Development and Validation Method for the Determination of Rare Earth Impurities in High Purity Neodymium Oxide by ICP-MS

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INTRODUCTION

Trace rare earth element (REE) determination is always an important field of study in analytical chemistry. As one of the major REE analytical methods, ICP-OES (inductively coupled plasma optical emission spectrometry) has been widely applied to the determination of trace REEs in metallurgy, geology, biology, the environment, and high purity rare earth material. However, in some cases, the sensitivity of ICP-OES is not enough to satisfy the demand of high purity REE material (99.99 %) analysis.

It has been shown that ICP-MS is the most effective modern analytical tool for trace element determination and possesses several advantages (1,2): high sensitivity, broad linear range, capability of multi-element analysis, and determination of isotope ratio. Compared with ICP-OES, the most obvious merit of ICP-MS in REE determination is its excellent detection capability, in which pg mL^{-1} detection limit levels can be obtained for REEs. Also, the sensitivity for single REEs is very close, and their difference in detection limit is less than one order of magnitude (3). Presently, ICP-MS is more widely applied for the analysis of high purity rare earth compounds (4,5).

However, it should be pointed out that interferences can be divided into spectral and non-spectral interferences (matrix interference), a ubiquitous problem in ICP-MS. In order to determine trace REE impurities in high purity rare

ABSTRACT

The analytical procedure for the determination of trace rare earth impurities in high purity neodymium oxide (Nd_2O_3) by ICP-MS is described. The effect of ICP-MS operating parameters on the REO(H)$^+$/RE$^+$ production ratio was studied in detail, and the optimal ICP operating conditions were established. In this context, the relationship between REO(H)$^+$/RE$^+$ production ratio and the bond strength of the rare earth oxides is also discussed briefly. For the correction of the spectral interference induced by the matrix (neodymium), a simple correction equation was used for correcting the interferences of the polyatomic ions NdO$^+$ and NdOH$^+$ with ^{159}Tb and $_{165}$Ho. The proposed method was applied to the determination of trace rare earth impurities in high purity Nd_2O_3, and the analytical results were in good agreement with the recommended reference values.

earth oxides, some effective measures can be taken to overcome the non-spectral interferences such as (a) matrix matching (6), (b) internal standard addition (7), and (c) sample dilution. For spectral interferences, however, the production ratio of REO$^+$/RE$^+$ is generally at the X‰ (thousandths) level or much lower, and the contribution of this kind of interference is quite low, just around ng/g. Even though the production ratio of REOH$^+$/RE$^+$ is much less, its contribution is negligible and spectral interferences between trace REE impurities can be ignored. However, in the determination of trace heavy rare earth impurities in a light rare earth oxide matrix, the REO(H)$^+$ interfer-

ence induced by the matrix (light REEs) has been reported and should be carefully considered (3,8).

Research on polyatomic response (including oxide interference) has been reported during the initial development of ICP-MS instrumentation (9,10). The identification of REO(H)$^+$ and the effect of instrumental operating parameters on the production ratio have been discussed in ICP-MS studies (11–13), but this is still an interesting research topic (14). Quantification of oxide (MO$^+$) and hydroxide (MOH$^+$) ions is generally expressed as the oxide production ratio (MO$^+$/M$^+$) and hydroxide production ratio (MOH$^+$/M$^+$). It is documented that the metal oxide/hydroxide production ratio depends on operational parameters such as plasma power (15,16), carrier gas flow rate (11,15,17), sampling depth and the sampler and skimmer orifice sizes (11,15,17). High plasma power and a low nebulizer gas flow rate were used to reduce the oxide production ratio (<2 % CeO/Ce) (17,18).

