

# Uncertainty propagation through correction methodology for the determination of rare earth elements by quadrupole based inductively coupled plasma mass spectrometry

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## Abstract

Determination of rare earth elements by quadrupole based inductively coupled plasma mass spectrometry (ICP-QMS) shows several spectroscopic overlaps from  $M^+$ ,  $MO^+$  and  $MOH^+$  ions. Especially, the spectroscopic interferences are observed from the atomic and molecular species of lighter rare earth elements including Ba during the determination of Eu, Gd and Tb. Mathematical correction methods, knowing the at.% abundances of different interfering isotopes, and the extent of formation of molecular species determined experimentally, have been used to account for various spectroscopic interferences. However, the uncertainty propagated through the mathematical correction limits its applicability. The uncertainty propagation increases with the increase in contribution from interfering species. However, for the same extent of total contribution, the overall error decreases when the interfering species are more than one. In this work, chondrite as well as a few geological reference materials containing different proportions of various rare earth elements have been used to study the contributions of different interfering species and the corresponding uncertainty in determining the concentrations of rare earth elements. A number of high abundant isotopes are proposed for determining the concentrations of various rare earth elements. The proposed isotopes are tested experimentally for determining the concentrations of different rare earth elements in two USGS reference materials AGV-1 and G-2. The interferences over those isotopes are corrected mathematically and the uncertainties propagated due to correction methodology are determined for those isotopes. The uncertainties in the determined concentrations of rare earth elements due to interference correction using the proposed isotopes are found to be comparable with those obtained by the commonly used isotopes for various rare earth elements.

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## 1. Introduction

Rare earth elements represent a group of elements from La to Lu, which shows similar physical and chemical properties. They play an important role in various fields ranging from geology to electronics, which demand their determination from percentage level to ultra-trace level [1]. Increasing use of

rare earth elements for different applications increases their release into the environment. As a consequence, determination of rare earth elements is also needed for environmental and biological science [2,3].

High selectivity and sensitivity along with multi-elemental detection capability of quadrupole based inductively coupled plasma mass spectrometry (ICP-QMS) have made this technique as a useful analytical tool for ultra-trace determination of different elements including rare earths. Since the launch of the first commercial ICP-QMS system in 1984, a number of papers have appeared in literature on its use for multi-elemental determinations in different matrices. This tech-

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nique is particularly attractive for determination of rare earth elements especially in geological samples without any chemical separation or pre-concentration [4]. As a result, many reports have been published for the determination of rare earth elements in geological samples by ICP-QMS [5–11]. However, the mass spectra are plagued by spectroscopic interferences from various species, e.g. oxides and hydroxides, which poses serious problem for determination of middle and heavier rare earth elements by ICP-QMS, particularly when the concentration ratio of lighter rare earths to heavier rare earths is high. In addition, Ba is one of the most abundant elements in many samples and its oxides and hydroxides also interfere with determination of some of the rare earth elements, e.g. Eu.

Reduction of oxide and hydroxide formation in plasma has been the focus of research for many years. Several methods including desolvation techniques like ultrasonic nebuliser [12], membrane dryer [13] and cryogenic desolvation [8] have been adopted to reduce the metal oxide formation in the ICP torch. Other attempts such as changes in plasma gas composition [14,15], changes in sampler and skimmer orifice size [16], optimization of the distance between them [17], and changes in sampling depth [13] have also been demonstrated to reduce the oxide formation. The dynamic reaction cell has also been introduced in the commercial ICP-QMS instruments, which makes use of collision/reaction with a gas to reduce the level of oxides present in the ion beam [18,19].

In spite of reduction in the formation of oxide and hydroxide species, mathematical correction methodology has to be adopted to account for the oxide and hydroxide overlap problem [20,21]. Vaughan and Horlick compared the use of multiple component analysis method with Gauss elimination for rare earth elements determination by ICP-QMS [22]. Dulski reported a degree of interference during rare earth elements determination by ICP-QMS under the routine conditions [7]. However, these publications do not allow the estimation of uncertainties due to interference correction in the corrected rare earth elements signals. As is obvious, due to large corrections required, coupled with increased uncertainty in the correction, this method has not been preferred for determination of lighter rare earth elements specifically Eu in presence of relatively high concentrations of Ba. Jarvis used doubly charged Eu ions for its determination to circumvent the spectroscopic interferences from oxide and hydroxide species of Ba [23]. Unusual severe loss of sensitivity limited the use of doubly charged ions in Eu determination at ultra-trace level. Cao et al. used chromatographic separation for Ba to avoid large mathematical correction at Eu [24]. Though the separation is required only in very unusual and exceptional samples, yet the procedure is tedious and time consuming.

The speed as well as ease of application of mathematical correction methodology without any additional experimental step motivated us to study in detail, the advantages and drawbacks of this approach. This was done by estimating the contributions from various interfering species

using experimental data on the formation of oxides and hydroxides and the corresponding uncertainty associated with them for the determination of rare earth elements by ICP-QMS.

A discussion of the best choice of isotopes on the basis of degree of oxide formation of potential interfering elements to be used for rare earth elements analysis was reported by Longerich et al. [25]. However, some of the high abundant isotopes of rare earth elements showing relatively more but correctable interferences have not been considered in those discussions. In this work, four different geological reference materials, chondrite and a synthetic mixture were used to identify the most suitable isotopes for determination of different rare earth elements. It is demonstrated that in many cases, more than one isotope can be used for determining the rare earth element concentrations by ICP-QMS, without worrying about the number of interfering species. Though, conventionally one isotope has been preferred due to more interferences on the other isotopes, however, the use of more than one isotope enhances the confidence in the concentration values obtained using ICP-QMS. It also helps in identifying isotopic anomalies, if any, in case of non-natural isotopic composition of the element, e.g. in natural reactor popularly known as OKLO phenomenon or in case of samples from a nuclear reactor or irradiation experiments.

## 2. Experimental

### 2.1. Apparatus

A SCIEX ELAN 6000 ICP-QMS (Perkin-Elmer, USA), with cross flow nebuliser described elsewhere [26], was used for analyzing various samples. The sampling depth between the sampler tip and top coil was fixed at 9 mm for all data acquisition. The coolant gas flow rate and the auxiliary gas flow rate were fixed at 15.0 and 1.0 L/min. The aerosol gas flow rate and the r.f. power were optimized daily using 10 ppb Ce solution to optimize the sensitivity along with fraction oxide formation. The typical values were 0.95 L/min for aerosol gas flow and 1250 W as the r.f. power.

### 2.2. Reagents

De-ionized water (Millipore, USA) was used for the preparation of solutions. Indium (1000 ppmw) was procured from Merck. All the rare earth elements solutions 10 ppmw each and Ba (1000 ppmw) standard solution were purchased from High-Purity Standards, USA and diluted to desired concentrations by 1% HNO<sub>3</sub>. Rock samples AGV-1 and G-2 with recommended values for rare earth elements and Ba were obtained from the United States Geological Survey. Trace pure grade HNO<sub>3</sub> and supra pure grade HF obtained from Merck were used for digestion and dissolution of rock samples. Finally, all the solutions and samples were prepared in 1% HNO<sub>3</sub> for ICP-QMS analysis.

### 2.3. Rock sample preparation

Ultrasonication [27] in conc. HF and conc. HNO<sub>3</sub> medium was employed for the extraction of rare earth elements from solid silicate matrices. An amount of 25 mg of AGV-1 was dissolved in PTFE beaker using a mixture of 0.5 mL conc. HF and 5 mL conc. HNO<sub>3</sub>, by heating on a hot plate followed by ultrasonication, for 1.5–2 h. To extract the ultra-trace heavier rare earth elements in G-2, the above digestion medium was modified to 1:1 HCl–HNO<sub>3</sub> in place of HNO<sub>3</sub>. The ultrasonication extraction time was also increased from 2 to 5 h. The dissolved solutions showed no residue after the ultrasonic extraction. It may be added that undissolved minerals, if left, during the dissolution procedure are most likely zircons containing heavier rare earths and hence it was essential to carry out quantitative dissolution. The dissolved solutions were evaporated to dryness to remove the excess of fluorides and chlorides from HF and HCl, respectively. They were further treated 2–3 times with conc. HNO<sub>3</sub> to evaporate till dryness, followed by their dilution to the desired volume with 1% HNO<sub>3</sub> for ICP-QMS analysis.

