Investigations for determination of Gd and Sm isotopic compositions in spent nuclear fuels samples by MC ICPMS

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Abstract

Precise isotopic determination of gadolinium and samarium in spent nuclear fuels is necessary to validate neutronic calculation codes. This study presents an analytical strategy to correct mass bias phenomenon inherent to MC ICPMS for precise and accurate samarium and gadolinium isotope measurements. An external standard bracketing approach to correct for mass discrimination and an exponential law fractionation correction have been applied in this work. Due to the lack of isotopic reference materials for Gd and Sm, the reproducibility of all of the isotopic ratios has been evaluated on the basis of natural spex solution commonly used for ICPMS. These solutions have been analysed for comparison and discussion about their representative isotopic values by thermal ionization mass spectrometry.

On the basis of TIMS and MC ICPMS investigations, it was observed that: (1) the choice in representative isotopic values of the elements are essential to obtain accurate isotopic results and (2) the dependence of the mass bias of gadolinium and samarium masses must be taken into account for precise and accurate isotopic results.

A reproducibility better than 0.1% was obtained with extensive measurements of Gd and Sm solutions by MC ICPMS. When measured isotope intensities were high enough, standard deviation of Gd and Sm isotopic ratios for purified fractions of Gd and Sm fuel samples were better than 0.2%.

From the results obtained in this study, the potential of MC ICPMS techniques for determination of precise and accurate Gd and Sm isotopic compositions was clearly demonstrated for nuclear applications.
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1. Introduction

Multiple-collector inductively coupled plasma mass spectrometry (MC ICPMS) is now commonly used for routine ratio measurement of elements. The advantages of MC ICPMS are the high sensitivity of the ion source [1], associated with multicollector detection system. This technique has opened several research fields particularly in earth sciences, cosmochemistry and oceanography [2]. In nuclear industry the knowledge of isotopic and elemental compositions of all of the fission product and actinides in spent nuclear fuel is crucial for qualification of neutronic calculation codes, management of nuclear wastes or for high burn-up with state of the art reactors. Rare earth elements

(REE) are of prime interest and Gd and Sm isotopic composition in spent nuclear fuel samples must be obtained with high accuracy and precision, since these two elements presents under six (^{154}Gd, ^{155}Gd, ^{156}Gd, ^{157}Gd, ^{158}Gd and ^{160}Gd) and seven isotopic forms (^{147}Sm, ^{148}Sm, ^{149}Sm, ^{150}Sm, ^{151}Sm, ^{152}Sm and ^{154}Sm). In the nuclear field, isotopic measurements are commonly performed by thermal ionization mass spectrometry (TIMS). This method is very reliable but is time consuming and requires strict analytical procedures [3]. Optimum heating conditions of evaporation and ionization filaments have to be precisely known for the determination of true isotopic ratios [4–6]. For a given element, a reference material with a known isotopic composition is required. Its analysis makes it possible to determine a correction coefficient for each element. The analytical parameters are carefully recorded to establish the operating procedure to be used subsequently for analysis of unknown samples of the same element. One of the major drawbacks of this

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method is that the degree of similarity between the operating calibration method and the one adopted for the unknown sample is difficult to assess. Frequently, the sample is not as pure as the isotopic reference material and the amount deposited is less accurately known.

The MC ICPMS technique has the potential to improve the determination of precise and accurate isotopic composition of spent nuclear fuel samples [7] due to the high sensitivity of its source and time saving compare to TIMS (15 min versus 3 h). However a variable mass bias effect was observed in many ICPMS systems and is much more important than mass discrimination effects observed with TIMS. Studies have demonstrated that internal normalization of MC ICPMS data with an exponential law can produce results that agree with TIMS reference values within about 50–100 ppm [8]. In nuclear applications internal normalization with an invariant ratio of the same element is not possible, thus reproducible and accurate measurements using an external normalization must be performed. Furthermore, because no reference isotope materials for Gd and Sm are available, the representative values of natural spex solutions used to correct mass bias for these elements, must be evaluated.

In this paper a method is proposed for the precise and accurate determination of Gd and Sm isotopic compositions by MC ICPMS on spent nuclear fuel samples. First, the choice for representative isotopic ratios for natural spex solutions is discussed based on previous data found in the literature and on data obtained in our laboratory by TIMS (presented in this study). Then, long-term reproducibility of isotopic measurements is evaluated based on natural isotopic measurements performed on an Isoprobe MC ICPMS. Finally results on separated fractions of Gd and Sm obtained from spent nuclear fuel samples after chromatographic separation are presented.

