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Determination of rare earth impurities in high purity samarium oxide using inductively coupled plasma mass spectrometry after extraction chromatographic separation

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Abstract

A method for the determination of trace of 14 rare earth elements (REEs) as impurities in high purity samarium oxide (Sm_2O_3) using inductively coupled plasma mass spectrometry (ICP-MS) was described. Analytes, such as La, Ce, Pr, Nd, Eu, Gd, Tb, Lu and Y were measured without Sm matrix separation because of no interference problems occurring that could affect the analysis of these elements. On the other hand, analytes, such as Dy, Ho, Er, Tm and Yb were carried out after Sm matrix being eliminated completely by means of 2-ethylhexyl hydrogen-ethylhexy phosphonate (EHEHP) extraction chromatographic separation. The inherent problem associated with matrix-induced suppression was effectively compensated with spiking In as internal standard element and the mass spectra isobaric interferences of atomic and molecular ions arose from Sm matrix had been overcome after the removal of Sm matrix. The limits of quantitations (LOQ) for 14 REEs impurities were from 0.01 to 0.07 $\mu g\, g^{-1}$ together with the recoveries of spiking sample of 14 REEs were found to be in the range of 85–110% and the proposed method precision was less than 5%. A synthetic standard Sm_2O_3 sample with well-known 14 REEs concentrations was prepared and analysed in order to prove the accuracy and precision of the proposed method together with another high purity Sm_2O_3 was also measured using ICP-MS. The methodology had been found to be suitable for the determination of trace of 14 REEs in 99.999–99.9999% high purity Sm_2O_3.

Keywords: Rare earth impurity; High purity samarium oxide; Inductively coupled plasma mass spectrometry; Extraction chromatographic separation

1. Introduction

High purity rare earth materials are extensively employed in various applications connected with electronics, nuclear technical materials, phosphor materials and other industrial applications of importance. In many of these applications, the properties are considerably affected by the concentrations of impurity elements. It is, therefore, essential to have sensitive, rapid and reliable methods for the determination of trace of REEs so as to satisfy the needs for quality control, certification and evaluation of material performance.

In recent years, glow discharge mass spectrometry (GD-MS), ICP-MS and laser ablation ICP-MS (LA-ICP-MS) have been widely applied as the most important inorganic mass spectrometric methods for the analysis of trace or ultratrace elements in analytical fields, such as high purity materials, environment, metallurgy etc. due to their capability to provide a very sensitive multielemental analysis. However, the quantification of the analytical results acquired from GD-MS and LA-ICP-MS are sometimes difficult because of a lack of matrix-fitted multielement standard reference materials for many solid samples. Comparing with GD-MS and LA-ICP-MS techniques, ICP-MS has its excellent analytical abilities and this makes the quantification simple for solid samples after sample dissolution. Today, ICP-MS has been widely used in many fields of material science and technology [1–18]. Many papers described the widely

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applications of ICP-MS for the determination of trace or ultra-trace REEs as impurities exist in other high purity rare earth samples or other materials in spite of some potential problems encountered in the analytical procedures, such as matrix suppression and isobaric interferences of atomic and molecular ions [2–4,11–13,16,18–29]. The matrix suppression could be compensated by means of adding internal standard because the intensity of internal standard element and analytes of interest decreased at the same time with matrix concentration increasing [2,17,19–25]. However, the problem of mass spectra interferences could critically restrict ICP-MS analytical capabilities of the analysis of many high purity rare earth materials [19–20]. Separation matrix as well as other methodologys could be taken in order to solve this inherent interfering problems. Takaku et al. [21] reported a method of doubly charged ions for analysis of REEs in 99.99% Gd_2O_3 using high-resolution ICP-MS. However, the sensitivities of these analytes were not high enough. Zhang et al. [22] described the detection of REEs impurities in high purity Eu_2O_3. Unfortunately, isobaric interferences arose from Eu^+, such as $^{153}EuO^+$ and $^{153}Eu^{18}OH^+$ ions seriously interfered the analysis of $^{169}Tm^+$ and $^{172}Yb^+$. Kawabata et al. [23] evaluated the analysis of high purity La_2O_3 and Gd_2O_3 using ICP-MS combined with ion chromatographic (IC) after matrix being completely removed on-line, respectively. Day et al. successfully developed an analytical procedure using capillary electrophoresis coupled on-line to a double-focusing sector field ICP-MS (CE-ICP-MS) for the analysis of mixtures of REEs in aqueous samples [16]. Otherwise, ICP-MS coupled on-line to liquid chromatographic (LC-ICP-MS) were also used in the analytical procedures in high purity rare earth samples [24–27]. On the other hand, some chemical separation procedures, such as liquid–liquid extraction [12], solvent extraction [13,30] and chromatographic extraction [28,29] were also used prior to ICP-MS detection for the analysis of high purity rare earth materials and other materials. Cao et al. [28] and Zhang et al. [29] investigated the analysis of high purity Gd_2O_3 and metal Yb by ICP-MS after extraction chromatographic separation using EHEHP. In their works, isobaric interferences of atomic and molecular ions arose from matrix were eliminated effectively. In the case of the analysis of 99.999–99.9999% Sm_2O_3, isobaric interferences lead to the failure of the detection of Dy, Ho, Er, Tm and Yb. Fewer of paper evaluated the determination of high purity Sm_2O_3 using ICP-MS. Zhang et al. [31] investigated the determination of trace of REEs as impurities in high purity metal Sm using ICP-MS with a matrix-fitted methodology. However, the problem encountered with the method was difficult to grasp sometimes in terms of acquiring homogenous standards which matched the samples in chemical and physical characteristics. By referring to this, the determinate purity of Sm was only realized to 99.9% in spite of its purity approaching to 99.999–99.9999% because the isobaric interferences of atomic and molecular ions were not eliminated using this method described above.

The aim of this work was to develop a reliable and effective method based on EHEHP extraction chromatographic separation for trace of REEs impurities and Sm matrix prior to ICP-MS detection.