## 3. Mathematical correction method

### 3.1. Correction for polyatomic (oxide or hydroxide) isobaric species

The correction methodology depends on the measurement of oxide and hydroxide yields of the interfering rare earth elements and Ba, under the experimental conditions employed. The contribution due to these oxide/hydroxide species should be eliminated from the observed intensity of rare earth element to get corrected intensity. The estimation of this contribution can be explained with the help of an example as follows.

Let us take the example of Sm determination using <sup>147</sup>Sm and the isobaric interference of <sup>130</sup>BaOH at <sup>147</sup>Sm. Since <sup>138</sup>Ba has no isobaric interference, has high abundance and can be monitored without any problem, the contribution ( $I_{C(\text{BaOH})}$ ) from <sup>130</sup>BaOH at <sup>147</sup>Sm in the sample can be calculated as follows

$$\left(\frac{I_{^{130}\text{BaOH}}}{I_{^{130}\text{Ba}}}\right)_{\text{sample}} = \left(\frac{I_{^{138}\text{BaOH}}}{I_{^{138}\text{Ba}}}\right)_{\text{sample}} \quad \text{or}$$

$$I_{^{130}\text{BaOH}(\text{sample})} = \frac{I_{^{138}\text{BaOH}(\text{sample})}}{I_{^{138}\text{Ba}(\text{sample})}} I_{^{130}\text{Ba}(\text{sample})} \quad \text{or}$$

$$I_{^{130}\text{BaOH}(\text{sample})} = \frac{I_{^{138}\text{BaOH}(\text{sample})}}{^{138}\text{Ba}(\text{at.}\%) } ^{130}\text{Ba}(\text{at.}\%) K \quad (1)$$

where  $K$  is the mass discrimination factor of the instrument under those experimental conditions and is defined as  $K = [I_{^{130}\text{Ba}}/I_{^{138}\text{Ba}}]_{\text{sample}}/[^{130}\text{Ba}(\text{at.}\%)/^{138}\text{Ba}(\text{at.}\%)]_{\text{IUPAC}}$ .

$$\text{Assuming } (I_{^{138}\text{BaOH}}/I_{^{138}\text{Ba}})_{\text{sample}} = (I_{^{138}\text{BaOH}}/I_{^{138}\text{Ba}})_{\text{standard}}$$

$$I_{^{138}\text{BaOH}(\text{sample})} = \left(\frac{I_{^{138}\text{BaOH}}}{I_{^{138}\text{Ba}}}\right)_{\text{standard}} I_{^{138}\text{Ba}(\text{sample})} \quad (2)$$

Substituting Eq. (2) into Eq. (1)

$$I_{^{130}\text{BaOH}(\text{sample})} = \left(\frac{I_{^{138}\text{BaOH}}}{I_{^{138}\text{Ba}}}\right)_{\text{standard}} I_{^{138}\text{Ba}(\text{sample})} \frac{^{130}\text{Ba}(\text{at.}\%) }{^{138}\text{Ba}(\text{at.}\%) } K \quad \text{or}$$

$$I_{^{130}\text{BaOH}(\text{sample})} = (Y_{\text{BaOH}}) I_{^{138}\text{Ba}(\text{sample})} \frac{^{130}\text{Ba}(\text{at.}\%) }{^{138}\text{Ba}(\text{at.}\%) } K \quad (3)$$

where,  $Y_{\text{BaOH}} = (I_{^{138}\text{BaOH}}/I_{^{138}\text{Ba}})$  denotes the yield of BaOH<sup>+</sup> and  $I_{^{138}\text{Ba}(\text{sample})}$  is the intensity of <sup>138</sup>Ba in the sample. If  $I_{^{147}\text{Sm}(\text{sample})}$  is the observed intensity of <sup>147</sup>Sm in the sample, then the corrected intensity  $I'_{^{147}\text{Sm}(\text{sample})}$  of <sup>147</sup>Sm used for its determination in the sample will be

$$I'_{^{147}\text{Sm}(\text{sample})} = I_{^{147}\text{Sm}(\text{sample})} - I_{^{130}\text{BaOH}(\text{sample})} \quad (4)$$

In generalized form, the Eqs. (3) and (4) can be written as:

$$I_C = Y I_{B(\text{sample})} \frac{b}{b'} K \quad (5)$$

$$I'_{A(\text{sample})} = I_{A(\text{sample})} - I_C \quad (6)$$

where A is the isotope for the analyte of interest to be determined, B the isotope (used as a monitor) of interfering element,  $b$  and  $b'$  are the IUPAC recommended at.%'s of interfering isotope and monitored isotope of interfering element,  $I_{B(\text{sample})}$  the intensity of interfering element,  $I_C$  the contribution from interfering species,  $I_{A(\text{sample})}$  and  $I'_{A(\text{sample})}$  are the observed and corrected intensities of the particular isotope in the sample. The methodology is based on the yield ( $Y$ ) determined using the major abundant isotope of the interfering element and hence would allow more accurate interference correction.

### 3.2. Correction for atomic isobaric species

For atomic isobaric species  $Y = 1$ , hence, Eq. (5) becomes

$$I_C = I_{B(\text{sample})} \frac{b}{b'} K \quad (7)$$

### 3.3. Correction for multiple isobaric species

When the analyte isotope has interference from more than one interfering species, the net contribution ( $I_C$ ) from different species can be calculated as

$$I_C = I_{C1} + I_{C2} + \dots + I_{Cn} \quad (8)$$

where,  $I_{C1}$ ,  $I_{C2}$ , ...,  $I_{Cn}$  the contributions from different interfering species 1, 2, ...,  $n$ , respectively, can be obtained as

follows

$$I_{C1} = Y_1 I_{B1(\text{sample})} \frac{b_1}{b'_1} K_1$$

$$I_{C2} = Y_2 I_{B2(\text{sample})} \frac{b_2}{b'_2} K_2$$

$$I_{Cn} = Y_n I_{Bn(\text{sample})} \frac{b_n}{b'_n} K_n$$

followed by Eq. (6)

### 3.4. Corrected concentration of analyte in sample

From the corrected intensity of analyte in sample ( $I'_{A(\text{sample})}$ ) obtained by Eq. (6) and the intensity of analyte in its standard solution ( $I_{A(\text{standard})}$ ), the correct concentration of analyte [A] in the sample using a appropriate dilution factor ( $D$ ) can be obtained as follows

$$[A] = \frac{I'_{A(\text{sample})}}{I_{A(\text{standard})}} D \quad (9)$$

## 4. Propagation of measurement uncertainties

### 4.1. For polyatomic (oxide or hydroxide) isobaric species

ICP-QMS determination of rare earth elements involves several experimental measurements, which are subjected to indeterminate uncertainties, which finally contribute to net indeterminate error in the final result. For instance, Eq. (5) in combination with Eq. (6) used for oxide or hydroxide correction is considered for error propagation. The uncertainties in the variables in Eq. (5) propagate in the final corrected intensity. The uncertainty propagation through Eq. (5) can be calculated as follows

$$\sigma_{I_C} = I_C \sqrt{\left(\frac{\sigma_Y}{Y}\right)^2 + \left(\frac{\sigma_{I_{B(\text{sample})}}}{I_{B(\text{sample})}}\right)^2 + \left(\frac{\sigma_b}{b}\right)^2 + \left(\frac{\sigma_{b'}}{b'}\right)^2 + \left(\frac{\sigma_K}{K}\right)^2} \quad (10)$$

### 4.2. For atomic isobaric species

For atomic isobaric interference correction as  $Y = 1$ , Eq. (10) will change as follows

$$\sigma_{I_C} = I_C \sqrt{\left(\frac{\sigma_{I_{B(\text{sample})}}}{I_{B(\text{sample})}}\right)^2 + \left(\frac{\sigma_b}{b}\right)^2 + \left(\frac{\sigma_{b'}}{b'}\right)^2 + \left(\frac{\sigma_K}{K}\right)^2} \quad (11)$$

