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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.

Keywords: Isotopic analysis; Rare earth elements; Thermal ionization; Inductively coupled plasma source mass spectrometry

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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

100 and 200 ppb. A Pt guard electrode was inserted between the torch and the load coil to increase the sensitivity [9], resulting in total signal of $(6–7) \times 10^{-11}$ A per ppm of Gd and Sm. The baseline was measured at half masses and directly corrected during each measurement. The sample analysis baseline was recorded after cleaning the sample introduction system with a 1 M HNO_3 solution, followed by a 0.5 M HNO_3 solution. The Gd and Sm data were acquired in static multicollection mode. The Faraday amplifier gain was calibrated on a daily basis prior to analytical session. The instrument was equipped with an array of nine faraday cups with 10^{11} Ω positive feedback resistors and a Daly ion counting system (not used in this study) inserted immediately behind a retarding filter (WARP). Reproducibility of the electric gains was better than 20 ppm/day.

2.2. Reagents

Aqueous solutions presenting a natural isotopic composition of Gd and Sm at a concentration of 1000 ng ml^{-1} were diluted in 0.5 M nitric acid. Nitric acid (Normatom Prolabo) and milli-Q de-ionized water (Millipore) were used for dilutions and for blank solutions.

Nuclear fuel samples were supplied as diluted nitric solutions with concentrations in the range of 4–5 mg ml^{-1} for U, 1–2 μg ml^{-1} for Gd and 5–6 μg ml^{-1} for Sm.

2.3. Chromatographic separation of Gd and Sm in the nuclear fuel samples

Gd and Sm were separated from all the actinides and fission products present in the spent nuclear fuel samples. First, the separation of uranium and plutonium was performed using an anion exchange Dowex AG1X4 (100–200 mesh, from Bio Rad laboratory) [3]. Then the separation of Gd and Sm fractions, to prevent isobaric interferences (^{154}Gd and ^{154}Sm), was developed using high performance liquid chromatography (HPLC) with an on-line UV detection. This separation was performed with a UPTISPHERE SA column and used 2-hydroxy-methylbutyric acid (HMB, Sigma–Aldrich) as the eluting solution. The pH of the mobile phase was adjusted with a 25% ammonia buffer solution. All the steps of the entire procedure were strictly controlled to minimize natural contamination. The purity of nitric acid and HMB acid was evaluated by HR-ICP-MS (Element2, ThermoFinnigan) prior to use.

3. Results and discussion

3.1. Evaluation of representative isotopic values for natural gadolinium and samarium solutions from the literature

TIMS is used primarily for isotopic measurements of REE and is very reliable for high precision measurements. With this technique, measurements are corrected for the effect of instrumental mass fractionation by normalization of the measured ratio to an invariant isotope ratio of the same element. This procedure, called internal normalization, commonly uses either a linear, power, or exponential law correction [10–12]. One of the major drawbacks for high precision isotopic ratios measurements in nuclear applications is that internal normalization, with a natural isotopic ratio cannot be considered because nuclear fuel samples do not possess such a ratio. Nevertheless the problem of isotopic fractionation can be resolved by TIMS using the total evaporation method [13,14]. This method, in which the data acquisition is performed continuously until the entire sample is ionized, is the most reliable technique for isotope ratio measurements. Because it takes into account the integration of all the ions formed during analysis, the effects of isotope fractionation in the evaporation process are virtually eliminated. This hypothesis has been verified experimentally in the analysis of NBS-certified uranium and plutonium reference materials [14] or compared with values obtained by other techniques [15]. This method, originally developed for the analysis of uranium and plutonium, has been applied to the analysis of neodymium, samarium, gadolinium and lutetium [16]. The values proposed for natural gadolinium and samarium isotopic composition are reported in Table 2 and compared with reference values data found in the literature. Most of the reference values found in the literature have been obtained by TIMS using the procedure of internal normalization. For Gd and Sm isotopic values, the following ratios have been commonly chosen: ^{156}Gd/^{160}Gd = 0.9361 [17] and ^{147}Sm/^{152}Sm = 0.56083 [18] (Table 2). If we compare the values obtained by total evaporation [16] and the values internally normalized, the relative difference varied between 0.1 and 1.5% (for the ^{152}Gd/^{158}Gd ratio). These relative differences may have some implications if we want to achieve isotopic compositions determination with an accuracy better than 0.2%. The total evaporation method is the more reliable way to approach true values of Gd and Sm isotopic composition. To discuss about the validity of absolute reference values proposed in [16] several deposits of Gd and Sm spex solutions were analysed by TIMS, with an analytical procedure adapted from the one presented in the experimental part.