2. Experimental

2.1. Instrumentation of ICP-MS

A Perkin-Elmer SCIEX ELAN 9000 ICP-MS (Perkin-Elmer, Inc., Wellesley, MA, USA) equipped with a integrated peristaltic pump and a cross flow nebulizer combined with a Scott spray chamber which was made from Ryton^{TM} material was used. The instrument conditions are listed in Table 1. Checking the instrumental performance using a mixture $10\,\mu g\,L^{-1}$ solution contained In, Mg, Pb, Ce and Ba (also obtained from Perkin-Elmer, Inc). Confirming that the sensitivity was more than about 4.0×10^5 counts per second (cps) for ^{115}In, 3.0×10^5 cps for ^{24}Mg and 4.0×10^5 cps for ^{208}Pb, respectively, together with the percentage ratios of $^{140}Ce^{16}O^+/^{140}Ce^+$ and $^{137}Ba^{2+}/^{137}Ba^+$ were less than 1.0% as well as the background was less than 5 cps at mass number 220. Table 1 also lists the conditions of ELAN 6000 ICP-MS.

2.2. Instrumentation connected with chemical separation

A model 78-1 magnetism heated pulsator (Leqing, Zhejiang, PR China) was used to help EHEHP resin to be sublimated. A model 501 thermostatic bath (Shanghai, PR China) was also used to accurately control the temperature at 50 ± 0.5 °C during the separation procedures. On the other hand, a four glass column (Ø 25 mm × 700 mm) with heating jacket obtained from Beijing Glass Instrument Factory (Beijing, PR China) was used for the extraction chromatographic separation.

In the separation procedures using ion exchange chromatographic column, EHEHP resin was used as stationary phase together with different acid concentration of HCl solutions as mobile phase. Cation exchange realized between the rare earth ions and the H^+ ions in the radical of EHEHP. Finally, trace of REEs impurities and a large amount of matrix were separated completely by means of eluting with different acid concentration of HCl solutions. In this work, ICP-MS was used as an off-line detector in order to detect the REEs impurities in high purity Sm_2O_3. A schematic diagram of the chemical separation procedures is shown in Fig. 1.

Table 1
Operating condition of ELAN 9000 and ELAN 6000 ICP-MS

	ELAN 9000	ELAN 6000
RF power (W)	900	900
Nebulizer gas flow ($L\,min^{-1}$)	0.90	0.90
Lens voltage (V)	6.75	8.25
Analog stage voltage (V)	−1950	−2100
Pulse stage voltage (V)	1100	1100
Discriminator threshold (V)	70	10
Ac rod offset (V)	−6	−6
Resolution ($m/\Delta m$)	0.60–0.70	0.60–0.70
Detector	Dual	Dual
Solution uptake rate ($mL\,min^{-1}$)	1.1	1.0
Sweeps/reading	3	3
Replicates	3	3
Scan mode	Peak hopping	Peak hopping
Dwell time (ms)	50	50

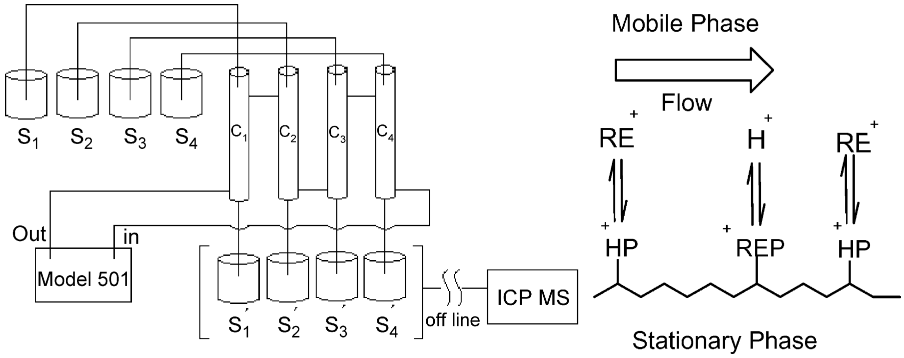

Fig. 1. Schematic diagram of the chemical separation procedures using ion exchange chromatographic column S_1, S_2, S_3 and S_4, sample solution; C_1, C_2, C_3 and C_4, ion exchange chromatographic column; S'_1, S'_2, S'_3 and S'_4, collective solution; model 501, thermostatic bath; RE^+, rare earth ions; ^+HP, radical of EHEHP; mobile phase, different acid concentration of HCl solutions; stationary phase, EHEHP resin.

2.3. Reagent and labware

The superpure HNO_3 ($14\,mol\,L^{-1}$) and HCl ($10\,mol\,L^{-1}$) used in this work were acquired from analytical-reagent grade HNO_3 and HCl under sub-boiling condition. H_2O_2 ($9.7\,mol\,L^{-1}$) and NH_4Cl were also analytical-reagent grade. All of these reagents were purchased from Shanghai Chemical Reagent Co., Ltd. (Shanghai, PR China). EHEHP resin was acquired from Baotou Research Institute of Rare Earth (Baotou, Inner Mongolia, PR China). Sample solution and finally washed water for all labwares including purification of resin and chromatographic columns was prepared from a TYUV05 purified water unit with resistivity being more than $18.3\,M\Omega\,cm$ (Tao Yuan Co., Ltd., Nanchang, PR China).

A 100 mL beakers and volumetric flasks made of glass were all obtained from Beijing Glass Instruments Factory (Beijing, PR China). In order to reduce blank value, all of these labwares used in this work were carefully washed with 10% HNO_3 (v/v) and then washed repeatedly with ultrapure water.

2.4. Standard calibration solution preparation

Two series of mixed standard solutions were prepared from the stock solutions of 14 REEs with concentration of $100\,\mu g\,L^{-1}$, individually (also obtained from Perkin-Elmer, Inc.). A group of the mixed standard solutions including La, Ce, Pr, Nd, Eu, Gd, Tb, Lu and Y were used in the determination of these analytes of interest and a other group of the mixed calibration solutions including Dy, Ho, Er, Tm and Yb were used in the measurement of these analytes after removal of Sm matrix by means of extraction chromatographic separation. The concentrations linked with the two series of these mixed standard solutions were 5 and $10\,\mu g\,L^{-1}$, respectively. Moreover, In was spiked as internal standard in each of the standard solutions as well as the final acid concentration was adjusted to 1% HNO_3 (v/v).