### 4.3. For multiple isobaric species

When the contribution is from more than one interfering species as shown in Eq. (8), the propagated uncertainty in the net contribution ( $\sigma_{I_C}$ ) can be calculated as follows

$$\sigma_{I_C} = \sqrt{(\sigma_{I_{C1}})^2 + (\sigma_{I_{C2}})^2 + \dots + (\sigma_{I_{Cn}})^2} \quad (12)$$

### 4.4. For corrected measured intensity of analyte

If  $\sigma_{I_C}$  and  $\sigma_{I_{A(\text{sample})}}$  are the uncertainties in the estimated contribution ( $I_C$ ) and in the observed intensity of analyte [ $I_{A(\text{sample})}$ ], then, the final uncertainty ( $\sigma_{I'_{A(\text{sample})}}$ ) in the corrected intensity [ $I'_{A(\text{sample})}$ ] propagated through Eq. (6) will be

$$\sigma_{I'_{A(\text{sample})}} = \sqrt{(\sigma_{I_{A(\text{sample})}})^2 + (\sigma_{I_C})^2} \quad (13)$$

### 4.5. For corrected concentration of analyte in the sample

The uncertainty propagated through Eq. (9) can be net uncertainty obtained in the determination of analyte in the given sample. This can be obtained using the following equation

$$\sigma_{[A]} = [A] \sqrt{\left(\frac{\sigma_{I'_{A(\text{sample})}}}{I'_{A(\text{sample})}}\right)^2 + \left(\frac{\sigma_{I_{A(\text{standard})}}}{I_{A(\text{standard})}}\right)^2} \quad (14)$$

## 5. Results and discussion

Spectroscopic interferences due to oxides and hydroxides formed from the analyte itself, the matrix component, the solvent and the plasma gases during ICP-MS are well recognized. Almost all the elements form  $MO^+$  and  $MOH^+$  ions to some extent. However, rare earth elements form the strongest oxide and hydroxide ions in ICP-QMS [28]. Moreover, the yields of oxides and hydroxides of lighter rare earth elements are much higher than those for heavier rare earth elements. These species occur at 16 and 17 amu above the parent ion and present a potential analytical problem for determination of low abundant heavier rare earth elements. In addition, the seven naturally occurring isotopes of Ba occur adjacent to the lighter rare earth elements, forming oxides and hydroxides. The oxide and hydroxide species of Ba are potential source of interference on the isotopes of middle rare earth elements, especially Eu. Both the isotopes of Eu ( $^{151}\text{Eu}$  and  $^{153}\text{Eu}$ ), suffer serious overlaps from oxides and hydroxides of Ba isotopes, particularly when Ba:Eu concentration ratio is greater than 200:1.

The correction methodology based on single element oxide measurement can be used to correct for these interferences. To achieve high sensitivity and good precision for the determination of any element, isotopes having high natural abundance should be selected. The interferences at the high abundant isotopes can be corrected using correction method-

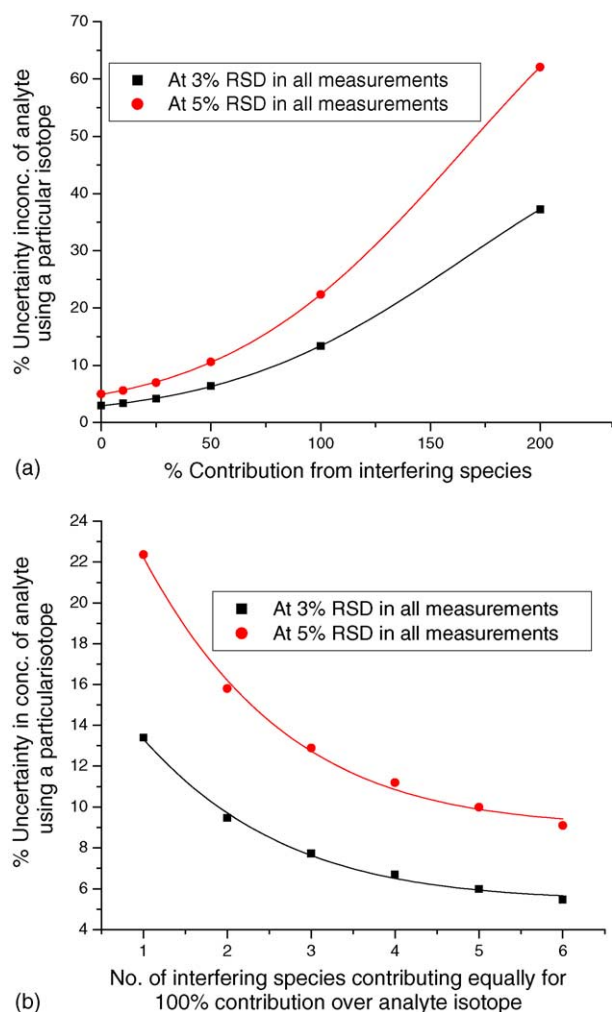


Fig. 1. Dependence of uncertainty propagation on (a) contribution from interfering species, as that of single species (b) number of contributing interfering species for the same total contribution divided equally among various species.

ology, however, the uncertainty propagated through the correction method would decide their suitability. The uncertainty due to correction depends on (a) the precision of analytical measurements, (b) the magnitude of contribution to be corrected, (c) the type of interfering species and (d) the number of contributing species. Fig. 1a and b show the dependence of uncertainty propagated on the % contribution of interfering species and the number of interfering species. As is obvious, for a fixed R.S.D. in analytical measurements, the uncertainty in the corrected signal of an isotope increases with increase in the contribution from interfering species. As shown in Fig. 1a, there is an exponential increase in uncertainty in corrected concentration of analyte using a particular isotope with increase in contribution from interfering species. This exponential increase is also dependent upon relative standard deviation of measurement, e.g. 5% R.S.D. versus 3% R.S.D. However, for the same extent of total % contribution, the overall uncertainty decreases with the increase in number of contributing species as shown in Fig. 1b. As can be seen,

Table 1

Certified (recommended/provisional) concentrations in ppmw of rare earth elements in geological standards and in chondrite

Rare earth element	AC-E <sup>a</sup>	AGV-1 <sup>b</sup>	G-2 <sup>b</sup>	GSP-1 <sup>b</sup>	Chondrite <sup>c</sup>
La	59	38	89	184	0.235
Ce	155	67	160	399	0.603
Pr	22.2	7.6	18	52	0.089
Nd	92	33	55	196	0.452
Sm	24.2	5.9	7.2	26.3	0.147
Eu	2.0	1.6	1.4	2.33	0.056
Gd	26	5	4.3	12.1	0.197
Tb	4.8	0.7	0.48	1.34	0.036
Dy	29	3.6	2.4	5.5	0.243
Ho	6.5	0.67	0.4	1.01	0.056
Er	17.7	1.7	0.92	2.7	0.159
Tm	2.6	0.34	0.18	0.38	0.024
Yb	17.4	1.72	0.8	1.7	0.163
Lu	2.45	0.27	0.11	0.21	0.024
Ba <sup>d</sup>	55	1230	1880	1310	2.3
Hf <sup>d</sup>	28.7	5.1	7.9	15.5	0.12

<sup>a</sup> Refers to GIT-IWG geological standard (Ref. [31]).

<sup>b</sup> Refers to USGS geological standards (Ref. [32]).

<sup>c</sup> Refers to chondrite often used for normalization of rare earth elements contents in geological standards (Ref. [33]).

<sup>d</sup> Refers to spectroscopically interfering elements during determination of rare earth elements by ICP-QMS.

the uncertainty of 22.4% in the corrected concentration of analyte, assuming 100% contribution from single species at 5% R.S.D. in all analytical measurements decreases to 11.2% when the same contribution is from four equally contributing interfering species. Normally, the uncertainty would lie within 11.2–22.4%, as all the four interfering species would never contribute equally. However, this suggests that for a particular isotope, even if the contributing species are more, it can be selected for determining the concentration of a rare earth element using correction methodology.