3.2. Results of Gd and Sm isotopic measurements by TIMS

A total of eight analysis of Gd have been performed. All the isotopes from ^{152}Gd to ^{160}Gd have been monitored. Fig. 1a represents the evolution of the ^{156}Gd/^{160}Gd ratio versus time for the two last steps of the procedure (when ion current intensity in the procedure is 7.5×10^{-12} A) and Fig. 1b shows the evolution of the ion current intensity on mass 158. In both figures, each point represents the average value of isotopic ratios and intensity, respectively, obtained from the eight Gd deposits. The ion current intensity of mass 158 decreases progressively between 90 and 130 min. The data acquisition was stopped before the sample was fully ionized. The evolution of the ^{156}Gd/^{160}Gd with time is in good agreement with the usual mass discrimination law. The ^{156}Gd/^{160}Gd ratio decreases from 0.9437 to 0.9371 (relative difference of 0.7%) between 90 and 130 min of acquisition time. The reference value given by Dubois et al. [16] is obtained at about 110 min whereas value given by Eugster et al. [17] is not reached (or probably after 140 min). In Table 3 are presented the normalized values of isotopic ratios to the ratio

Table 2
Summary of Gd and Sm isotopic ratio measurements in the literature data

Ref.	Normalization ratio	^{152}Gd/^{158}Gd	^{154}Gd/^{158}Gd	^{155}Gd/^{158}Gd	^{156}Gd/^{158}Gd	^{157}Gd/^{158}Gd	^{160}Gd/^{158}Gd
[16]		0.00828(2)	0.08822(4)	0.59785(13)	0.82595(12)	0.63088(5)	0.87863(22)
IUPAC [23]		0.00805(43)	0.0878(15)	0.5958(65)	0.8241(60)	0.6300(26)	0.8800(101)
[24]		0.00837(49)	0.0910(22)	0.6163(124)	0.8408(167)	0.6408(130)	0.8816(171)
[17]	^{156}Gd/^{160}Gd: 0.9361	0.00817(2)	0.08782(2)	0.59593(13)	0.82410(7)	0.63024(9)	0.88036(7)
[25]	^{155}Gd/^{160}Gd: 0.6754; ^{158}Gd/^{160}Gd: 1.1353	0.00816(3)	0.08773(6)	0.59484(11)	0.82305(9)	0.63100(6)	0.88082(6)
[26]	^{156}Gd/^{160}Gd: 0.9361	0.00817(1)	0.08781(3)	0.59593(7)	0.82416(4)	0.63028(6)	0.88042(4)
[27]	^{156}Gd/^{160}Gd: 0.9361		0.087778(5)	0.59593(2)	0.82411(1)	0.63023(2)	0.88037(2)
[28]	^{156}Gd/^{160}Gd: 0.9361	0.00816(1)	0.08779(1)	0.59588(1)	0.82413(1)	0.63021(1)	0.880389(1)