Nevertheless, the reduction or elimination of spectral inter-ferences and the development of an effective method for ICP-MS determination of trace REE impurities in high pure RE oxides (especially trace heavy rare earth impurities in a light rare earth matrices) is still an unsolved problem which continues to puzzle analytical chemists. Various approaches have been reported to reduce or eliminate the spectral interference in ICP-MS determination of REEs in various matrices. Chemical separation based on the separation of the matrix, such as ion chromatography (19), ion

exchange chromatography (18), liquid chromatography (20), and solvent extraction (21), has proven to be efficient. However, chemical separations are time-consuming and laborious. Also, high concentrations of organic eluents and buffer reagents might lead to carbon deposition on the sampling orifice of ICP-MS systems or might cause clogging of the ICP torch, resulting in a drift in instrument sensitivity. High resolution ICP-MS (HR-ICP-MS) can, in some cases, separate analyte signals from the interfering oxides; its validity has been demonstrated for the determination of REEs in rocks (22). However, HR-ICP-MS is very expensive, and most ICP-MS users still work with quadrupole ICP-MS instruments. An alternative method to solve the above problems is to use a suitable mathematical method to correct the raw data. Zhu and co-workers (23) developed a PLSR (Partial Least Squares Regression) model to eliminate or correct the REO, REOH, and isotope interferences in the determination of REEs by ICP-MS. Likewise, Elokhin et al. (24) used a simplex approach for data processing and claimed that the main features of the simplex approach were adequate automatic correction for all possible spectral overlaps. A routine method for oxide and hydroxide interference correction was also proposed for ICP-MS determination of trace REEs in geological sample (25). However, it should be noted that most of this research involves the determination REEs in geological and environmental samples; only a few are reported for the determination of REE impurities in high purity rare earth oxides.

The purpose of the present study is to examine the effect of ICP operating parameters on the $REO(H)^+/RE^+$ production ratio, to explore the relationship between the $REO(H)^+/RE^+$ production ratio and the bond strength of corre-sponding rare earth oxide, and to develop a simple and effective method to determine trace rare earth impurities in high purity Nd_2O_3 by ICP-MS.

EXPERIMENTAL

Instrumentation

Rare earth element determination was performed by a quadrupole (Q) ICP-MS (Model Agilent 7500a, Hewlett-Packard, Yokogawa Analytical Systems, Tokyo, Japan) with a Babington nebulizer; the instrumental operating parameters are given in Table I.

Chemicals and Standard Solution

The rare earth element standard stock solutions were prepared by dissolving the appropriate amount of corresponding SpecPure (Shanghai No. 1 Reagent Factory, Shanghai, P.R. China) rare earth oxides.

A standard solution of REEs was prepared by diluting the stock solution of each element in 2% (v/v) HNO_3. The high purity Nd_2O_3 reference material was provided by Jiahua Rare Earth Corporation of Jiangyin, P.R. China, and the high purity Nd_2O_3 sample was provided by Yuelong Rare Earth Research Institute of Shanghai, P.R. China. Other chemicals were of SupraPure grade. Double distilled water was used throughout the experiment.

Sample Preparation

50.00 mg Nd_2O_3 powdered sample was weighed into a 50-mL beaker and 5 mL (1+1) (v/v) HNO_3 was added, then heated on a graphite plate. After cooling, it was diluted to 50 mL in a flask to obtain a 1.0 g L^{-1} Nd_2O_3 concentration. Then, 100 mg L^{-1} and 10 mg L^{-1} Nd_2O_3 samples were obtained by diluting the 1.0 g L^{-1} Nd_2O_3 sample concentration.