In this work, the uncertainty due to the interference correction is used as a parameter for proper choice of rare earth element isotope with maximum isotopic abundance. Table 1 gives the recommended concentration values of different reference materials used in the present work for experimental and/or calculation purposes. Table 2 a shows all rare earth elements isotopes in the mass range of 138–176, their natural abundances and the possible isobaric interferences from atomic, oxide or hydroxide species of rare earth elements, Hf and Ba, theoretically calculated. Table 2b shows the data on other interfering elements viz. Ba and Hf, for their different isotopes with natural abundances. The isotopes suggested by Longerich et al. and normally used by different researchers for determination of various rare earth elements are given in bold in Table 2a. It can be seen that the major isotopes of La and Ce are free from isobaric interferences along with Pr, which is mono-isotopic. However, the interferences on high abundant isotopes of rare earth elements occur from Nd to Yb. <sup>144</sup>Nd, <sup>152</sup>Sm, <sup>160</sup>Gd, <sup>164</sup>Dy, <sup>166</sup>Er and <sup>174</sup>Yb are the isotopes of the high natural abundance of these rare earth elements. Comparative evaluation of contribution from

Table 2

(a) Spectroscopic interferences and the corresponding uncertainties due to their corrections during the determination of rare earth elements by ICP-QMS

RE	Mass	At.%	Interference	Synthetic mixture <sup>a</sup>		AC-E		AGV-1		G-2		GSP-1		Chondrite	
				% Contribution <sup>b</sup>	% Uncertainty <sup>b</sup>	% Contribution <sup>b</sup>	% Uncertainty <sup>b</sup>	% Contribution <sup>b</sup>	% Uncertainty <sup>b</sup>	% Contribution <sup>b</sup>	% Uncertainty <sup>b</sup>	% Contribution <sup>b</sup>	% Uncertainty <sup>b</sup>	% Contribution <sup>b</sup>	% Uncertainty <sup>b</sup>
La	138	0.090 (1)	<sup>138</sup> Ce, <sup>138</sup> Ba	*	–	*	–	*	–	*	–	*	–	*	–
	<b>139</b>	<b>99.910 (1)</b>	–	0	3.0	0	3.0	0	3.0	0	3.0	0	3.0	0	3.0
Ce	136	0.185 (2)	<sup>136</sup> Ba	*	–	*	–	*	–	*	–	*	–	*	–
	138	0.251 (2)	<sup>142</sup> Nd, <sup>138</sup> Ba	*	–	*	–	*	–	*	–	*	–	*	–
	<b>140</b>	<b>88.450 (51)</b>	–	0	3.0	0	3.0	0	3.0	0	3.0	0	3.0	0	3.0
	142	11.114 (51)	<sup>142</sup> Nd	*	–	*	–	*	–	*	–	*	–	*	–
Pr	141	100	–	0	3.0	0	3.0	0	3.0	0	3.0	0	3.0	0	3.0
Nd	142	27.2 (5)	<sup>142</sup> Ce	42	5.5	70	8.8	84	11	*	–	85	11	55	6.9
	<b>143</b>	<b>12.2 (2)</b>	–	0	3.0	0	3.0	0	3.0	0	3.0	0	3.0	0	3.0
	<b>144</b>	<b>23.8 (3)</b>	<sup>144</sup> Sm	13	3.5	3.4	3.1	2.3	3.1	1.7	3.1	1.7	3.1	4.2	3.1
	145	8.3 (1)	–	0	3.0	0	3.0	0	3.0	0	3.0	0	3.0	0	3.0
	<b>146</b>	<b>17.2 (3)</b>	<sup>130</sup> BaO	0.0006	3.0	0.0004	3.0	0.02	3.0	0.02	3.0	0.004	3.0	0.003	3.0
	148	5.7 (1)	<sup>148</sup> Sm, <sup>132</sup> BaO	*	–	50	6.3	34	4.9	25	4.2	26	4.2	62	7.8
	150	5.6 (2)	<sup>150</sup> Sm, <sup>134</sup> BaO	*	–	34	4.9	25	4.1	19	3.8	18	3.7	43	5.6
Sm	144	3.07 (7)	<sup>144</sup> Nd	*	–	*	–	*	–	*	–	*	–	*	–
	<b>147</b>	<b>14.99 (18)</b>	<sup>130</sup> BaOH	0.0007	3.0	0.0007	3.0	0.14	3.0	0.18	3.0	0.016	3.0	0.005	3.0
	148	11.24 (10)	<sup>148</sup> Nd, <sup>132</sup> BaO	51	6.5	*	–	*	–	*	–	*	–	*	–
	149	13.82 (7)	<sup>132</sup> BaOH	0.0003	3.0	0.0008	3.0	0.07	3.0	0.09	3.0	0.02	3.0	0.005	3.0
	150	7.38 (1)	<sup>150</sup> Nd, <sup>134</sup> BaO	76	9.6	*	–	*	–	*	–	*	–	*	–
	<b>152</b>	<b>26.75 (16)</b>	<sup>152</sup> Gd, <sup>136</sup> CeO, <sup>136</sup> BaO, <sup>135</sup> BaOH	0.8	3.0	0.9	3.0	9	3.3	11	3.4	2.4	3.1	1.7	3.1
	154	22.75 (29)	<sup>154</sup> Gd, <sup>142</sup> NdO, <sup>138</sup> CeO, <sup>138</sup> BaO, <sup>137</sup> BaOH	11	3.4	12	3.4	78	8.7	93	11	22	3.8	19	3.7
Eu	<b>151</b>	<b>47.81 (3)</b>	<sup>135</sup> BaO, <sup>134</sup> BaOH	0.01	3.0	0.4	3.0	11	3.4	19	3.8	8.1	3.3	0.6	3.0
	153	52.19 (3)	<sup>137</sup> BaO, <sup>136</sup> BaOH	0.03	3.0	0.7	3.0	19	3.7	34	4.6	14	3.5	1	3.0
Gd	152	0.20 (1)	<sup>152</sup> Sm, <sup>136</sup> CeO, <sup>136</sup> BaO, <sup>135</sup> BaOH	*	–	*	–	*	–	*	–	*	–	*	–
	154	2.18 (3)	<sup>154</sup> Sm, <sup>138</sup> BaO, <sup>137</sup> BaOH, <sup>142</sup> NdO, <sup>138</sup> CeO	*	–	*	–	*	–	*	–	*	–	*	–
	155	14.80 (12)	<sup>138</sup> BaOH, <sup>139</sup> LaO	11	3.4	24	4.1	*	–	*	–	*	–	15	3.5
	156	20.47 (9)	<sup>156</sup> Dy, <sup>140</sup> CeO	9.9	3.4	58	7.2	*	–	*	–	*	–	30	4.5
	<b>157</b>	<b>15.65 (2)</b>	<sup>141</sup> PrO	15	3.6	12	3.5	22	4.0	61	7.6	63	7.8	6.6	3.2
	158	24.84 (7)	<sup>158</sup> Dy, <sup>142</sup> CeO, <sup>142</sup> NdO	3.8	3.1	15	3.5	29	4.2	67	7	71	7.3	9	3.3
	<b>160</b>	<b>21.86 (19)</b>	<sup>160</sup> Dy, <sup>144</sup> SmO, <sup>144</sup> NdO	14	3.5	21	3.8	24	4.0	37	4.8	43	5.4	20	3.8
Tb	<b>159</b>	<b>100</b>	<sup>143</sup> NdO	0.3	3.0	4.8	3.2	12	3.4	29	4.4	36	5.1	3.1	3.1
Dy	156	0.06 (1)	<sup>156</sup> Gd, <sup>140</sup> CeO	*	–	*	–	*	–	*	–	*	–	*	–
	158	0.10 (1)	<sup>158</sup> Gd, <sup>142</sup> CeO, <sup>142</sup> NdO	*	–	*	–	*	–	*	–	*	–	*	–
	160	2.34 (8)	<sup>160</sup> Gd, <sup>144</sup> NdO, <sup>144</sup> SmO	*	–	*	–	*	–	*	–	*	–	*	–
	161	18.91 (24)	<sup>145</sup> NdO	0.9	3.0	2.8	3.1	8	3.3	20	3.9	31	4.6	1.6	3.1
	162	25.51 (26)	<sup>162</sup> Er, <sup>146</sup> NdO	2.4	3.1	4.9	3.2	13	3.5	31	4.6	49	6.2	3.2	3.1
	<b>163</b>	<b>24.90 (16)</b>	<sup>147</sup> SmO	0.2	3.0	0.1	3.0	0.3	3.0	0.5	3.0	0.7	3.0	0.09	3.0
	<b>164</b>	<b>28.18 (37)</b>	<sup>164</sup> Er, <sup>148</sup> SmO, <sup>148</sup> NdO	12	3.4	8.2	3.3	9.2	3.3	14	3.5	20	3.8	8.2	3.3
Ho	165	100	<sup>149</sup> SmO	0.03	3.0	0.1	3.0	0.06	3.0	0.6	3.0	0.9	3.0	0.09	3.0
Er	162	0.14 (1)	<sup>162</sup> Dy, <sup>146</sup> NdO	*	–	*	–	*	–	*	–	*	–	*	–
	164	1.61 (3)	<sup>164</sup> Dy, <sup>148</sup> SmO, <sup>148</sup> NdO	*	–	*	–	*	–	*	–	*	–	*	–
	<b>166</b>	<b>33.61 (35)</b>	<sup>150</sup> SmO, <sup>150</sup> NdO	0.4	3.0	1.8	3.1	7	3.2	20	3.9	25	4.1	1	3.0
	<b>167</b>	<b>22.93 (17)</b>	<sup>151</sup> EuO	0.06	3.0	0.007	3.0	0.05	3.0	0.09	3.0	0.05	3.0	0.02	3.0
	<b>168</b>	<b>26.78 (26)</b>	<sup>168</sup> Yb, <sup>152</sup> SmO, <sup>152</sup> GdO	0.7	3.0	0.8	3.0	1.4	3.0	2.6	3.1	2.8	3.1	0.7	3.0
	170	14.93 (27)	<sup>170</sup> Yb, <sup>154</sup> GdO, <sup>154</sup> SmO	20	3.9	20	3.9	21	3.9	24	4.1	14	3.5	21	3.9
Tm	<b>169</b>	<b>100</b>	<sup>153</sup> EuO	0.01	3.0	0.01	3.0	0.07	3.0	0.1	3.0	0.09	3.0	0.03	3.0