	Normalization ratio	^{144}Sm/^{149}Sm	^{147}Sm/^{149}Sm	^{148}Sm/^{149}Sm	^{150}Sm/^{149}Sm	^{152}Sm/^{149}Sm	^{154}Sm/^{149}Sm
[16]		0.22383(14)	1.08680(16)	0.81419(6)	0.53366(15)	1.93040(32)	1.64008(35)
[29]		0.2283(95)	1.0889(218)	0.8143(162)	0.5397(105)	1.9241(382)	1.6279(324)
[30]		0.2185(21)	1.0738(60)	0.8119(45)	0.5355(30)	1.9392(92)	1.6556(91)
[24]		0.2256(37)	1.0809(149)	0.8130(122)	0.5351(81)	1.9019(280)	1.6067(258)
IUPAC [23]		0.2221(62)	1.0847(185)	0.8133(114)	0.5340(34)	1.9356(214)	1.6462(293)
[31]	^{147}Sm/^{154}Sm: 0.65918	0.22248(6)	1.08507(7)	0.81347(12)	0.53399(8)	1.93476(23)	1.64607(11)
[18]	^{147}Sm/^{152}Sm: 0.56083	0.22246(12)	1.08549(11)	0.81384(16)	0.53472(12)	1.93559(19)	1.64683(27)
[11]	^{148}Sm/^{154}Sm: 0.49419	0.22248(2)	1.08507(7)	0.81348(3)	0.53300(5)	1.93477(13)	1.64609(5)
[27]	^{147}Sm/^{152}Sm: 0.56083	0.22242(3)	1.08512(1)	0.81350(1)	0.53403(1)	1.93484(1)	1.64619(7)
[28]	^{147}Sm/^{152}Sm: 0.56083	0.22242(1)	1.085067(1)	0.81348(1)	0.53400(1)	1.93475(1)	1.64613(2)
[32]		0.22241(9)	1.08499(27)	0.81342(21)	0.53402(17)	1.93518(73)	1.64644(71)

^{156}Gd/^{160}Gd = 0.9400 given in [16], using a linear law. All these normalized isotopic ratios with their respective standard deviations are in good agreement with the one determined by Dubois et al. in [16]. The only exception is the ^{157}Gd/^{158}Gd ratio which could be explained by an interference due to BaF as mentioned by Eugster et al. [17]. The Gd isotopic ratios obtained by the total evaporation procedure [16] agree relative to a mass fractionation factor with the precise values determined using the internal normalization procedure.

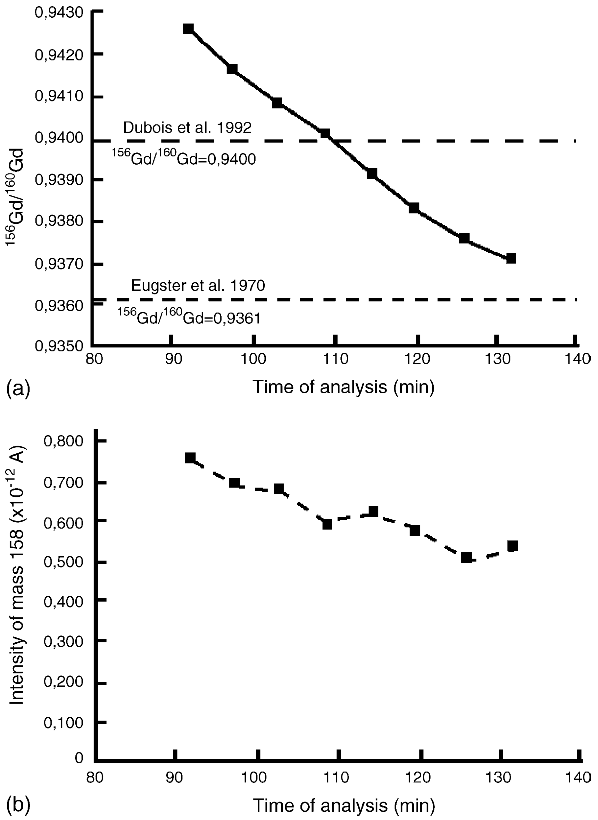

Fig. 1. Evolution of the ^{158}Gd/^{160}Gd isotopic ratio (a) and 158 mass intensity (b) during time of analysis using TIMS technique.