TABLE I
ICP-MS Operating Parameters

| Plasma		Ion Lenses	
Incident Power	1300 W	Extract 1	−143.5 V
RF Natching	1.6 V	Extract 2	−67 V
Carrier Gas (Ar) Flow Rate	1.16 L min^{-1}	Einzel 1,3	−94 V
External Gas (Ar) Flow Rate	15 L min^{-1}	Einzel 2	0 V
Sampling Depth	7 mm	Plate Bias	0 V
Sample Uptake Rate	0.4 mL min^{-1}	Omega Bias	−27 V
Q-Pole		Omega (+)	2.7 V
AMU Gain	126	Omega (−)	−0.1 V
AMU Offset	126	QP Focus	7.3 V
Axis Gain	0.9998		
Axis Offset	0.02	Integration Time	0.1 s
QP Bias	1.2 V	Nebulizer	Babington
Detector		Torch	Fassel (quartz)
Discriminator	8.7 mV		
Analog	1460 V	Sampler	Ni, 1.0 mm diameter orifice
Pulse HV	900 V	Skimmer	Ni, 0.4 mm diameter orifice
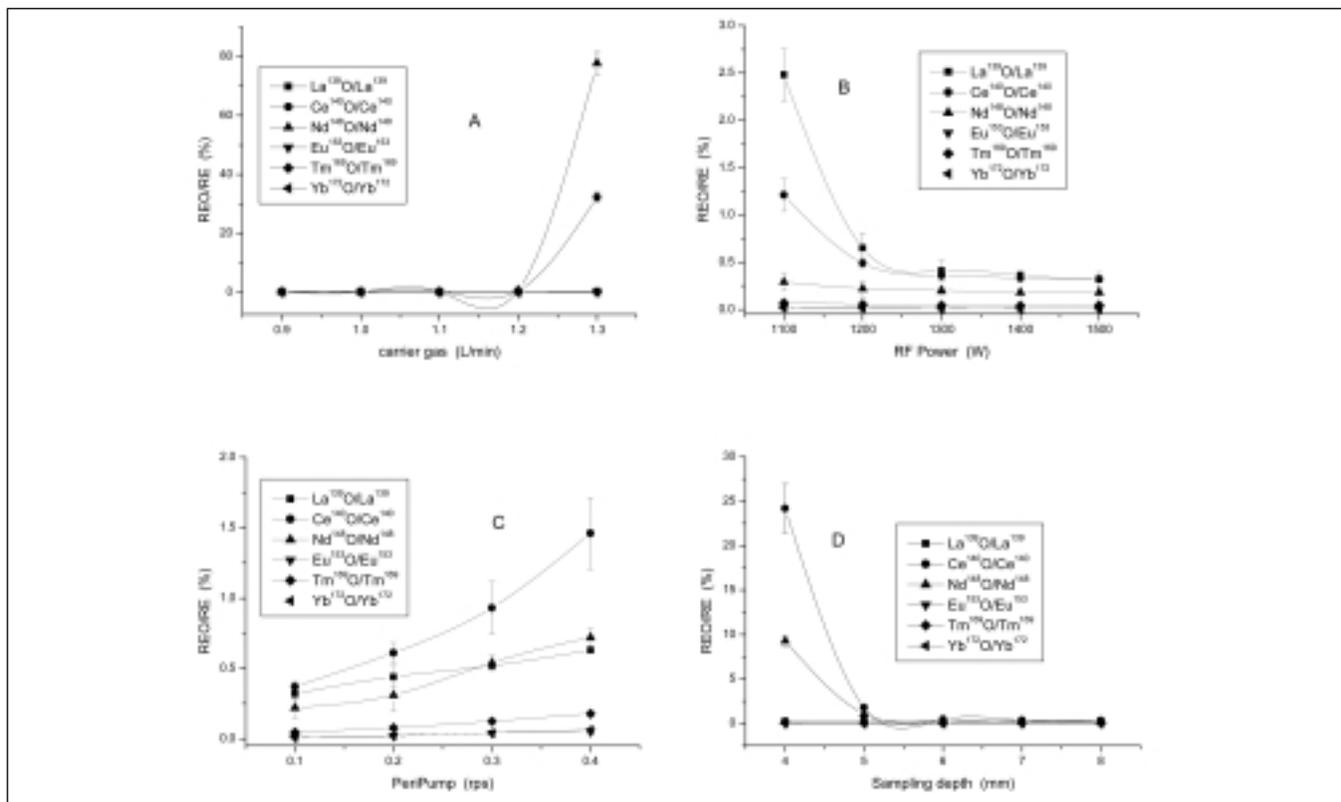
Fig. 1 (A–D). Factors affecting the production ratio of REO⁺/RE⁺. Error bar indicates two times the standard deviation (n=3). A=Carrier gas flow rate. B=RF power. C=Sample solution uptake rate. D=Sampling depth.