Yb	168	0.13 (1)	<sup>168</sup> Er, <sup>152</sup> GdO, <sup>152</sup> SmO	*	–	*	–	*	–	*	–	*	–	*	–
	170	3.04 (15)	<sup>170</sup> Er, <sup>154</sup> GdO, <sup>154</sup> SmO	*	–	*	–	*	–	*	–	*	–	*	–
	<b>171</b>	<b>14.28 (57)</b>	<b><sup>155</sup>GdO</b>	1.1	3.0	1.6	3.0	3.1	3.1	5.7	3.2	7.6	3.3	1.3	3.0
	172	21.83 (67)	<sup>156</sup> DyO, <sup>156</sup> GdO	0.9	3.0	1.4	3.0	2.8	3.1	5.2	3.2	6.8	3.2	1.2	3.0
	<b>173</b>	<b>16.13 (27)</b>	<b><sup>157</sup>GdO</b>	1.0	3.0	1.5	3.0	2.9	3.1	5.4	3.2	7.1	3.2	1.2	3.0
	<b>174</b>	<b>31.83 (92)</b>	<b><sup>174</sup>Hf, <sup>158</sup>DyO, <sup>158</sup>GdO</b>	1.2	3.0	1.8	3.1	3.4	3.1	7.8	3.3	8.9	3.3	1.2	3.0
	176	12.76 (41)	<sup>176</sup> Lu, <sup>176</sup> Hf, <sup>160</sup> GdO, <sup>160</sup> DyO	52	5.6	53	6.3	93	11.4	*	–	*	–	27	4.1
Lu	<b>175</b>	<b>97.41 (2)</b>	<b><sup>159</sup>TbO</b>	1.0	3.0	1.9	3.1	2.6	3.1	4.5	3.1	6.5	3.2	1.5	3.0
	176	2.59 (2)	<sup>176</sup> Yb, <sup>176</sup> Hf, <sup>160</sup> GdO, <sup>160</sup> DyO	*	–	*	–	*	–	*	–	*	–	*	–

Element	Isotope	At.%
(b) Other interfering elements in rare earth elements determination by ICP-QMS		
Ba	130	0.106 (1)
	132	0.101 (1)
	134	2.417 (18)
	135	6.592 (12)
	136	7.854 (24)
	137	11.232 (24)
	138	71.698 (42)
Hf	174	0.16 (1)
	176	5.26 (7)
	177	18.60 (9)
	178	27.28 (7)
	179	13.62 (2)
	180	35.08 (16)

Note: Bold isotopes are often used for quantitative determination of rare earth elements by several researchers. Bold and italic isotopes are more abundant isotopes proposed in this work for quantitative determination of rare earth elements. Bold interfering species are the major contributing species of spectroscopic interference over the particular isotope. \*: Two to six orders of magnitude higher contribution as well as higher uncertainty; hence not suitable for analytical determinations. Column 3 in a and b contains at.% of different isotopes and the parenthesis indicates the uncertainties on the last digits as per recommended by IUPAC in 1997.

<sup>a</sup> Synthetic mixture containing all rare earth elements in equal proportion of ppmw.

<sup>b</sup> Calculated assuming an error of 3% on each isotope signal determination and using the contributions of different interfering species. For atomic isobaric species, isotope abundances are used and for molecular isobaric species (oxide and hydroxide), the experimentally determined oxide and hydroxide yields by pneumatic nebuliser are used.

interfering species and the measured uncertainty in those isotopes due to interference correction, in different samples with varying element composition, can decide the suitability of their choice for quantitative determination of rare earth elements. Using the recommended concentrations listed in Table 1, total contribution from different interfering species and the corresponding uncertainty were calculated for all the isotopes of various rare earth elements in a synthetic mixture of all rare earth elements in equal proportion as well as

in different geological reference materials having different elemental compositions (AC-E, AGV-1, G-2, GSP-1). Similar calculation was also performed for chondrite normally used for obtaining chondrite-normalised curves. A measurement uncertainty of 3% was assumed for the sake of calculation and comparison. The contribution and the corresponding uncertainties are listed in Table 2a. The selection of more than one isotope for different rare earth elements is discussed below.