A total of eight analysis of Sm have also been performed, where all its isotopes from mass ^{144}Sm to ^{154}Sm have been monitored. Fig. 2a presents the evolution of the ^{147}Sm/^{152}Sm ratio versus time for the last two steps of the procedure, whereas Fig. 2b shows the evolution of the ion current intensity of mass 152. The ion current intensity of mass 152 remains almost constant between 100 and 185 min. The sample was not entirely ionized at the end of this procedure. The evolution of the ^{147}Sm/^{152}Sm ratio is in good agreement with the usual mass discrimination law at the level of precision achievable with TIMS, although it never reaches the reference values given by Dubois et al. [16] or by Lugmair and Marty [18]. Instead, the ^{147}Sm/^{152}Sm ratio decreases from 0.57111 to 0.56785 (relative difference of 0.6%) between 105 and 185 min. As for Gd, in Table 3 are presented the normalized values of isotopic ratios to the ratio ^{147}Sm/^{152}Sm = 0.56299 given in [16], using a linear law. All these normalized isotopic ratios with their respective standard deviations are in good agreement with the one determined by Dubois et al. in [16].

In order to perform accurate analysis of Gd and Sm isotopic compositions by TIMS, analytical procedures must be strictly controlled and carefully reproduced. For routine measurements of unknown samples, this is a rather difficult task. The MC ICPMS technique offers the opportunity to obtain isotopic ratio with an accuracy and precision similar to TIMS and moreover is less time consuming. Therefore, the isotopic measurements of Gd and Sm isotopic composition by MC ICPMS were explored and the long-term reproducibility of the results,

Table 3
Measured Gd and Sm isotope ratios obtained by TIMS normalized using a linear law to ^{158}Gd/^{160}Gd = 0.9400 ratio [16] and ^{147}Sm/^{152}Sm = 0.56299 [16] for the analysis period, compared to TIMS values[a] given in [16]

	^{152}Gd/^{158}Gd	^{154}Gd/^{158}Gd	^{155}Gd/^{158}Gd	^{156}Gd/^{158}Gd	^{157}Gd/^{158}Gd	^{160}Gd/^{158}Gd
TIMS [16] spex solutions	0.00828(2)	0.08822(4)	0.59785(13)	0.82595(12)	0.63088(5)	0.87863(22)
Average value (n = 8)	0.00826	0.08820	0.59801	0.82594	0.63111	0.87863
Standard deviation	0.00002	0.00001	0.00006	0.00003	0.00003	0.00003
	^{144}Sm/^{149}Sm	^{147}Sm/^{149}Sm	^{148}Sm/^{149}Sm	^{150}Sm/^{149}Sm	^{152}Sm/^{149}Sm	^{154}Sm/^{149}Sm
TIMS [16] spex solutions	0.22383(14)	1.08680(16)	0.81419(6)	0.53366(15)	1.93040(32)	1.64008(35)
Average value (n = 8)	0.22340	1.08674	0.81426	0.53373	1.93041	1.64117
Standard deviation	0.00001	0.00003	0.00005	0.00002	0.00010	0.00242

Accuracy is defined as the relative difference in % between MC ICPMS and TIMS values.

[a] All reproducibilities are 2 standard deviations.

taking into account the choice of reference values for Gd and Sm natural isotopic compositions, was evaluated.

3.3. Results of Gd and Sm isotopic measurements by MC ICPMS

A significant feature of plasma source mass spectrometry is the large instrumental mass bias, which is related to the enhanced extraction and transmission of the heaviest ions [19]. The mass bias effect is around 1.5% amu^{-1} for Gd and Sm with the Isoprobe instrument and is an order of magnitude larger than the mass fractionation observed with TIMS.