2.5. Analytical procedure

2.5.1. Determination without matrix separation

A sample of 99.999% high purity Sm_2O_3 which was acquired from Hunan Institute of Rare Earth Material (Hunan, PR China) was weighted with two parts of 0.1000 g, respectively, into 100 mL beakers and decomposed with 10 mL ultrapure water and 2 mL superpure HNO_3 on a hot plate which was heated approximately to about 80 °C. In addition, a 0.5 mL H_2O_2 was added while Sm_2O_3 was decomposing. After the dissolving solution cooled, transferred it into a 100 mL volumetric flask, individually, and finally diluted with ultrapure water. The concentration of Sm_2O_3 in solution was $1000\,\mu g\,mL^{-1}$ and In was also spiked as internal standard with the concentration of $10\,\mu g\,L^{-1}$. Prepared blank solution like this at the same time and completed the analysis of the analytes of interest using ICP-MS. On the other hand, considering the lack of a certified high purity Sm_2O_3 standard material, a synthetic Sm_2O_3 standard sample was prepared from a 99.999% Sm_2O_3 (also obtained from Hunan Institute of Rare Earth Material, Hunan, PR China). The final solution contained $1000\,\mu g\,mL^{-1}$ Sm_2O_3 and the concentration of REEs, such as La, Ce, Pr, Nd, Eu, Gd, Tb, Lu and Y was $2.0\,\mu g\,L^{-1}$, individually, and that of In was $10\,\mu g\,L^{-1}$.

2.5.2. Extraction chromatographic separation measurement

2.5.2.1. Purification of EHEHP resin. A 400 g EHEHP resin mixed with 1000 mL 1:1 HCl (v/v) in a 2000 mL beaker on the plate of the magnetism heated pulsator was constantly whisking for about 12 h with the temperature setting to about 40 °C. Shutting off the magnetism heated pulsator after this procedure completed and let the solution stay without any whisking through all night in order to divaricate the solution in two layers automatically. Then the aqueous phase was discarded and the organic phase including EHEHP resin was purified with ultrapure water on the pulsator. Repeating this procedure described above until the concentration of Fe^{3+} in the discard of aqueous phase was near to the value of the blank solution (detected by ICP-MS). Finally, mixing the EHEHP resin with ultrapure water to prepare the separation column.

2.5.2.2. Preparation of separation column. Loading the purified EHEHP resin into the glass column with natural deposition. When the resin bed reached a height of about 65 cm, covering the top of the resin bed with glass wool and then added the ultrapure water into the column and keeping a 2 cm height over the top of the resin bed.

2.5.2.3. Determination of the extraction chromatographic separation. Three parts of the same high purity Sm_2O_3 were weighted with 50 mg, respectively, into 50 mL beakers and digested like the part of Section 2.5.1 described. Keeping the volume of the solution with about 5 mL and then loading the solution into the separation column, individually. Eluting the column with different acid concentrations of HCl. After all, the eluted solution about 200 mL including Dy, Ho, Er, Tm, Yb and fewer fraction of Tb was collected and then the solution was evaporated to near 80 mL on a hot plate. After the solution cooled, transferred it into a 100 mL volumetric flask and finally diluted with ultrapure water. In was also spiked with concentration of $10\,\mu g\,L^{-1}$. Preparing blank solution like this separation procedure described above and taking the determination of the analytes of interest using ICPMS. As has been already pointed out like the part of Section 2.5.1, a synthetic Sm_2O_3 standard sample was also prepared from the same high purity Sm_2O_3 sample. Before the separation procedure, the synthetic standard sample solution with volume of about 5 mL contained 50 mg Sm_2O_3 and the additional quantity of Dy, Ho, Er, Tm and Yb was 200 ng, respectively. Finally, the synthetic standard collective solution was also evaporated and transferred into a 100 mL volumetric flask. In was also spiked with concentration of $10\,\mu g\,L^{-1}$.

2.6. ICP-MS determination

In the procedures of determination of trace of 14 REEs impurities in high purity Sm_2O_3 using ELAN 9000 ICP-MS, setting the instrumental mass resolution value to $0.7m/\Delta m$ for the measurement of $^{89}Y^+$, $^{139}La^+$, $^{140}Ce^+$, $^{141}Pr^+$, $^{157}Gd^+$, $^{159}Tb^+$, $^{161}Dy^+$, $^{165}Ho^+$, $^{167}Er^+$, $^{169}Tm^+$, $^{174}Yb^+$ and that to $0.6m/\Delta m$ for the analysis of $^{143}Nd^+$ and $^{151}Eu^+$. The matrix solutions with concentrations of 0, 300, 500, 700 and $1500\,\mu g\,mL^{-1}$, respectively, were used to take the matrix suppression experiment. Moreover, higher abundant isotopes of the analytes of interest were selected along with considering that the analytes were free from the isobaric interferences of atomic and molecular ions.

3. Results and discussion

3.1. Mass spectra interferences arose from Sm matrix

Many publishers have evaluated the isobaric interferences of atomic and molecular ions generated from matrix in the case of determination for the trace of REEs as impurities exist in other high purity rare earth materials using ICP-MS [2,16,19–23,28–31]. Sm has seven naturally occurring isotopes, such as ^{144}Sm, ^{147}Sm, ^{148}Sm, ^{149}Sm, ^{150}Sm, ^{152}Sm and ^{154}Sm. Table 2 lists the circumstance of mass spectra isobaric interferences arose from Sm matrix combined with oxygen and hydrogen and the determinate apparent concentrations of these molecular ion formation generated from $500\,\mu g\,mL^{-1}$ Sm_2O_3

Table 2
Isobaric interferences and the apparent concentrations ($\mu g\,mL^{-1}$, $n = 3$) of the molecular ion formation generated from $500\,\mu g\,mL^{-1}$ Sm_2O_3 (with purity of 99.999%) solution