RESULTS AND DISCUSSION

Factors Affecting the Production Ratio of REO⁺/RE⁺

Carrier Gas

The carrier gas flow rate plays an important role in the formation quality of the analyte aerosol and its transport. Figure 1A shows the effects of carrier gas flow rate on the ratio of REO⁺/RE⁺. As can be seen, no obvious variation of the REO⁺/RE⁺ ratios was found in a flow rate range of 0.9 L min⁻¹ ~1.2 L min⁻¹; the ratios were very low. However, when the flow rate exceeds 1.2 L min⁻¹, the ratio of LaO⁺/La⁺, CeO⁺/Ce⁺, and NdO⁺/Nd⁺ increases sharply, while no large ratio change was observed for Eu, Tm, and Yb. These experimental results demonstrate that a low carrier gas flow rate is benefi-

cial for a low and stable production ratio of REO⁺/RE⁺. The reason for this may be that the amount of the aerosol transported into the ICP source in a unit of time would increase rapidly when a much higher carrier gas flow rate is used. As a result, this would cause an overload of the ICP and lead to the rapid increase of the REO⁺/RE⁺ ratio (3). This situation is much worse for some RE oxides (LaO, CeO, NdO) with higher dissociation energies. In contrast, the permissible variation range for the carrier gas flow rate is much broader for the REO (EuO, TmO, YbO) with a lower dissociation energy.

RF Power

Generally, higher RF power benefits the dissociation of REO and results in a decrease of the

REO⁺/RE⁺ ratio. The influence of RF power on the REO⁺/RE⁺ ratio was studied, and the results are shown in Figure 1B. For some REO (EuO, TmO, YbO) with a low dissociation energy, the production ratio of REO+ is low and little REO⁺/RE⁺ ratio change can be found when the RF power is varied from 1.1 kW to 1.5 kW. Thus, a low RF power can be chosen for the determination of these REEs. But for REO (LaO, CeO) with a higher dissociation energy, a higher RF power is necessary for their determination. The mid-RF power is required for the determination of Nd.

Sample Solution Uptake Rate

The sample solution uptake rate indicates the amount of analyte that is transferred into the nebulizer per unit time, and is determined by the rotation rate of the pump. Figure 1C
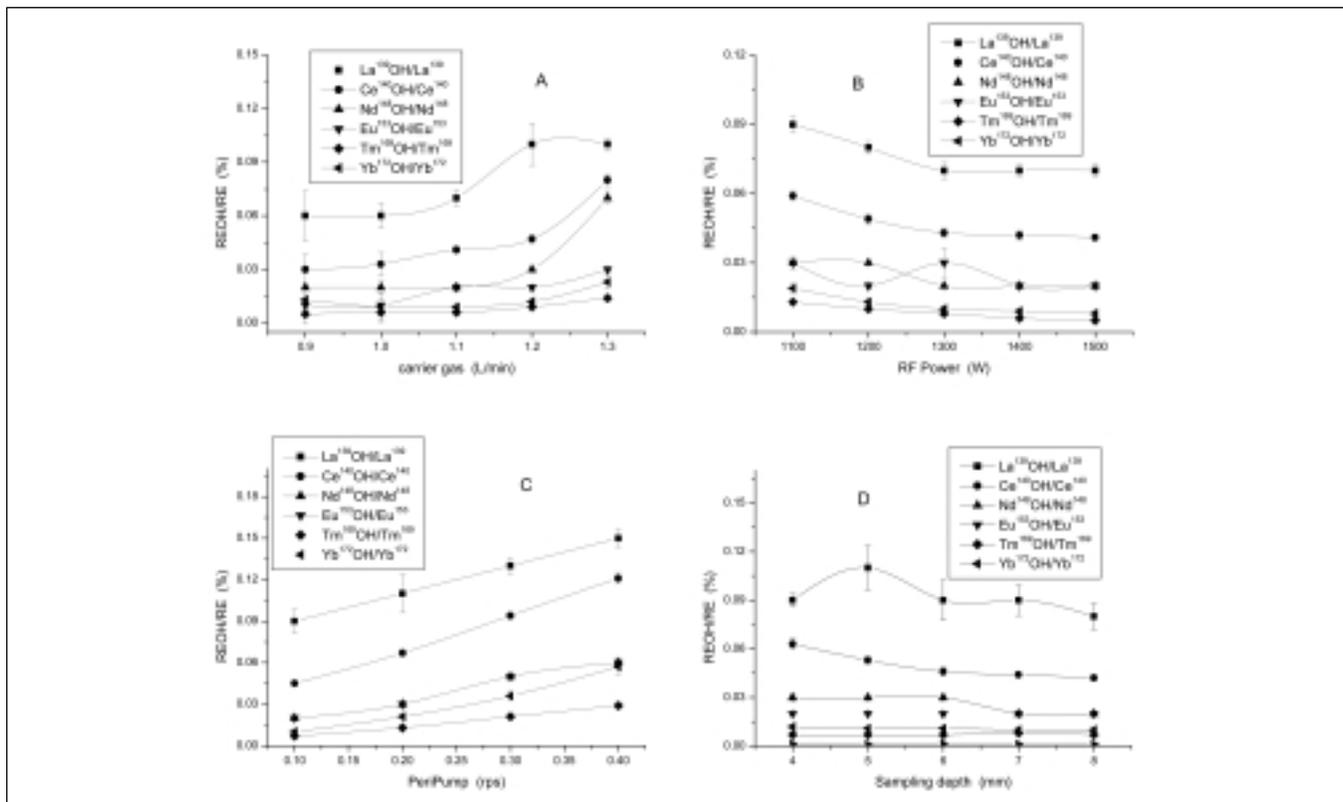
Fig. 2 (A–D). Factors affecting the production ratio of REOH⁺/RE⁺. Error bar indicates two times the standard deviation (n=3). A=Carrier gas flow rate. B=RF power. C=Sample solution uptake rate. D=Sampling depth.