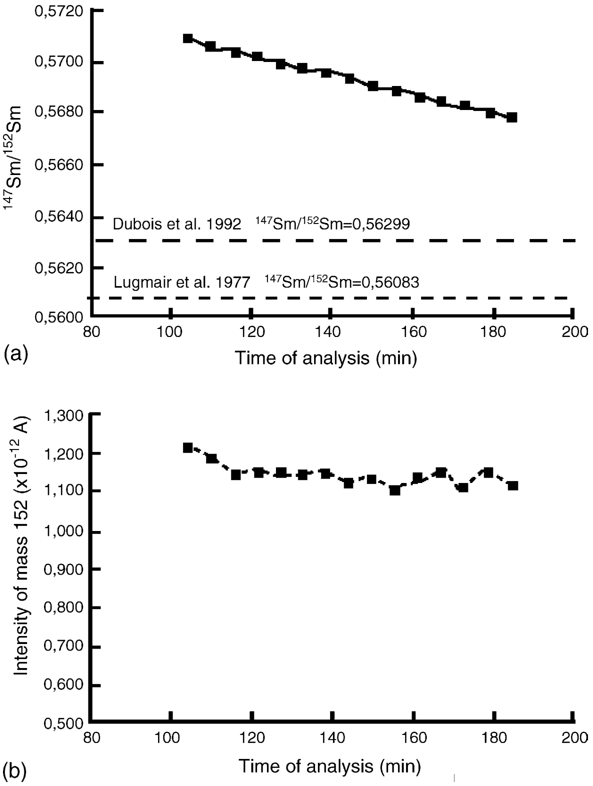

Fig. 2. Evolution of the ^{147}Sm/^{152}Sm isotopic ratio (a) and 152 mass intensity (b) during time of analysis using TIMS technique.

3.3.1. Gd and Sm reproducibility on natural solutions

During the analytical session (over 1 year) 42 analyses of natural solutions of Gd solutions and 40 analyses of natural solution of Sm were performed. The analyses used two blocks, each data block corresponds to the completion of 20 cycles of 10 s integration time each. For Gd internal precision varied from 0.002 to 0.2%, the worst value was found for the ^{152}Gd/^{158}Gd ratio. For Sm, internal precision varied from 0.002 to 0.02%, the worst value was found for the ^{144}Sm/^{149}Sm ratio.

Table 4 shows the data obtained on our natural spex solutions, by normalizing the measured isotope ratios to the following ratios: ^{160}Gd/^{158}Gd = 0.87863 [16] and ^{147}Sm/^{149}Sm = 1.08680 [16], using the equation given in [10]:

$$R_{\text{true}} = R_{\text{meas}}(m_1/m_2)^{\beta} \tag{1}$$

where R_{true} and R_{meas} are the true and the measured isotope ratios of the two isotopes 1 and 2; m_1 and m_2 the respective atomic masses of these isotopes; and β is the correction factor called Mass Bias Beta Factor.

Reproducibility of the data obtained is better than 0.05% for all ratios, except for the ^{152}Gd/^{158}Gd ratio where reproducibility is around 0.4%, due to the very low signal intensity on mass 152 (<5 mV). Accuracy, defined as the relative difference in % between MC ICPMS and TIMS, is not better than 0.2% for ratios such as ^{154}Gd/^{158}Gd, ^{144}Sm/^{149}Sm and ^{154}Sm/^{149}Sm. Furthermore accuracy improves when the normalizing ratio used is closer in mass to the ratio to be normalized: it is better for the ^{157}Gd/^{158}Gd ratio (−0.03% deviation) than for the ^{154}Gd/^{158}Gd ratio (−0.23% deviation). Fig. 3 shows the beta values for the Gd isotope ratios (using Eq. (1) and ratios given in [16]), normalized to the beta value for the ^{156}Gd/^{158}Gd ratio and plotted as a function of the numerical average masses in the numerator and denominator. Beta value is not constant across the limited range of Gd isotope ratios (calculated using ratios given in [16]). The same observation is made for Sm isotopic data and was previously observed on an Isoprobe instrument for all Nd isotopes [20]. Table 5 represents Gd and Sm isotopic ratios corrected with a beta value for which the average mass between numerator and denominator masses is the same or close to the mass of the ratio to be normalized. In this table are presented the ratio used for normalization, the reproducibility and accuracy of the results. If