Isotopes (abundance %)	Molecular ion formation					Interfered isotopes (abundance %)
	SmH^+	SmO^+	$SmOH_{1-3}{}^+$			
^{144}Sm (3.1)	$^{144}SmH^+$	$^{144}SmO^+$	$^{144}SmOH^+$	$^{144}SmOH_2{}^+$	$^{144}SmOH_3{}^+$	^{145}Nd (8.3), ^{160}Gd (21.7), ^{160}Dy (2.3), ^{161}Dy (18.9), ^{162}Dy (25.5), ^{162}Er (0.14), ^{163}Dy (24.9)
Concentration	0.00022	0.16	0.0043	0.00088	0.00001	
R.S.D. (%)	3.9	3.7	2.3	2.9	4.3	
^{147}Sm (15.0)		$^{147}SmO^+$	$^{147}SmOH^+$	$^{147}SmOH_2{}^+$	$^{147}SmOH_3{}^+$	^{148}Nd (5.7), ^{163}Dy (24.9), ^{164}Dy (28.2), ^{164}Er (1.6), ^{165}Ho (100), ^{166}Er (33.4)
Concentration		0.74	0.021	0.00421	0.0006	
R.S.D. (%)		4.7	3.3	2.7	4.4	
^{148}Sm (11.2)		$^{148}SmO^+$	$^{148}SmOH^+$	$^{148}SmOH_2{}^+$	$^{148}SmOH_3{}^+$	^{148}Nd (5.7), ^{164}Dy (28.2), ^{164}Er (1.6), ^{165}Ho (100), ^{166}Er (33.4), ^{167}Er (22.9)
Concentration		0.55	0.016	0.0031	0.00004	
R.S.D. (%)		2.9	3.7	2.2	4.2	
^{149}Sm (13.8)		$^{149}SmO^+$	$^{149}SmOH^+$	$^{149}SmOH_2{}^+$	$^{149}SmOH_3{}^+$	^{150}Nd (5.6), ^{165}Ho (100), ^{166}Er (33.4), ^{167}Er (22.9), ^{168}Er (27.0), ^{168}Yb (0.14)
Concentration		0.68	0.019	0.0038	0.00006	
R.S.D. (%)		2.7	2.3	3.3	3.9	
^{150}Sm (7.4)	$^{150}SmH^+$	$^{150}SmO^+$	$^{150}SmOH^+$	$^{150}SmOH_2{}^+$	$^{150}SmOH_3{}^+$	^{150}Nd (5.6), ^{151}Eu (47.8), ^{166}Er (33.4), ^{167}Er (22.9), ^{168}Er (27.0),^{168}Yb (0.14), ^{169}Tm (100)
Concentration	0.00052	0.36	0.01	0.002	0.00003	
R.S.D. (%)	2.6	2.7	3.7	3.5	3.2	
^{152}Sm (26.7)	$^{152}SmH^+$	$^{152}SmO^+$	$^{152}SmOH^+$	$^{152}SmOH_2{}^+$	$^{152}SmOH_3{}^+$	^{152}Gd (0.20), ^{153}Eu (52.2), ^{168}Er (27.0), ^{168}Yb (0.14), ^{169}Tm (100),^{170}Er (15.0), ^{170}Yb (3.0), ^{171}Yb (14.3)
Concentration	0.0018	1.32	0.037	0.0074	0.0001	
R.S.D. (%)	2.2	4.4	3.2	4.7	3.2	
^{154}Sm (22.8)	$^{154}SmH^+$	$^{154}SmO^+$	$^{154}SmOH^+$	$^{154}SmOH_2{}^+$	$^{154}SmOH_3{}^+$	^{154}Gd (2.2), ^{155}Gd (14.9), ^{170}Er (15.0), ^{170}Yb (3.0), ^{171}Yb (14.3), ^{172}Yb (21.9), ^{173}Yb (16.2)
Concentration	0.0014	1.13	0.032	0.0064	0.0001	
R.S.D. (%)	2.3	4.9	3.7	1.5	2.5	

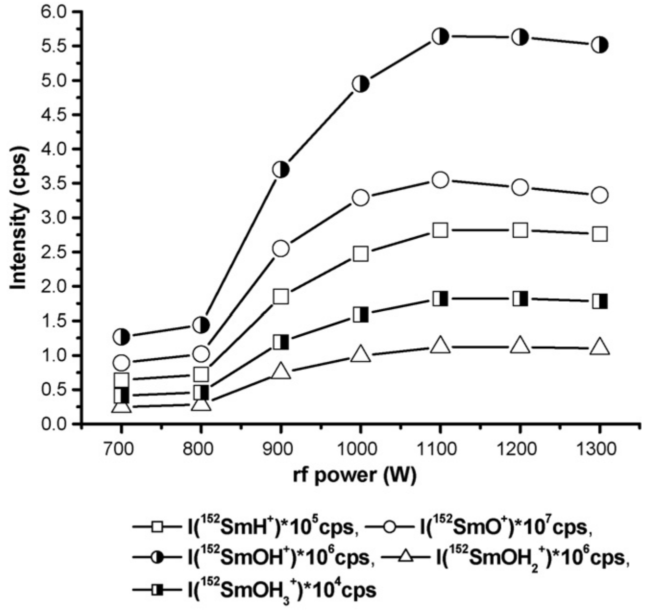

Fig. 2. Intensity of molecular ion formation of $^{152}Sm^+$ in 500 μg mL^{-1} Sm_2O_3 (99.999%) solution vs. RF power. Mass resolution, 0.70*m*/Δ*m*; Nebulizer gas flow rate, 0.90 L min^{-1}.

(with purity of 99.999%) solution. It can be seen from Table 2 that the determination of trace of REEs, such as Nd, Eu, Gd, Dy, Ho, Er, Tm and Yb suffered from the mass spectra interferences. Interferences arose from Sm matrix overlapping on $^{143}Nd^+$ and $^{151}Eu^+$ can be neglected by means of setting the mass resolution value to 0.6*m*/Δ*m* during analytical procedure [20] and the analysis of Gd could carry out through selecting the isotope of ^{157}Gd in order to avoid the isobaric interferences, such as $^{152}Sm^+$, $^{154}Sm^+$ on $^{152}Gd^+$, $^{154}Gd^+$, individually, and $^{154}SmH^+$ on $^{155}Gd^+$. But considering with the molecular ion interferences, such as SmO^+ and $SmOH_{1-3}{}^+$ that seriously affect the determination with precision and accuracy connecting with Dy, Ho, Er, Tm and Yb. By referring to Table 2, the apparent concentrations of the molecular ion formation arose from 500 μg mL^{-1} Sm_2O_3 matrix solution ranged from 0.00001 to 1.32 μg mL^{-1} and the interfering formation, such as SmO^+ was the most serious interference covered on the analytes of interest.