shows the dependence of REO^+/RE^+ ratio on the sample solution uptake rate. The results indicate that the REO^+/RE^+ ratio increased with the increase of the sample solution uptake rate, but this increase is different for different rare earth oxides owing to their different bond strength of REO. In other words, the maximum allowable amount of REEs to produce a consistently low level of oxide in the ICP source varies by element; REOs with high dissociation energy have much lower allowable amounts than those with lower dissociation energy.

Sampling Depth

The effect of sampling depth on REO^+/RE^+ production ratio is shown in Figure 1D. As can be seen, in a broad range of the sampling depth, no obvious REO^+/RE^+

ratio variation appears for rare earth oxides with low dissociation energy. However, for those REO with higher dissociation energy, the REO^+/RE^+ ratio decreases with the increase of the sampling depth. Therefore, a compromise sampling depth should be selected for the determination of light/heavy REEs simultaneously.

Factors Affecting Production Ratio of REOH⁺/RE⁺

Figure 2 shows the effects of the above parameters (carrier gas flow rate, RF power, sample consumption, and sampling depth) on the production ratio of $REOH^+/RE^+$. It was found that these parameters have a similar influence on REOH with the only difference being that the production ratio of REOH+/RE+ is much lower than that of REO+/RE+.

Relationship Between REO(H)+/RE+ Production Ratio and REE Concentration

The variation of $REO(H)^+/RE^+$ production ratio with the change of REE concentration was investigated; the results are given in Table II. It can be seen that the $REO(H)^+/RE^+$ production ratio is stable roughly with REE concentrations varying from 1~100 mg L⁻¹. This indicates that the variation of $REO(H)^+/RE^+$ production ratio depends only on the ICP operating parameters instead of the REE concentration in solution.