2. Experimental

2.1. Instrumentation and measurement procedures

2.1.1. TIMS measurements

Analyses were performed on a sector 54 mass spectrometer from GV Instruments (Manchester, UK). The source was placed inside a glove-box to be able to handle radioactive samples. Removable triple filament arrangements were used in order to control independently the sample evaporation and ionization temperatures. The two evaporating filaments were made of tantalum and the ionizing filament was made of rhenium. Around 500 ng of Gd and 300 ng of Sm were deposited on a pure tantalum filament, previously degassed. In a first step the temperature of the ionizing filament was increased until an ion current on $^{187}Re^+$ of about 8×10^{-13} A was reached. Then, in order to take into account the fractionation effect, the temperature of the evaporation filament was increased in five different steps.

These steps corresponded for Gd to ion currents intensities on $^{158}Gd^+$ of, respectively, 0.5×10^{-12}, 1.3×10^{-12}, 2.5×10^{-12}, 7.5×10^{-12} and 7.5×10^{-12} A. For the first three steps the isotopic ratio measurements were based on the completion of 30 cycles with a 5 s integration time each, and the last two steps on 90 cycles with a 5 s integration time each. Data were

acquired in automatic mode and the total time needed was about 130 min. For mass 158, maximum ion beam intensity was around 7×10^{-12} A, with the exception of three analyses where the maximum ion beam intensity was around 4×10^{-12} A. Internal precision at the maximum ion beam intensity varied from 0.002 to 0.06% for the $^{152}Gd/^{158}Gd$ ratio (^{152}Gd is the less abundant isotope).

The five different evaporation steps for Sm corresponded to different ion currents intensities on $^{152}Sm^+$ of, respectively, 0.5×10^{-12}, 1×10^{-12}, 2.5×10^{-12}, 5×10^{-12} and 10×10^{-12} A. For the first three steps the isotopic ratio measurements were based on the completion of 20 cycles with a 5 s integration time each, and the last two steps, respectively, on 60 and 90 cycles with a 5 s integration time each. Data were acquired in automatic mode and the time required for the completion of this procedure was about 190 min. For mass 152 maximum ion beam intensity was around 1.2×10^{-11} A. Internal precision at the maximum ion beam intensity varied from 0.001 to 0.02% for the $^{144}Sm/^{152}Sm$ isotope ratio (^{144}Sm is the less abundant isotope).

All isotopic measurements were performed in static multicollection mode using Faraday cups. The instrument is equipped with seven Faraday cups with 10^{11} Ω positive feedback resistors. The Faraday amplifier gain was calibrated on a daily basis prior to analytical sessions. Reproducibility of the electric gains was better than 20 ppm/day.

2.1.2. MC ICPMS measurements

The MC ICPMS used in this study was an Isoprobe-N from GV instruments (Manchester, UK) modified to handle radioactive samples. Two glove-box were specifically added to the ICPMS system for this purpose. The sampling interface, the plasma torch, the torch box and the spray chamber with the nebulizer were located in the first glove-box. The peristaltic pump was located in the second glove-box, which was connected to the first one, and used to handle solutions. The operating conditions and data acquisition procedure are summarized in Table 1. All standards and samples were prepared in a 0.5 M HNO$_3$ solution and introduced in free aspiration mode via a PTFA micro concentric nebulizer. Sample uptake flow was around 0.1 ml min^{-1}. The ion beam intensity was optimized on the most abundant isotope (^{158}Gd and ^{152}Sm) on a daily basis by adjusting the torch position, gas flows, ion focusing and magnet field settings. The concentrations of Gd and Sm in sample solutions were between

Table 1
Typical operating conditions and data acquisition procedure for MC ICPMS measurements

RF power (W)	1350
Plasma gas flow rate (l min^{-1})	15
Auxiliary gas flow rate (l min^{-1})	1
Nebulizer gas flow rate (l min^{-1})	0.8
Sample uptake rate (ml min^{-1})	0.1
Nebulizer type	Micro concentric nebulizer
Spray chamber type	Cyclonic
Detector type	Faraday
Acquisition mode	Static