According to Table 2, Table 3 presents the apparent concentration of each of the interfered mass number. It is evident from Table 3, if we determined the trace of Dy, Ho, Er, Tm and Yb without considering the separation of Sm matrix, we could only realize to get a 99.0% purity even if the purity of Sm_2O_3 was from 99.999–99.9999% because of the isobaric interferences of molecular ion formation.

3.2. Influence of RF power and nebulizer gas flow rate on molecular ion formation

Figs. 2 and 3 illustrate the influence of RF power and nebulizer gas flow rate of ICP-MS on the molecular ion formation of $^{152}Sm^+$ which is a isotope having the highest abundance among the naturally occurring isotopes of Sm.

Table 3
Apparent concentration (μg mL^{-1}, $n = 3$) of interfered mass number arose from 500 μg mL^{-1} Sm_2O_3 (with purity of 99.999%) solution

	Interfered mass																	
	145	151	153	155	160	161	162	163	164	165	166	167	168	169	170	171	172	173
Concentration	0.00022	0.00052	0.0018	0.0014	0.16	0.0043	0.00088	0.74	0.57	0.70	0.37	0.014	1.32	0.037	1.14	0.032	0.0064	0.0001
R.S.D.	3.3	4.2	1.8	3.0	3.5	2.2	2.6	3.3	2.5	2.1	2.3	3.0	4.0	2.1	4.2	3.3	1.6	3.0

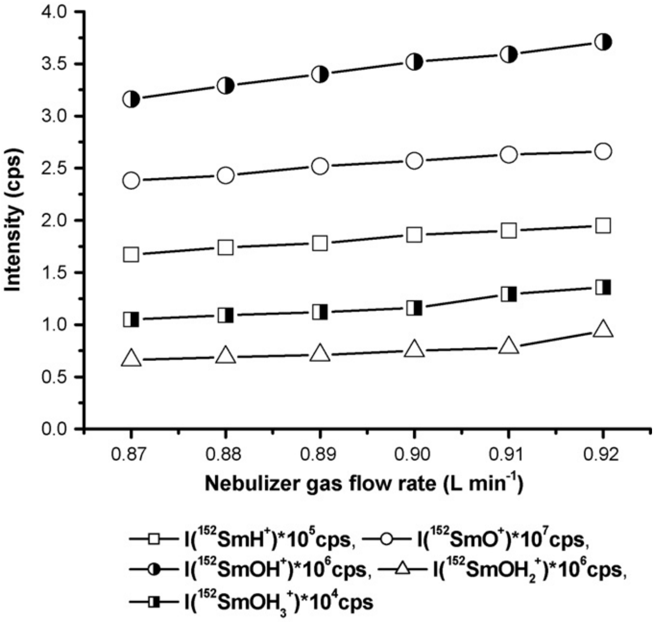

Fig. 3. Intensity of molecular ion formation of $^{152}Sm^+$ in 500 μg mL^{-1} Sm_2O_3 (99.999%) solution vs. Nebulizer gas flow rate. Mass resolution, 0.70$m/\Delta m$; RF power, 900 W.

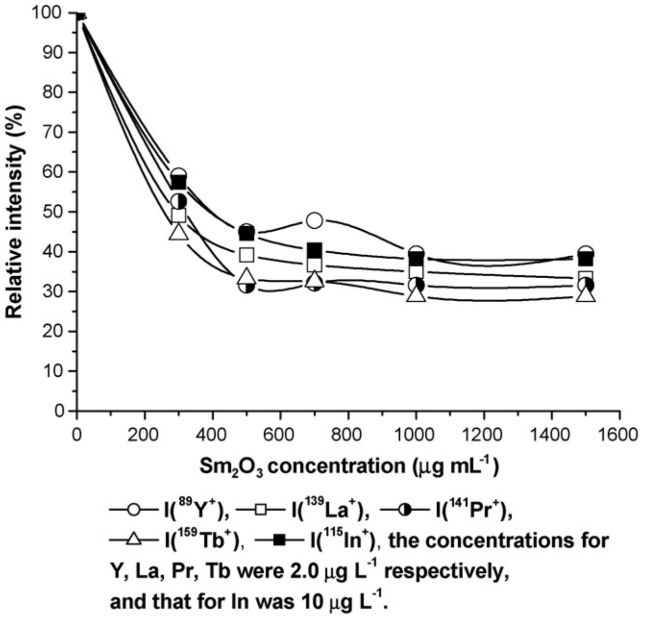

Fig. 4. Relative intensity vs. Sm_2O_3 matrix concentration.

A 500 μg mL^{-1} Sm_2O_3 (99.999%) solution was used to carry out these tests. It can been seen from Fig. 2 that the intensity of the molecular ion formation of $^{152}Sm^+$, such as $^{152}SmH^+$, $^{152}SmO^+$ and $^{152}SmOH_{1-3}{}^+$ continuous increase with the RF power increase and finally, remain slightly decrease after the value of RF power equal to 1100 W. A lower RF power was usually used in order to decrease the productive ratios of these molecular ion formation. As shown in Fig. 3, the intensity of these molecular ion formation mentioned above increase slightly with the nebulizer gas flow rate continuous increase. It was favorable for decrease the productive ratios of molecular ion formation with decrease the nebulizer gas flow rate.

3.3. Matrix suppression effect and internal standard

Matrix suppression effect is an inherent problem during rare earth materials being analyzed using ICP-MS [1,2,19, 20,22,24–26,28–31]. In this work, six solutions of 99.999% high purity Sm_2O_3 matrix with 0, 300, 500, 700, 1000 and 1500 μg mL^{-1} spiked with Y, La, Pr, Tb of 2.0 μg L^{-1}, respectively, were used to carried out this tests as well as 10 μg L^{-1} In was also spiked in these solutions as internal standard.