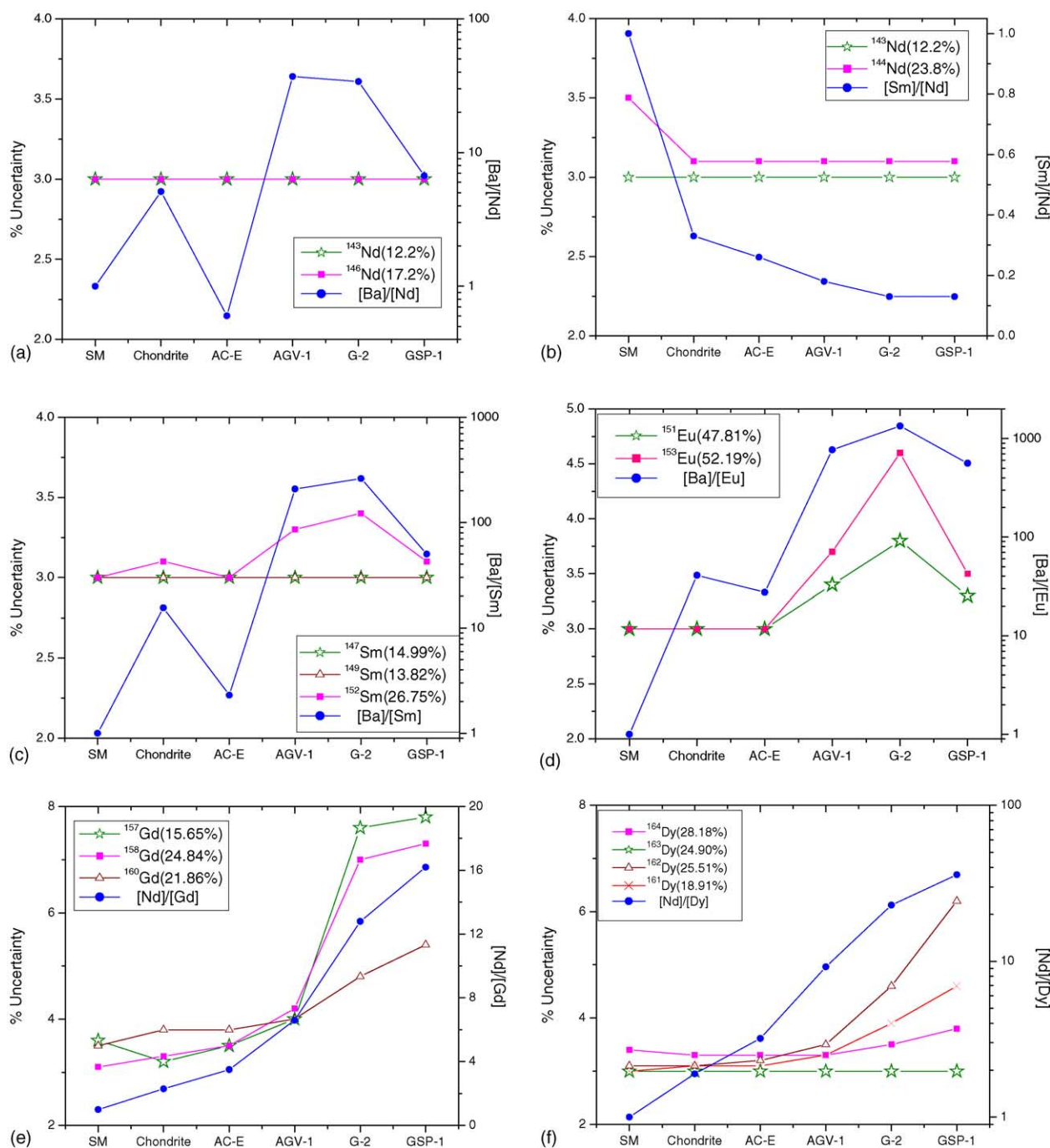


Fig. 2. Uncertainty propagation in the corrected rare earth elements in a synthetic mixture containing all rare earth elements in equal proportion and in different geological materials of different rare earth elements composition.



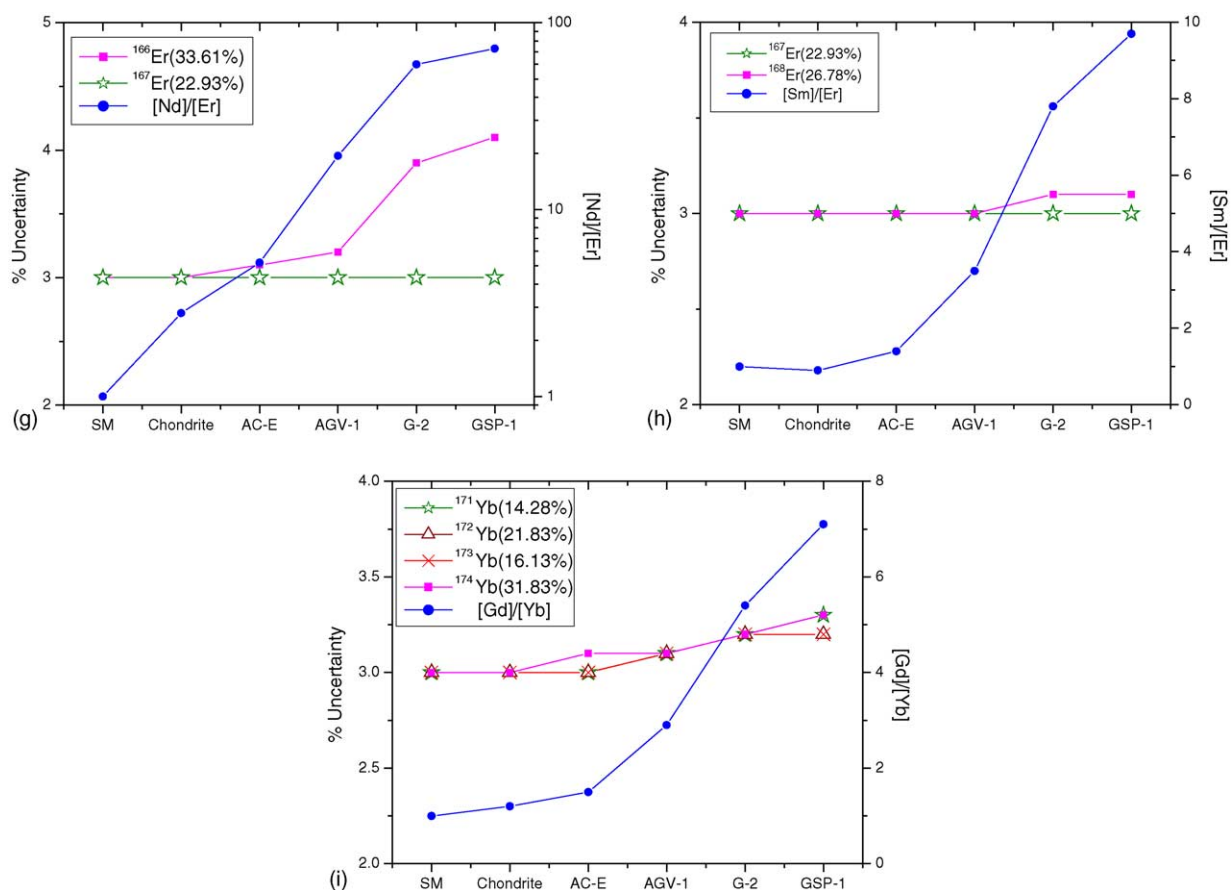


Fig. 2. (Continued).

### 5.1. Selection of isotopes for determination of rare earth elements by ICP-QMS

As mentioned in the introduction, a discussion on the choice of isotopes for determination of rare earths by ICP-QMS was given by Longerich et al. [25]. However, the discussion given below justifies the use of more than one isotope for various rare earths considering the uncertainty involved due to the interference corrections.

#### 5.1.1. Nd

In many of the reports of rare earth elements determinations by ICP-QMS,  $^{143}\text{Nd}$  (12.2 at.%) or  $^{146}\text{Nd}$  (17.2 at.%) isotopes have been used for Nd determination [3,6,12,25,29,30]. As given in Table 2a,  $^{143}\text{Nd}$  has no interference. However,  $^{146}\text{Nd}$  has interference from  $^{130}\text{BaO}$ . Fig. 2a and b show the uncertainties in determination of different Nd isotopes in various samples (synthetic mixture (SM), chondrite and different rock samples normally used as reference materials).  $^{144}\text{Sm}$  (3.07 at.%) interferes with  $^{144}\text{Nd}$  (23.8 at.%) which is the isotope of Nd having the highest abundance. However, in most of the rock samples, concentration of Sm is less than that of Nd (Fig. 2b). Hence,  $^{144}\text{Nd}$  can also be used with small correction for  $^{144}\text{Sm}$  as given in Table 2a and as shown in Fig. 2b. Other Nd isotopes viz.

$^{142}\text{Nd}$ ,  $^{145}\text{Nd}$ ,  $^{148}\text{Nd}$  and  $^{150}\text{Nd}$  have either large interferences or small isotopic abundances and are, therefore, not recommended for Nd determination using ICP-QMS.

#### 5.1.2. Sm

In case of Sm, there is no single isotope, which is interference free. Hence,  $^{147}\text{Sm}$  (14.99 at.%) [3,6,9,12,25,29,30] is the isotope used by different investigators for the determination of Sm by ICP-QMS due to extremely small contributions from  $^{130}\text{BaOH}$ . Fig. 2c shows the uncertainty in the determination of Sm in different samples with different Ba/Sm concentration ratios. The highest abundant  $^{152}\text{Sm}$  isotope (26.75 at.%) has interferences from  $^{152}\text{Gd}$ ,  $^{136}\text{CeO}$  and oxide and hydroxide of Ba. However, major contribution is from  $^{136}\text{BaO}$  and  $^{135}\text{BaOH}$ . As seen in Fig. 2c, the uncertainty in determination of Sm increases from 3 to 3.5% in G-2 with Ba/Sm concentration ratio  $>200$ .  $^{152}\text{Sm}$  with nearly double the at.% abundance as those of  $^{147}\text{Sm}$  and  $^{149}\text{Sm}$  can also be used and would improve the detection sensitivity by a factor of 2.

