rods [2] and has been proposed as a burnable poison to be used in Compact Light Water Reactors. This highly refractory compound is stable to irradiation and undergoes minimum swelling under reactor operating conditions.

GdAlO<sub>3</sub> is synthesized by solid state mixing of gadolinia (Gd<sub>2</sub>O<sub>3</sub>) and alumina (Al<sub>2</sub>O<sub>3</sub>) powders followed by heat treatments and sintering at relatively high temperatures (1600–1700 °C) [3]. Apart from being used as a burnable poison, GdAlO<sub>3</sub> also finds application as phosphor [4–6], scintillator [3] and potential host systems for oxygen ion conducting materials [7,8].

In India Gd<sub>2</sub>O<sub>3</sub> is manufactured from monazite ore. As monazite ore is a rich source of rare earth elements (REEs), the purified Gd<sub>2</sub>O<sub>3</sub> is always accompanied by traces of other REEs. It is desirable to know the exact amount of all the other REEs to arrive at the correct estimate of microscopic neutron absorption cross section of the overall gadolinium aluminate matrix prior to its use as a burnable poison. The applicability of an analytical method requires the presence of a matrix matched certified reference material or the elimination of matrix effect. The matrix effect can be eliminated by complete removal of the matrix. The accurate and precise determination of traces of other REEs subsequent to their chemical separation from Gd matrix is a challenging task due to a similar chemical behavior of matrix and the analytes of interest and till date there is no report dealing with such work. Under such circumstances it was necessary to dilute the matrix to minimize its effect on the quantification of analytes. However dilution of the

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matrix lowers the analyte concentration to a level where only a highly sensitive multielemental technique like Inductively Coupled Plasma Mass Spectrometer (ICP-MS) can be employed. The application of other sensitive multi-elemental spectroscopic technique, viz., ICP-AES in such a case is ruled out due to complicated line rich emission spectra of the matrix. The effects of different matrix levels on analyte intensities were studied to arrive at that level of matrix concentration where the matrix effect was minimum and reproducible. It is well known that the light REEs (LREEs), in the form of their oxides, cause isobaric interferences in the middle and heavy REEs (MREEs and HREEs) under plasma operating conditions thereby restricting their precise determination by ICP-MS. Several methods have been utilized to reduce the metal oxide formation such as changes in plasma gas composition [9–11], cooling the spray chamber [12,13], changes in sampling depth [14], changes in sampler and skimmer orifice size [15] and optimization of the distance between them [16]. Many workers [17–20] have carried out mathematical corrections for isobaric interferences in the determination of REEs by ICP-MS. It has been reported [21,22] that the use of aerosol desolvating device as sample introduction system in ICP-MS enhances the analyte sensitivity as well as limits the barium (Ba) and LREEs oxide ion interferences on MREEs and HREEs. In the present work, an analytical methodology, employing an ultrasonic nebulizer (USN)-desolvating sample introduction system was used for the quantification of ten trace REEs viz., La, Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho and Tm, in GdAlO<sub>3</sub> by ICP-MS. A microwave digestion procedure was optimized for quantitative dissolution of this refractory oxide. Even though the use of desolvating sample introduction system minimizes the polyatomic isobaric interferences, the accuracy and precision of the method was enhanced by studying the individual oxide ion formation yield in matrix matched solution, for our system, and applying the interference correction equations for the quantification of the analytes. In the literature [23,24], indium (In) has been reported as an internal standard for the REEs. The feasibility of using <sup>115</sup>In as an internal standard was studied in the presence of matrix before using it for correcting the matrix effect as well as the sensitivity variations of the analytes in the plasma. The proposed method was validated by carrying out recovery studies employing a standard addition technique [25–27]. The above mentioned method was applied to the analysis of three real samples. These samples were also analyzed, for europium (Eu) and neodymium (Nd), by an isotopic dilution mass spectrometric (IDMS) technique [28–31], using two enriched REE spikes to enhance our confidence in the method.