Fig. 4 presents the results connected with $^{89}Y^+$, $^{139}La^+$, $^{141}Pr^+$, $^{159}Tb^+$ and $^{115}In^+$. Each point represents its intensity relative to that of Sm_2O_3 matrix free solution. On the other hand, Fig. 5 shows the compensable effect of In using the ratios of the intensity of each analyte to that of In. It is evident from Fig. 4 that the relative intensity of $^{89}Y^+$, $^{139}La^+$, $^{141}Pr^+$, $^{159}Tb^+$ continuous decrease with the matrix concentration constantly increase. When the matrix concentration equals to 500 μg mL^{-1}, the relative intensity of those analytes remain approximately constant. The phenomenon of $^{115}In^+$ changing with Sm_2O_3 matrix is very similar to that of $^{89}Y^+$, $^{139}La^+$, $^{141}Pr^+$, $^{159}Tb^+$. In this work, sample dilution factor of 1000 was used for the determination of the trace of REEs impurities without matrix separation, the signal intensity decreased ratios of the analytes of interest ranged about from 60% to 70%. However, that for In was also from about 60% to 70%.

As shown in Fig. 5 that the ratios of the intensity of $^{89}Y^+$, $^{139}La^+$, $^{141}Pr^+$ and $^{159}Tb^+$ to that of $^{115}In^+$ at different Sm_2O_3 matrix concentration keep approximately a straight line, individually. We can conclude spiking In as internal standard can effectively compensate the potential problem associated with matrix suppression.

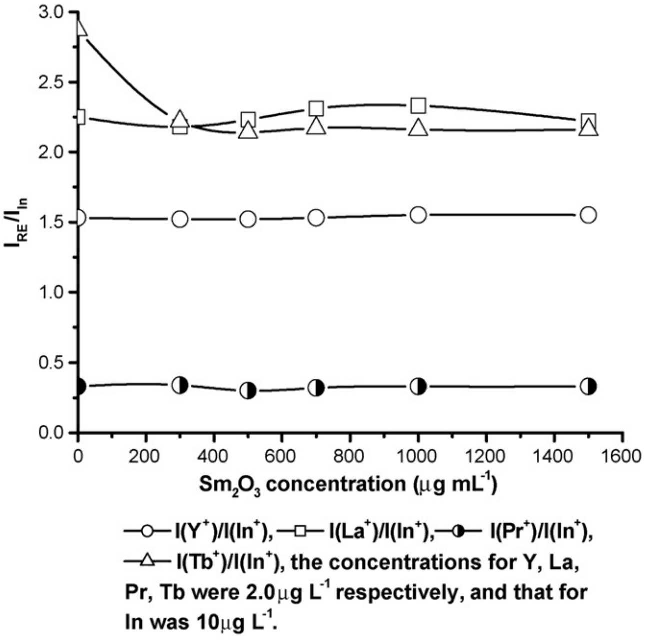

Fig. 5. Compensable effects of In vs. Sm_2O_3 concentration.

3.4. Features dealing with extraction chromatographic separation

In order to overcome the isobaric interferences of atomic and molecular ion, some critical features dealing with extraction chromatographic separation must be considered: blank value of separation procedure, eluted acid concentration control and separation efficiency.

3.4.1. Blank value of separation procedure

It was necessary that purifying EHEHP resin repeatedly like the part of Section 2.5.2.1 before loading up the columns and this could efficiently reduce the blank value of the analytes of interest. In this work, the concentration of the analytes containing in the discarded solution during purified procedures, such as Dy, Ho, Er, Tm and Yb was also carried out by ICP-MS in order to monitor the purification effects of the EHEHP resin. Experimental results presented that the blank value of separation procedures for the analytes of interest might only reach the levels ranging from $0.000x$ to $0.00x$ $\mu g\,L^{-1}$. It was evident that this could not affect the determination of trace of rare earth analytes, such as Dy, Ho, Er, Tm and Yb in high purity Sm_2O_3 after extraction chromatographic separation using EHEHP.

3.4.2. Eluted acid concentration control

A series of different concentration of HCl eluted solutions with 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 1.0, 2.0, 3.0, 4.0 and 4.5 $mol\,L^{-1}$, respectively, were selected to carry out the extraction chromatographic separation in order to remove Sm matrix as well as 0.6 $mol\,L^{-1}$ NH_4Cl solutions were also used with each group of HCl eluted solutions. Experimental results represented when the concentration of HCl was less than 0.20 $mol\,L^{-1}$, the eluted solution volume was much more than 500 mL together with consuming a long eluted time although the fraction containing La^+, Ce^+, Pr^+ and Nd^+ could be eluted completely. When the concentration of HCl was less than 0.3 $mol\,L^{-1}$, the eluted solution volume was large to get 400 mL and the determination for the analytes of interest would suffer from a few portion of Sm^+ existing in the eluted solution. When the HCl concentration equaled to 0.35 $mol\,L^{-1}$, the fraction containing Eu^+, Gd^+, Tb^+ and Dy^+ might be eluted to arrive before we expected and this affected the recovery dates of the analytes of interest in spite of Sm matrix being eluted completely as well as the eluted volume was littler. Selecting the concentration of 0.30 $mol\,L^{-1}$ HCl eluted solution gave attention to the two features of considering the eluted volume of completely separating Sm matrix and realizing the separation completely between Sm matrix and the trace of rare earth analytes, such as Dy, Ho, Er, Tm and Yb. On the other hand, when the concentration was much more than 1.0 $mol\,L^{-1}$, but less than 4.0 $mol\,L^{-1}$, the recovery values of the analytes of interest were lower and the separation procedures would consume a long time. Finally, a 4.0 $mol\,L^{-1}$ HCl eluted solution was selected considering the features with satisfying the recoveries of analytes of interest and shortening the separation procedures. Fig. 6 presents the gradient elution curve of REEs impurities in high purity Sm_2O_3 (99.999%).