Table 4
Measured Gd and Sm isotope ratios obtained by MC ICPMS normalized using an exponential law to ^{160}Gd/^{158}Gd = 0.87863 ratio [16] and ^{147}Sm/^{149}Sm = 1.08680 [16] for the analysis period, compared to TIMS values[a] given in [16]

	^{152}Gd/^{158}Gd	^{154}Gd/^{158}Gd	^{155}Gd/^{158}Gd	^{156}Gd/^{158}Gd	^{157}Gd/^{158}Gd	^{160}Gd/^{158}Gd
TIMS [16]	0.00828(2)	0.08822(4)	0.59785(13)	0.82595(12)	0.63088(5)	0.87863(22)
^{160}Gd/^{158}Gd: 0.87863	0.00820(3)	0.08802(4)	0.59729(15)	0.82550(13)	0.63072(8)	
Accuracy%	−0.91	−0.23	−0.09	−0.05	−0.03	
	^{144}Sm/^{149}Sm	^{147}Sm/^{149}Sm	^{148}Sm/^{149}Sm	^{150}Sm/^{149}Sm	^{152}Sm/^{149}Sm	^{154}Sm/^{149}Sm
TIMS [16]	0.22383(14)	1.08680(16)	0.81419(6)	0.53366(15)	1.93040(32)	1.64008(35)
^{147}Sm/^{149}Sm: 1.0868	0.22332(7)		0.81407(5)	0.53345(7)	1.92862(23)	1.63689(28)
Accuracy %	−0.23		−0.01	−0.04	−0.09	−0.19

[a] All reproducibilities are 2 standard deviations.

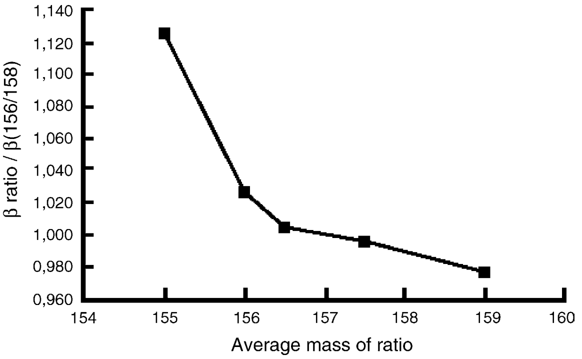

Fig. 3. Variation in exponential mass bias with mass for the Gd mass range plotted as a function of the average mass of the normalized ratio. Each point represents the average of 42 separate analyses over a period of 1 year.

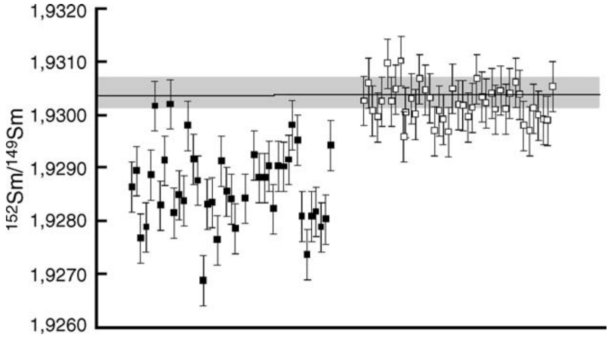

Fig. 4. ^{152}Sm/^{149}Sm ratio of the natural solutions normalized to ^{147}Sm/^{154}Sm ratio (open square) compared to ^{152}Sm/^{149}Sm normalized to ^{147}Sm/^{149}Sm ratio (black square). Error bars represent 0.025% relative error.