Stability of REO(H)⁺/RE⁺ Production Ratio

As mentioned above, low $REO(H)^+/RE^+$ production ratio can be achieved by optimizing the ICP operating parameters. It is also very

TABLE II
Relationship Between REO(H)$^+$/RE$^+$ Production Ratio (%) and REE Concentration

Ratio	REE Concentration (µg mL^{-1})				Ratio	REE Concentration (µg mL^{-1})			
(%)	1	10	20	100	(%)	1	10	20	100
LaO$^+$/La$^+$	0.37	0.37	0.37	0.38	LaOH$^+$/La$^+$	0.06	0.06	0.06	0.06
CeO$^+$/Ce$^+$	0.45	0.46	0.45	0.45	CeOH$^+$/Ce$^+$	0.08	0.09	0.09	0.09
NdO$^+$/Nd$^+$	0.20	0.21	0.21	0.21	NdOH$^+$/Nd$^+$	0.03	0.03	0.03	0.03
EuO$^+$/Eu$^+$	0.03	0.02	0.02	0.02	EuOH$^+$/Eu$^+$	0.02	0.02	0.02	0.02
TmO$^+$/Tm$^+$	0.04	0.04	0.05	0.06	TmOH$^+$/Tm$^+$	0.01	0.01	0.01	0.01
YbO$^+$/Yb$^+$	0.01	0.01	0.01	0.01	YbOH$^+$/Yb$^+$	0.01	0.01	0.01	0.01

TABLE III
Stability of the REO(H)+/RE+ Production Ratio (%RSD, n=11)

	LaO+/La+	CeO+/Ce+	NdO+/Nd+	EuO+/Eu+	TmO+/Tm+	YbO+/Yb+
RSD(%)	4.2	3.8	7.1	2.8	2.1	7.6
	LaOH+/La+	CeOH+/Ce+	NdOH+/Nd+	EuOH+/Eu+	TmOH+/Tm+	YbOH+/Yb+
RSD(%)	5.0	1.5	1.5	3.1	5.2	5.4

TABLE IV
Bond Strength of REO (KJ mol^{-1})

Element	Bond Strength	Element	Bond Strength
Y - O	715	Tb - O	707
La - O	799	Dy - O	711
Ce - O	795	Ho - O	619
Pr - O	753	Er - O	611
Nd - O	703	Tm - O	557
Sm - O	573	Yb - O	418
Eu - O	470	Lu - O	695
Gd - O	716		

Fig. 3. Relationship between the REO$^+$/RE$^+$ production ratio and the bond strength of REO.
Error bar indicates two times the standard deviation (n=11).

important to keep the production ratio stable. For this reason, under the compromise conditions, stability of the REO(H)$^+$/RE$^+$ production ratios of most rare earth elements were observed for eleven times sequentially (one determination for every 30 min, total of 330 min); the results are shown in Table III. It can be concluded that the REO(H)$^+$/RE$^+$ production ratio remains stable as long as the experimental conditions remain stable.

Relationship Between REO$^+$/RE$^+$ Production Ratio and Bond Strength of REO

The bond strength of rare earth oxides (26) is listed in Table IV. Under the compromise conditions, the relationship between the REO$^+$/RE$^+$ production ratio and the bond strength of their corresponding REO was plotted in Figure 3. It can be seen that the REO$^+$/RE$^+$ production ratio is low when the bond strength of the corresponding REO is low. In contrast, the greater the bond strength of rare earth oxide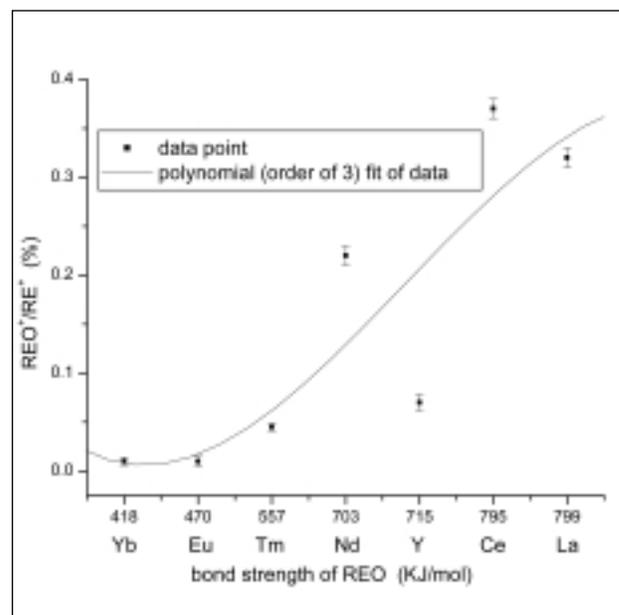, the higher the REO$^+$/RE$^+$ production ratio. The reason for this is that the higher the bond strength/ dissociation energy of rare earth oxides, the higher the thermal stability of the rare earth oxides, and the more difficult it is for the rare earth oxides to dissociate. Thus, compromise ICP operating parameters are required to obtain a low and stable REO$^+$/RE$^+$ production ratio.