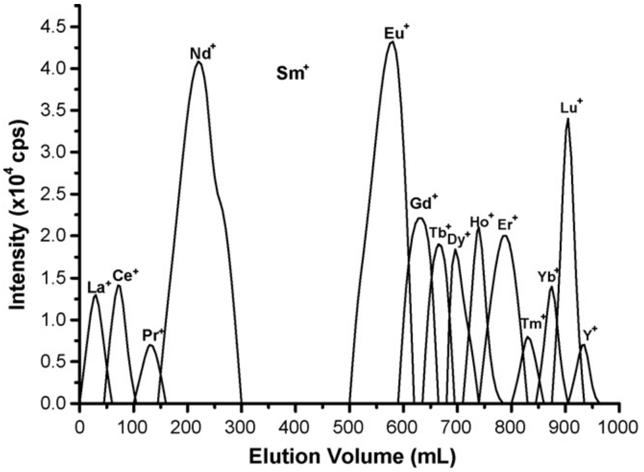

Fig. 6. Gradient elution curve of rare earth impurities in high-purity Sm_2O_3 (99.999%).

It can be seen from Fig. 6 that the analytes of interest, such as Dy, Ho, Er, Tm and Yb were completely separated from Sm matrix with the eluted solution volume about to 200 mL and the fewer of Tb fraction remained in Dy eluted solution did not affect the determination of the trace of analytes of interest.

3.4.3. Separation efficiency

Experimental results presented that the quantity of Sm matrix remained in the eluted solutions which would be used to carry out the analysis of analytes using ICP-MS was less than 20 $\mu g\,L^{-1}$ after 50 mg Sm_2O_3 was removed by means of extraction chromatographic separation. The separation efficiency could be calculated as following equation: $(m_1 - m_2)/m_1 \times 100\%$, where, m_1 refers to the quantity of Sm matrix before separation ($50\,mg \times 300.8/348.8 = 43.1192\,mg$), m_2 refers to the quantity of Sm matrix remained in the solutions of interest ($<20\,\mu g\,L^{-1} \times 10^{-3} \times 10^{-3} \times 100 = 0.002\,mg$). It was evident from the equation that the separation efficiency connected with the extraction chromatographic separation for the removal of Sm matrix was much more than 99.995%.

3.4.4. Interferences of remaining Sm matrix

Table 4 lists the concentration of different isotopes of Sm remained in the eluted solution containing analytes of interest and the apparent concentration of molecular ion formation arose from Sm matrix combined with oxygen, such as SmO^+ which was considered to be the most serious interference by referring back to Table 3.

In the case of determination of REEs impurities in high purity Sm_2O_3 using ICP-MS, the percentage ratio of SmO^+/Sm^+ was less than 1.0%. So, it can be seen from Table 4 that the isobaric interferences on the analytes of interest arose from Sm matrix remained in the measured solution with concentration of less than 20 $\mu g\,L^{-1}$ were much slighter with a range of less than 0.006–0.053 $\mu g\,L^{-1}$. But in fact, this slighter interferences could also be overcome by means of selecting isotopes, such as ^{161}Dy, ^{167}Er and ^{174}Yb that did not suffer from the mass spectra interferences. Ho has only one naturally occurring isotope

Table 4
Concentration of different isotopes of Sm and apparent concentration of SmO^+ ($\mu g\,L^{-1}$)

	Isotope (abundance %)						
	^{144}Sm (3.1)	^{147}Sm (15.0)	^{148}Sm (11.2)	^{149}Sm (13.8)	^{150}Sm (7.4)	^{152}Sm (26.7)	^{154}Sm (22.8)
Concentration	<0.62	<3.0	<2.24	<2.76	<1.48	<5.34	<4.56
Mass of SmO^+	160	163	164	165	166	168	170
Apparent concentration	<0.006	<0.03	<0.022	<0.027	<0.014	<0.053	<0.045
Interfered species	^{160}Dy (2.3)	^{163}Dy (24.9)	^{164}Dy (28.2), ^{164}Er (1.6)	^{165}Ho (100)	^{166}Er (33.4)	^{168}Er (27.0), ^{168}Yb (0.14)	^{170}Er (15.0), ^{170}Yb (3.0)

Table 5
Method precision (%) and Limit of quantitation ($\mu g\,g^{-1}$)

	Analyte								
	^{139}La	^{140}Ce	^{141}Pr	^{143}Nd	^{151}Eu	^{157}Gd	^{159}Tb	^{175}Lu	^{89}Y
LOQ	0.01	0.014	0.011	0.07	0.05	0.019	0.02	0.014	0.01
Precision	3.0	2.1	4.4	3.9	4.7	1.0	2.4	2.4	2.9

of ^{165}Ho and the isobaric interference generated from $^{149}SmO^+$ was less than 0.027 $\mu g\,L^{-1}$, this did not affect substantially the determination of Ho. The other analyte of Tm has also only one naturally occurring isotope of ^{169}Tm and the measurement for it mainly suffered from the isobaric interference of $^{152}SmOH^+$. In this work, the percentage ratio of $SmOH^+/Sm^+$ was less than 0.1%, so, the apparent concentration of $^{152}SmOH^+$ was less than 0.0053 $\mu g\,L^{-1}$ and this much slighter isobaric interference on ^{169}Tm could also be neglected.

3.5. Method precision and limit of quantitation

According to the IUPAC definition, the limit of quantitation (LOQ) is defined as the corresponding concentration values of 10 times the standard deviation (10 s) in 11 determinations of 1% HNO_3 blank solution which is free from Sm_2O_3 matrix and with consideration of dilution factors of the samples. The method precision and LOQs of Dy, Ho, Er, Tm and Yb before matrix separation were carried out using a 1000 $\mu g\,mL^{-1}$ high purity Sm_2O_3 solution and that of those analytes after matrix separation were obtained by the separation blank solution. The results are listed in Tables 5 and 6, respectively.