#### 5.1.3. Eu

In case of Eu, both the isotopes have almost the same natural abundance and are interfered by oxide and hydroxide of

Table 3

Comparison of uncertainties ( $\sigma$ ) due to interference correction in the experimentally determined isotopes of rare earth elements in AGV-1 and G-2 using ICP-MS

RE	Isotope used	AGV-1			G-2		
		Recommended concentration	Observed concentration	Corrected concentration ( $\pm\sigma$ )	Recommended concentration	Observed concentration	Corrected concentration ( $\pm\sigma$ )
La	139	38 $\pm$ 3	39	39 $\pm$ 1.2	89 $\pm$ 8	93	93 $\pm$ 2.7
Ce	140	67 $\pm$ 5	71	71 $\pm$ 2.2	160 $\pm$ 10	170	170 $\pm$ 5.1
Pr	141	7.6 $\pm$ 1.1	8.6	8.6 $\pm$ 0.0.25	18 $\pm$ 2	17.4	17.4 $\pm$ 0.52
Nd	143	33 $\pm$ 3	31.4	31.4 $\pm$ 0.9	55 $\pm$ 6	54.7	54.7 $\pm$ 1.7
	144		33.5	32.8 $\pm$ 1.4		57.9	56.9 $\pm$ 2.4
	146		31.8	31.8 $\pm$ 1.3		54.7	54.7 $\pm$ 2.3
			Mean	32.0 $\pm$ 1.4 <sup>a</sup>		Mean	55.4 $\pm$ 2.5 <sup>a</sup>
Sm	147	5.9 $\pm$ 0.4	6.2	6.2 $\pm$ 0.25	7.2 $\pm$ 0.7	7.7	7.7 $\pm$ 0.30
	152		6.6	6.1 $\pm$ 0.15		8.5	7.8 $\pm$ 0.18
	154		9.9	6.0 $\pm$ 0.24		13.1	7.4 $\pm$ 0.40
			Mean	6.1 $\pm$ 0.24 <sup>a</sup>		Mean	7.6 $\pm$ 0.37 <sup>a</sup>
Eu	151	1.6 $\pm$ 0.1	1.8	1.6 $\pm$ 0.06	1.4 $\pm$ 0.1	1.7	1.5 $\pm$ 0.03
	153		2.0	1.7 $\pm$ 0.05		1.9	1.5 $\pm$ 0.05
			Mean	1.7 $\pm$ 0.09 <sup>a</sup>		Mean	1.5 $\pm$ 0.04 <sup>a</sup>
Gd	157	5.0 $\pm$ 0.5	6.1	4.7 $\pm$ 0.18	4.3 $\pm$ 0.8	7.1	4.5 $\pm$ 0.19
	160		6.2	5.0 $\pm$ 0.24		5.8	4.3 $\pm$ 0.22
	158		5.8	4.6 $\pm$ 0.22		6.9	4.6 $\pm$ 0.25
			Mean	4.8 $\pm$ 0.30 <sup>a</sup>		Mean	4.5 $\pm$ 0.27 <sup>a</sup>
Tb	159	0.7 $\pm$ 0.1	0.8	0.7 $\pm$ 0.02	0.48 $\pm$ 0.08	0.66	0.51 $\pm$ 0.02
Dy	163	3.6 $\pm$ 0.3	3.7	3.7 $\pm$ 0.11	2.4 $\pm$ 0.3	2.4	2.4 $\pm$ 0.09
	164		4.2	4.0 $\pm$ 0.17		2.9	2.5 $\pm$ 0.11
	161		3.9	3.6 $\pm$ 0.13		3.0	2.4 $\pm$ 0.07
	162		4.1	3.6 $\pm$ 0.14		3.3	2.4 $\pm$ 0.08
			Mean	3.7 $\pm$ 0.23 <sup>a</sup>		Mean	2.4 $\pm$ 0.10 <sup>a</sup>
Ho	165	0.67 $\pm$ 0.1	0.68	0.68 $\pm$ 0.02	0.40 $\pm$ 0.06	0.39	0.38 $\pm$ 0.01
Er	167	1.7 $\pm$ 0.2	1.9	1.9 $\pm$ 0.07	0.92 $\pm$ 0.18	0.93	0.92 $\pm$ 0.03
	166		2.0	1.9 $\pm$ 0.03		1.13	0.89 $\pm$ 0.04
	168		1.9	1.9 $\pm$ 0.07		0.92	0.88 $\pm$ 0.05
		Mean	1.9 $\pm$ 0.06 <sup>a</sup>		Mean	0.90 $\pm$ 0.05 <sup>a</sup>	
Tm	169	0.34 $\pm$ 0.13*	0.27	0.27 $\pm$ 0.01	0.18 $\pm$ 0.08*	0.12	0.12 $\pm$ 0.005
Yb	171	1.72 $\pm$ 0.19	1.77	1.69 $\pm$ 0.06	0.80 $\pm$ 0.17	0.69	0.62 $\pm$ 0.03
	174		1.74	1.66 $\pm$ 0.04		0.66	0.61 $\pm$ 0.05
	172		1.69	1.62 $\pm$ 0.04		0.69	0.63 $\pm$ 0.04
	173		1.78	1.71 $\pm$ 0.06		0.71	0.65 $\pm$ 0.04
		Mean	1.67 $\pm$ 0.06 <sup>a</sup>		Mean	0.63 $\pm$ 0.04 <sup>a</sup>	
Lu	175	0.27 $\pm$ 0.03	0.28	0.27 $\pm$ 0.01	0.11 $\pm$ 0.02	0.09	0.07 $\pm$ 0.003

<sup>a</sup> Mean corrected concentrations show net uncertainty due to correction ( $\sigma_{\text{total}}$ ), obtained from  $\sigma_{\text{external}}$  and  $\sigma_{\text{internal}}$ .

\* Provisional value.

Ba. However, the isotopes of Ba in the interfering oxide and hydroxide species over <sup>153</sup>Eu have high abundances and give marginally higher correction and the corresponding uncertainty (Fig. 2d). Hence, <sup>151</sup>Eu is a better isotope compared to <sup>153</sup>Eu for Eu determination. However, both the Eu isotopes may be used for its determination without any significant difference in the results.

#### 5.1.4. Gd

In case of Gd, <sup>156</sup>Gd (20.47 at.%), <sup>157</sup>Gd (15.65 at.%), <sup>158</sup>Gd (24.84 at.%) and <sup>160</sup>Gd (21.86 at.%) are the high abundant isotopes. <sup>156</sup>Gd is interfered by <sup>140</sup>CeO seriously. In most of natural rock samples, Ce concentration is the highest amongst all the rare earth elements. Hence, <sup>156</sup>Gd cannot be used for analysis due to large interference, which leads to large uncertainty. <sup>157</sup>Gd is the most common choice for Gd [3,6,9,25,30] and is interfered by <sup>141</sup>PrO. However, the uncertainty in Gd determination using <sup>157</sup>Gd depends on the Pr con-

centration in the sample and the error increases as Pr/Gd concentration ratio increases (Table 2a, G-2 and GSP-1). <sup>158</sup>Gd has the highest natural abundance. But large corrections need to be applied due to high oxide yielding Ce and Nd, which are normally present at higher concentrations than that of Gd in rock samples. As shown in Fig. 2e and Table 2a, <sup>160</sup>Gd is the best choice, since it has higher abundance than <sup>157</sup>Gd and the % uncertainty in the correction applied is less in different samples (Fig. 2e). Also <sup>138</sup>Ba<sup>19</sup>F is another possible interference over <sup>157</sup>Gd and its degree of interference depends on the presence of HF or F in the sample. However, there is no practical way of monitoring F and HF. Hence, <sup>160</sup>Gd should be the best choice for Gd determination in unknown samples.