Determination of RE Impurities in High Purity Nd_2O_3

As is well known, there is much less research on the determination of REE impurities in light rare earth matrices than in heavy rare earth matrices. One of the most important reasons for this is that the spectral interferences (REO^+, $REOH^+$, in particular) produced by the light REE matrix are much more severe than those produced by heavy REE matrices. Also, the interferences of light REEs with multiple isotopes are more complicated. Nd is a such an element, and has seven isotopes. Table V lists the possible spectral interferences produced by the matrix (Nd) on the other REEs. As can be seen, ^{159}Tb is interfered by both ^{142}NdOH and ^{143}NdO, while ^{165}Ho is interfered by ^{148}NdO. Therefore, it is impossible to accurately determine trace Ho and Tb in high purity Nd_2O_3, and an effective spectral interference correction should be performed. For the correction of these interferences, the following correction equations were adopted:

$$S_{Tb159} = S_{159} - S_{142} \times {}^{142}NdOH^+/Nd^+ - S_{143} \times {}^{143}NdO^+/Nd^+$$

$$S_{Ho165} = S_{165} - S148 \times {}^{148}NdOH^+/Nd^+$$

Where S_{Tb159} and S_{Ho165} are the net signal intensity of ^{159}Tb and ^{165}Ho, respectively; S_{159}, S_{142}, S_{165} and S_{148} are the total signal intensity of ^{159}Tb, ^{142}Nd, ^{165}Ho, and ^{148}Nd, respectively.

These correction equations were used to correct the interferences induced by the Nd matrix in the determination of Tb and Ho in Nd_2O_3. The analytical results for a reference material with and without corrections are shown in Table VI. The results obtained indicate that the spectral interferences induced by the Nd matrix are very serious for Tb and Ho, but they can be corrected by the correction equations described above. It should be noted that a low and stable $REO(H)^+/RE^+$ production ratio is a prerequisite for these corrections.

In order to demonstrate the validity of the analytical procedure, both reference and real samples of high purity Nd_2O_3 were analyzed; the analytical results, together with reference values and recoveries, are given in Tables VII and VIII, respectively. As can be seen, good agreement between the determined values and the reference values was obtained. For the real sample analysis, the recovery ranged from 93–115% for all RE impurities except that the recovery of Tb was 65–117%.

CONCLUSION

In this paper, the $REO(H)^+/RE^+$ production ratio of six REEs (La, Ce, Nd, Eu, Tm, Yb) and their effects on the ICP-MS determination of REEs were studied in detail. A simple, rapid, and effective ICP-MS method was developed for the determination of trace rare earth impurities in high purity Nd_2O_3. Based on the research results, the

TABLE V
Possible Spectral Interferences Induced by the Matrix (Nd)

Isotope of Nd	Abundance (%)[a]	Interference of NdO	Interference of NdOH
142	27.2	^{158}Gd (25%), ^{158}Dy (0.1%)	^{159}Tb (100%)
143	12.2	^{159}Tb (100%)	^{160}Gd (22%), ^{160}Dy (2.3%)
144	23.8	^{160}Gd (22%), ^{160}Dy (2.3%)	^{161}Dy (19%)
145	8.3	^{161}Dy (19%)	^{162}Dy (26%), ^{162}Er (0.14%)
146	17.2	^{162}Dy (26%), ^{162}Er (0.14%)	^{163}Dy (25%)
148	5.7	^{164}Dy (28%), ^{164}Er (1.6%)	^{165}Ho (100%)
150	5.6	^{166}Er (34%)	^{167}Er (23%)

[a] (%) Indicates isotope abundance of the element.