As listed in Tables 5 and 6, the proposed method precision was less than 5% and the LOQs for the trace of 14 REEs impurities ranged from 0.01 to 0.07 $\mu g\,g^{-1}$, this can completely satisfy the requirement for the analysis of 99.999–99.9999% high purity Sm_2O_3. It is evident from Table 6 that the LOQs of Dy, Ho, Er, Tm and Yb obtained from the method without matrix separation are very higher than that acquired from the proposed method with matrix separation and this will lead to the failure of the detection of 99.999–99.9999% high purity Sm_2O_3.

Table 6
Method precision (%) and Limit of quantitation ($\mu g\,g^{-1}$) before and after matrix separation

	Analyte				
	^{161}Dy	^{165}Ho	^{167}Er	^{169}Tm	^{174}Yb
LOQ (before)	43.0	1573.8	99.6	76.8	0.44
Precision (before)	4.7	3.6	2.9	4.7	2.9
LOQ (after)	0.015	0.025	0.030	0.022	0.025
Precision (after)	3.2	2.9	3.3	3.3	2.0

3.6. Recovery test

The recovery tests in terms of determination without Sm matrix separation and measurement after removal of Sm matrix by means of extraction chromatographic separation were carried out through using four solutions of 99.999% high purity Sm_2O_3 treated like the parts of Sections 2.5.1 and 2.5.2.3, respectively. According to the proposed method, La, Ce, Pr, Nd, Eu, Gd, Tb, Lu, Y and Dy, Ho, Er, Tm, Yb were spiked, individually, Dy, Ho, Er, Tm and Yb were added before 50 mg Sm_2O_3 solutions loading into the columns. The concentrations of the spiking analytes of 14 REEs were 2.0 and 5.0 $\mu g\,L^{-1}$, respectively, and In was also spiked with 10 $\mu g\,L^{-1}$ at each of the four solutions. The recovery values and R.S.D. acquired with a set of three replicates ($n = 3$) are listed in Table 7. By referring to Table 7, the recoveries for all of the 14 REEs were satisfactory with a range of 85–110% as well as the mean R.S.D. was less than 5%.

3.7. Sample analysis

A high purity Sm_2O_3 sample ($1^{\#}$, obtained from Hunan Institute of Rare Earth Material, Hunan, PR China) and a synthetic standard Sm_2O_3 sample with well-known 14 REEs concentrations were all determined by ELAN 9000 and ELAN 6000 ICP-MS running in our laboratory, respectively, using the proposed method described in this work. The analytical results are listed in Table 8. It can be seen from Table 8 that the total of 14 REEs impurities of sample $1^{\#}$ is below 10 $\mu g\,g^{-1}$ and the determinate concentrations of 14 REEs of the synthetic standard Sm_2O_3 sample keep in good agreement with the additional quantity of each of the 14 REEs.

Table 7
Spiking recovery (%) test ($n = 3$)

Analyte	99.999% Sm_2O_3 solution (1.0 g L^{-1})				Analyte	99.999% 50 mg Sm_2O_3 solution			
	2.0 μg L^{-1}	R.S.D. (%)	5.0 μg L^{-1}	R.S.D. (%)		2.0 μg L^{-1}	R.S.D. (%)	5.0 μg L^{-1}	R.S.D. (%)
^{139}La	97.4	2.3	102.0	2.7	^{161}Dy	107.3	4.3	96.1	2.9
^{140}Ce	99.6	1.7	97.6	2.3	^{165}Ho	110.0	3.7	89.6	3.4
^{141}Pr	100.3	1.3	99.8	3.4	^{167}Er	91.7	4.6	103.4	4.5
^{143}Nd	100.6	2.1	93.9	1.9	^{169}Tm	85.0	2.5	110.0	4.1
^{151}Eu	102.0	3.2	96.7	4.1	^{174}Yb	94.3	3.2	105.7	2.6
^{157}Gd	101.3	2.9	98.2	2.3					
^{159}Tb	100.0	3.3	94.9	1.1					
^{175}Lu	93.0	4.1	95.7	2.0					
^{89}Y	97.7	2.1	100.7	3.3					

Table 8
Analytical results ($n = 3$)

Analyte	Sample 1#				Synthetic standard Sm_2O_3 sample			
	ELAN 9000 (μg g^{-1})	R.S.D. (%)	ELAN 6000 (μg g^{-1})	R.S.D. (%)	ELAN 9000 (μg L^{-1})	R.S.D. (%)	ELAN 6000 (μg L^{-1})	R.S.D. (%)
La	0.17	3.1	0.19	2.2	1.96	2.1	1.99	3.3
Ce	0.22	2.3	0.22	3.7	1.99	3.3	1.95	2.7
Pr	0.10	1.9	0.10	4.1	1.97	4.0	2.02	3.5
Nd	1.92	4.7	1.83	4.0	2.04	3.7	1.99	2.7
Eu	2.41	4.3	2.34	3.3	1.99	3.4	2.08	1.9
Gd	0.54	2.6	0.51	2.1	2.07	2.7	1.95	3.1
Tb	0.50	2.4	0.42	1.9	2.06	3.1	2.11	2.6
Dy	0.21	3.6	0.21	4.4	1.83	4.3	1.91	4.3
Ho	0.24	3.7	0.24	2.3	2.15	3.6	2.18	2.5
Er	0.22	4.4	0.22	3.6	2.13	3.0	2.09	4.1
Tm	0.19	2.9	0.21	4.2	2.01	2.7	1.89	3.4
Yb	0.21	4.3	0.25	1.9	1.78	4.3	1.93	4.7
Lu	0.30	2.9	0.30	1.9	1.98	3.6	2.01	3.1
Y	0.07	1.3	0.10	2.6	2.02	1.9	1.97	2.6

4. Conclusion

A reliable, precise and accurate methodology for the determination of trace of 14 REEs as impurities in 99.999–99.9999% high purity Sm_2O_3 using ELAN 9000 ICP-MS was established. The mass spectra isobaric interferences of atomic and molecular ions generated from Sm matrix were completely eliminated by means of removal of Sm matrix through extraction chromatographic separation using EHEHP resin. In was spiked as internal standard to effectively compensate the matrix suppression. The proposed method is especially useful for the determination of trace of 14 REEs as impurities in Sm_2O_3 materials with purity of 99.999–99.9999%.

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