#### 5.1.5. Dy

<sup>163</sup>Dy is generally used for its determination due to negligible contribution from <sup>147</sup>SmO [3,6,9,12,25,29,30]. However, <sup>164</sup>Dy can also be used, especially in those samples

where Nd/Dy concentration ratio is  $<20$  as  $^{148}\text{NdO}$  is the major interfering species and there is no significant difference in the uncertainty as shown in Fig. 2f. The other isotopes viz.  $^{161}\text{Dy}$  and  $^{162}\text{Dy}$  may also be used for verifying the concentration of Dy obtained using  $^{163}\text{Dy}$  and  $^{164}\text{Dy}$  isotopes.

#### 5.1.6. Er

In determination of Er by ICP-QMS,  $^{167}\text{Er}$  is normally used due to very small interference from  $^{151}\text{EuO}$  in its determination [6,9,25,29]. However,  $^{166}\text{Er}$  having the highest natural abundance of 33.6% or  $^{168}\text{Er}$  with 26.8% natural abundance can also be used along with the commonly used  $^{167}\text{Er}$  (Fig. 2g and h).

#### 5.1.7. Yb

For Yb determination,  $^{171}\text{Yb}$  to  $^{174}\text{Yb}$  isotopes have been used in different publications [3,6,9,12,25,29,30]. However, Table 2a shows almost the same contribution on all the four isotopes of Yb in all samples, as GdO is the common interfering species. Hence, highest abundant  $^{174}\text{Yb}$  should be the best choice. Other than rare earth elements, Hf is another element, which gives interference at  $^{174}\text{Yb}$ . However, due to low abundance (0.16%) of  $^{174}\text{Hf}$  (Table 2b), its contribution over  $^{174}\text{Yb}$  is not significant.

For other rare earth elements, the selection of isotope is straightforward.  $^{139}\text{La}$ ,  $^{140}\text{Ce}$  and  $^{175}\text{Lu}$  are the isotopes with high abundances and there is no interference in case of La and Ce and small interference over Lu from  $^{159}\text{TbO}$ .  $^{141}\text{Pr}$ ,  $^{159}\text{Tm}$ ,  $^{165}\text{Ho}$  and  $^{169}\text{Tm}$  are the elements, which are mono-isotopic. Pr shows no interference and Ho and Tm show negligible interference contributions from SmO and EuO, respectively. However,  $^{159}\text{Tb}$  shows major interference from  $^{143}\text{NdO}$ , and the contribution depends on the Nd/Tb concentration ratio in sample. As the Nd/Tb ratio increases from chondrite to GSP-1, the uncertainty in the corrected Tb concentration increases from 3 to 5%.

### 5.2. Experimental demonstration of uncertainty propagation due to interference correction in determination of rare earth elements in AGV-1 and G-2 using the proposed high abundant isotopes

The use of different proposed isotopes of various rare earth elements has been demonstrated experimentally for the uncertainty propagation due to interference correction by analyzing two rock samples (AGV-1 and G-2) using ICP-QMS. The non-spectroscopic interferences that often arise due to matrix effect or due to instrumental fluctuations have been corrected using indium as an internal standard.  $^{115}\text{In}$  was used as an internal standard because of its high natural abundance. It shows isobaric interference with  $^{115}\text{Sn}$  (0.34%) and  $^{99}\text{RuO}$ . Hence, both the rock samples (AGV-1 and G-2) were checked for Sn and Ru. The concentration of Ru in both the samples is below the detection limits. Due to low natural abundance of  $^{115}\text{Sn}$ , its contribution to internal standard ( $^{115}\text{In}$ ) signal was  $<0.1\%$  and hence was neglected.

Table 3 shows the results of determination of rare earth elements in AGV-1 and G-2 using the commonly used as well as other proposed isotopes by ICP-QMS and their comparison on basis of uncertainty due to interference corrections. The measured intensities of the isotopes used in the calculations were blank subtracted and the net uncertainty obtained from the standard deviations of gross intensity and blank was used for determining the propagation uncertainty due to correction methodology. The R.S.D.% on the intensity values used for correction would lead unnecessarily larger errors than using R.S.D.% on ratios in cases when isotope ratios are measured with high precision using multi-collector detector system. However, the difference between the two approaches is marginal in the present case, since both the isotope ratios as well as intensity values have comparable uncertainties in view of the single detector used. The isotopes for each element are placed in the order of preference of their usage for particular rare earth element determination. As an example, in case of Nd,  $^{143}\text{Nd}$  (12.2 at.%) having no isobaric interference is quite often used for its determination by different researchers. The proposed  $^{144}\text{Nd}$  isotope in this work having almost double natural abundance (23.8 at.%) compared to  $^{143}\text{Nd}$  shows isobaric interference from  $^{144}\text{Sm}$ . After applying the interference correction for  $^{144}\text{Sm}$ , the uncertainty was found to be 4% in Nd determination using  $^{144}\text{Nd}$  compared 3% using  $^{143}\text{Nd}$  in both the rock samples (AGV-1 and G-2). Similarly in case of Sm,  $^{147}\text{Sm}$  (14.99 at.%) is the commonly used isotope for Sm determination by different researchers, due to negligible interference from  $^{130}\text{BaOH}$ . The proposed isotope  $^{152}\text{Sm}$  having almost double the natural abundance (26.75 at.%) compared to that of  $^{147}\text{Sm}$  shows interferences from  $^{136}\text{BaO}$  and  $^{135}\text{BaOH}$ . After accounting for the interferences, the uncertainty due to correction in the determination of Sm concentration using  $^{152}\text{Sm}$  should be more than that using  $^{147}\text{Sm}$  in AGV-1 and in G-2 rock samples (Table 2a). However, experimentally it was found that the uncertainty due to correction in the determination of Sm concentration using  $^{152}\text{Sm}$  is lesser (3% in AGV-1 and 2% in G-2) than that using  $^{147}\text{Sm}$  (4% in both AGV-1 and G-2) (Table 3). This is due to the more precised measurement of high abundant isotope ( $^{152}\text{Sm}$ ) of Sm than the low abundant one ( $^{147}\text{Sm}$ ).  $^{154}\text{Sm}$  is another high abundant isotope which was used for quantification. However, due to large corrections for  $^{138}\text{BaO}$  and  $^{137}\text{BaOH}$ , the uncertainty in the corrected concentration of Sm using this isotope is more than that obtained by using the other isotopes. In case of Gd,  $^{160}\text{Gd}$  isotope should be preferred compared to routinely used  $^{157}\text{Gd}$ , especially for G-2 or other samples where Pr/Gd amount ratio is likely to be higher. For other rare earth elements, having multiple choices of isotopes for quantification, the uncertainties due to interference corrections in the corrected concentrations are found to be practically same. Hence, high abundant isotopes amongst them are preferable for quantification. One should note that the corrected concentrations using those high abundant but relatively more interfered isotopes show comparable uncertainties. Hence, it is advisable to use

these isotopes also in quantification in order to improve the sensitivity.

Since, ICP-MS is a multi-elemental determination technique, the determination of more than one element along with their different isotopes is possible at a time. Also the time required for multiple isotopes determination is not significantly large. Using Microsoft Excel worksheet, correction methodology can be easily applied. With the speed and ease of application of correction methods without any additional experimental effort, the enhanced sensitivity using high abundant isotope is an added advantage, since, the uncertainty due to the corrections in most of the high abundant and the commonly used isotopes is practically same.

## 6. Conclusion

The propagation of measurement uncertainties through the correction methodology has been studied for different isotopes of rare earth elements in the range of  $m/z$  130–176. It has been shown that the uncertainty propagation through the correction methodology increases with the increase in contribution from interfering species. At the same time, assuming the same total contribution, the uncertainty decreases with the number of contributing species. The estimation of degree of interference and the corresponding uncertainty after its correction facilitates the choice for high abundant isotopes in determination of rare earth elements using ICP-QMS. The proposed isotopes have been tested experimentally in two geological samples (AGV-1 and G-2), which are commonly used as reference standards for rare earth elements determination by ICP-QMS. The comparable uncertainties due to interference correction are obtained in the corrected concentrations, by the commonly used and proposed isotopes. This proved the suitability of high abundant isotopes for sensitive detection, for some of the rare earth elements.

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