## 2. Experimental

### 2.1. Instruments

#### 2.1.1. Inductively Coupled Plasma Mass Spectrometer

An inductively coupled plasma orthogonal acceleration time of flight mass spectrometer (ICP-oo-TOF-MS), model: 8000R (GBC, Australia), was used for the determination of trace REEs in the GdAlO<sub>3</sub> matrix. The mass analyzer was calibrated for the mass range of 7–209 amu. Sample introduction was carried out by an USN-desolvating device, model: U5000AT<sup>+</sup> (CETAC). The instrumental operating conditions are given in Table 1. The instrumental operating conditions were arrived at so as to have maximum <sup>140</sup>Ce<sup>+</sup> intensity and minimum possible <sup>140</sup>CeO<sup>+</sup>/<sup>140</sup>Ce<sup>+</sup> ratio with minimum variation on signal intensities. The instrument has an inbuilt smartgate [32] which was utilized for blanking the mass peaks of matrix.

#### 2.1.2. Microwave digestion system

An Anton Par Multiwave 3000 microwave digestion system with 8 × rotor was used for dissolution of refractory GdAlO<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>.

**Table 1**  
Optimized operating conditions of ICP-MS and ultrasonic nebulizer.

	Values
<i>ICP-MS parameters</i>	
RF power	1220 W
Frequency	27.2 MHz
Plasma gas flow rate	11.5 L min <sup>-1</sup>
Auxiliary gas flow rate	0.55 L min <sup>-1</sup>
Nebulizer gas flow rate	0.97 L min <sup>-1</sup>
Sample uptake rate	0.6 mL min <sup>-1</sup>
Measurement mode	Dual (PC/analog)
Acquisition time	1 s
<i>USN parameters</i>	
Heating jacket	140 °C
Cooler	2 °C
Washing time	5 min (with 5% HNO <sub>3</sub> soln.)

### 2.2. Reagents and solutions

Suprapur® sulphuric acid (Merck), Suprapur® ortho-phosphoric acid (Merck) and ultrapure water (18 MΩ, Milli-Q) were used for dissolution of samples. Commercially available ICP standard solutions (Alfa Aesar) of individual elements, each of 1000 mg L<sup>-1</sup>, were used for preparing multi-element standard solutions by appropriate dilution with the same acid mixture as used for preparing sample solutions. Enriched europium oxide (<sup>151</sup>Eu<sub>2</sub>O<sub>3</sub>) and neodymium oxide (<sup>145</sup>Nd<sub>2</sub>O<sub>3</sub>) were used for preparing spike solutions to carry out isotope dilution mass spectrometry (IDMS). High purity Gd<sub>2</sub>O<sub>3</sub> (99.999%, Sigma Aldrich) and Al<sub>2</sub>O<sub>3</sub> (99.9%, Alfa Aesar) were used for studying the matrix effect. High purity Eu<sub>2</sub>O<sub>3</sub> (99.999%, Alfa Aesar) and Nd<sub>2</sub>O<sub>3</sub> (99.999%, Alfa Aesar) were used for calibration of the spike solution.

### 2.3. Preparation of sample solutions

The microwave digestion system was utilized for the dissolution of known weight of GdAlO<sub>3</sub> and then the resulting dissolved solutions were appropriately diluted. For investigating the effect of varying amounts of matrix on the analyte intensities, appropriate amounts of high purity Gd<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> were digested and diluted in a similar way. For validating the method, recovery studies by standard addition were carried out by adding pure elemental standards of the REEs, of interest, to known weights of nuclear grade GdAlO<sub>3</sub> sample, followed by digestion, dilution and analysis by ICP-MS.

### 2.4. Preparation and calibration of spike solutions

Known weights of enriched <sup>151</sup>Eu<sub>2</sub>O<sub>3</sub> and <sup>145</sup>Nd<sub>2</sub>O<sub>3</sub> were dissolved and stored in 3 M HNO<sub>3</sub>. Mettler Toledo microbalance, model: XP26, was used to reduce the uncertainty associated with weighing. These spike solutions of Eu and Nd were calibrated by reverse IDMS technique employing solutions of high purity Eu<sub>2</sub>O<sub>3</sub> and Nd<sub>2</sub>O<sub>3</sub> respectively in 3 M HNO<sub>3</sub>. These spike solutions were used for carrying out IDMS measurements.

### 2.5. Selection of REE nuclides

The monitored nuclides of the analytes under consideration, listed in Table 2a, were selected as that they do not suffer from atomic isobaric interferences and have minimum polyatomic interferences. The polyatomic ions causing the interferences may be formed from precursors having numerous sources, like sample matrix, reagents, plasma and atmospheric gases. For correcting interferences on the analyte intensities it was necessary to consider some of the nuclides which are listed in Table 2b.

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