TABLE VI
Determination Results (µg g^{-1}) of Tb and Ho in High Purity Nd_2O_3 Reference Sample With and Without Correction

Element	Spiked Amount (µg L^{-1})	Without Correction (µg g^{-1})	With Correction (µg g^{-1})	Reference Value (µg g^{-1})	Recovery (%)
Tb	0	169	5.12	–[a]	
Ho	0	4.6	<0.8	<1.7	
Tb	1.0	178	14.6		95
Ho	1.0	22.1	11.0		110
Tb	2.0	191	26.5		107
Ho	2.0	30.8	20.3		102
Tb	5.0	219	55.0		100
Ho	5.0	59.8	49.8		100

Spiked amount indicates the concentration of REEs spiked into the matrix (100 µg L^{-1}).
[a] No reference value.

TABLE VII
Analytical Results of Trace REEs (µg g^{-1})
in High Purity Nd$_2$O$_3$ Reference Sample by ICP-MS (n = 3)

Element	Mass	External Standard	Standard Addition	Reference Values
Y	89	13.7 ± 0.3	13.5 ± 0.4	14.4
La	139	47.9 ± 0.9	50.6 ± 1.2	53.8
Ce	140	3.67 ± 0.07	3.56 ± 0.10	4.6
Pr	141	250 ± 5	237 ± 5	226
Sm	152	50.2 ± 1.1	51.4 ± 1.3	---[b]
Eu	153	0.60 ± 0.02	0.55 ± 0.02	0.4
Gd	157	2.06 ± 0.07	2.14 ± 0.07	1.7
Tb[a]	159	5.12 ± 0.21	5.05 ± 0.24	---[b]
Ho[a]	165	<0.8	<0.8	<1.7
Er	168	1.89 ± 0.09	1.91 ± 0.08	1.9
Tm	169	0.28 ± 0.02	0.26 ± 0.02	0.3
Yb	172	1.58 ± 0.04	1.55 ± 0.03	1.4
Lu	175	0.21 ± 0.01	0.21 ± 0.01	0.3

Note: Results are means of three measurements ± standard deviation.
[a] The result of this element has been corrected by the correction equation.
[b] No reference value.

TABLE VIII
Analytical Results of Trace REEs in High Purity Nd$_2$O$_3$
by ICP-MS and Recovery of Spiked Sample

Element	Mass	External Standard (µg g^{-1})	Standard Addition (µg g^{-1})	(%) Recovery		
				1.0[a]	2.0[a]	5.0[a]
Y	89	1.5	1.9	94	105	110
La	139	2.3	2.6	93	100	115
Ce	140	1.2	0.8	98	99	103
Pr	141	6.2	5.3	103	100	104
Sm	152	1.9	2.6	105	110	109
Eu	153	0.5	0.4	96	105	108
Gd	157	1.8	1.4	102	101	102
Tb[b]	159	<0.2	<0.2	65	80	117
Ho[b]	165	1.2	1.0	94	98	99
Er	168	0.7	0.9	101	102	106
Tm	169	0.3	0.3	100	100	101
Yb	172	0.3	0.3	100	103	104
Lu	175	0.6	0.6	100	102	102

[a] The spiked amount of RE (µg L^{-1}) into 100 µg L^{-1} Nd$_2$O$_3$ sample solution.
[b] The result of this element has been corrected by the correction equation.

following conclusions can be drawn:

The influence of ICP operating parameters on the production ratio of REO$^+$ is similar to that of REOH$^+$, but the production ratio of the latter is much lower than that of the former.

This influence is related to the bond strength of corresponding RE oxides, instead of the concentration of REEs in the solution.

Under optimal ICP operating conditions, the stability (%RSD) of the REO(H)$^+$/RE$^+$ production ratio can be maintained at 10% over 5-1/2 hours.

The proposed method is simple and accurate, and no matrix matching is required. It can be extended to the ICP-MS analysis of trace rare earth impurities in other high purity rare earth oxides.

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