we compare accuracy of the Gd and Sm isotope ratios reported in Table 4 to accuracy reported in Table 5, we observe an increase of the accuracy for all the ratios. This is particularly true for the ratios ^{154}Gd/^{158}Gd (−0.07% relative to −0.23%), ^{155}Gd/^{158}Gd (−0.01% relative to −0.09%), ^{154}Sm/^{149}Sm (−0.06% relative to −0.19%) or ^{152}Sm/^{149}Sm (−0.01% relative to −0.09%). Furthermore the reproducibility increases for all the ratios, except for the ratio ^{155}Gd/^{158}Gd for which we do not have any explanation yet. Ratios are corrected using other mass discrimination laws (linear and power laws) but differences in terms of reproducibility and accuracy are not distinguishable with the current precision achieved in our study.

Fig. 4 illustrates the importance of the choice of the ratio of normalization for the particular ^{152}Sm/^{149}Sm ratio. The ^{152}Sm/^{149}Sm ratio has been internally normalized by the two isotopic ratios ^{147}Sm/^{149}Sm (data represented by black square) and ^{147}Sm/^{154}Sm (data represented by open square), with average masses of, respectively, 148 and 150.5. The two average ratios for the 40 analyses are, respectively, of 1.92862 ± 0.00023 (with an accuracy of −0.09%) and 1.93023 ± 0.00010 (with an accuracy of −0.01%). Reproducibility and accuracy are better when average masses between the normalizing ratio and the ratio use to do the normalization are similar (150.5).

Table 5
Replicate analyses of Gd and Sm natural solutions by MC ICPMS internally normalized using an exponential law

Ratio use for normalization	^{154}Gd/^{156}Gd ^{152}Gd/^{158}Gd	^{156}Gd/^{158}Gd ^{154}Gd/^{158}Gd	^{157}Gd/^{158}Gd ^{155}Gd/^{158}Gd	^{154}Gd/^{160}Gd ^{156}Gd/^{158}Gd	^{155}Gd/^{160}Gd ^{157}Gd/^{158}Gd	^{157}Gd/^{160}Gd ^{160}Gd/^{158}Gd
TIMS [16]	0.00828(2)	0.08822(4)	0.59785(13)	0.82595(12)	0.63088(5)	0.87863(22)
MC ICPMS (n = 42)	0.00825(3)	0.08815(3)	0.59779(26)	0.82612(10)	0.63084(6)	0.87852(8)
Accuracy %	−0.38	−0.07	−0.01	0.02	−0.01	−0.01
Ratio use for normalization	^{147}Sm/^{149}Sm ^{144}Sm/^{149}Sm	^{148}Sm/^{149}Sm ^{147}Sm/^{149}Sm	^{150}Sm/^{147}Sm ^{148}Sm/^{149}Sm	^{147}Sm/^{152}Sm ^{150}Sm/^{149}Sm	^{147}Sm/^{154}Sm ^{152}Sm/^{149}Sm	^{152}Sm/^{149}Sm ^{154}Sm/^{149}Sm
TIMS [16]	0.22383(14)	1.08680(16)	0.81419(6)	0.53366(15)	1.93040(32)	1.64008(35)
MC ICPMS (n = 40)	0.22332(7)	1.08746(22)	0.81397(7)	0.53355(7)	1.93023(10)	1.63916(13)
Accuracy %	−0.23	0.06	−0.03	−0.02	−0.01	−0.06

Ratio use for normalization, reproducibility and accuracy are indicated.

Table 6
Gadolinium and samarium isotopic ratios determined by MC ICPMS in spent nuclear fuel samples (MOX sample)

	MOX sample Gd				
	^{154}Gd/^{156}Gd	^{155}Gd/^{156}Gd	^{158}Gd/^{156}Gd	^{157}Gd/^{158}Gd	^{160}Gd/^{158}Gd
	0.11683	0.03302	0.20546	0.00461	0.07632
	0.11688	0.03309	0.20538	0.00474	0.07606
	0.11689		0.20540		
	0.11689		0.20537		
Mean	0.11687	0.03305	0.20540	0.00467	0.07619
Standard deviation %	0.03	0.15	0.02	1.84	0.24

	MOX Sm					
	^{147}Sm/^{150}Sm	^{148}Sm/^{150}Sm	^{151}Sm/^{150}Sm	^{152}Sm/^{150}Sm	^{154}Sm/^{150}Sm	^{149}Sm/^{150}Sm
	0.58855	0.61967	0.04329	0.36397	0.20289	0.00741
	0.58876	0.61979	0.04315	0.36348	0.20275	0.00741
	0.58892	0.61995	0.04313	0.36383	0.20277	0.00737
Mean	0.58874	0.61980	0.04319	0.36376	0.20280	0.00740
Standard deviation %	0.03	0.02	0.20	0.07	0.04	0.35

3.3.2. Applications: Gd and Sm measurements in nuclear fuel samples

Isotopic measurements have been performed using natural spex solution as the standard in the standard bracketing method: each sample is analysed between two standards. The isotopic ratios of the natural solution is measured and a mass bias correction factor is calculated. In relation to the observations done during the analysis of natural solutions, mass bias correction factor are determined using: (1) total evaporation values for Gd and Sm (representative of absolute compositions) and (2) normalization ratios with average masses close to the ratios that must be corrected, in relation to the dependence of the mass bias with masses. The magnitude of the bias depends on the operating conditions. In practice it is difficult to minimize this mass bias discrimination and the stability of the mass bias over time is more important than its magnitude. A little variation of mass bias during 1 day is the guarantee of the good reproducibility of the measurements. Nevertheless, this technique requires extremely strict sample purification [21]. Prior to mass spectrometry analysis of Gd and Sm in MOX (Mixte Oxide of uranium and plutonium) samples, these elements are separated from all the actinides and fission products present in nuclear fuel samples. Due to the large difference in isotopic compositions between fuel samples and natural standards (used for mass bias corrections) of solution of 0.1 M HNO_3 was used between samples analyses to avoid memory effects. Reproducibility of the entire procedure was tested on a fuel sample. Table 6 reports the results obtained on several purified Gd and Sm fractions for a MOX sample. The ratios for which signal intensity on the isotope of interest is less than 10 mV are distinguished on the right of the table (^{157}Gd/^{158}Gd, ^{160}Gd/^{158}Gd and ^{149}Sm/^{150}Sm ratios). On the Isoprobe instrument several precautions must be taken with low signal intensity due to blank and 1/2 masses corrections [22]. The results on the MOX fuel sample show the good reproducibility of the data. This reproducibility, expressed as the relative standard deviation (in %), is less than 0.2% for ratios where the signal intensity is better than 10 mV.

4. Conclusions

An analytical procedure has been successfully developed for Gd and Sm isotopic measurements in spent nuclear fuel samples by MC ICPMS, to obtain precise and accurate isotopic ratios. The MC ICPMS technique is time saving compared to TIMS.

Due to the impossibility to perform internal mass discrimination corrections, external standard bracketing approach is used. Isotopic composition of natural solutions of gadolinium and samarium must be referred to absolute isotopic compositions previously determined by TIMS using the total evaporation technique. Furthermore, extensive Gd and Sm measurements of natural solutions show that isotopic ratios are systematically more accurate when the average mass normalization is closer to the one of the normalizing ratio.

The isotopic compositions of gadolinium and samarium have been measured in a MOX sample and the relative standard deviation on several analyses of purified fractions of this sample was better than 0.2% (except for ratios for which mass intensity was not high enough), a precision which is required for nuclear applications.

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