Routine determination of trace rare earth elements in high purity Nd_2O_3 using the Agilent 8800 ICP-QQQ

Application note

Geochemistry, mining and materials science

Authors

Juane Song[1], Xiang-Cheng Zeng[1],
Dong Yan[1] and Wei-ming Wu[2]

1 Agilent Technologies, China

2 Jiangxi University of Science and Technology, Jiangxi, China

Introduction

Advanced technology products containing rare earth elements (REEs) continue to evolve at a rapid pace. Consequently, the use of REEs has extended from well-established applications such as glass polishing, to high-performance magnets, high-tech catalysts, electronics, glass, ceramics, and alloys. An alloy of the second most abundant REE, neodymium (Nd), with iron and boron (NIB) is an important material in the super permanent magnets that are used in vehicle components, computer data storage devices, MRI scanners, and loudspeakers. Nd is also used to make glass and safety glasses (didymium) used by glassblowers and welders. As REEs are increasingly used in high-tech products, control of any impurities is important. For example, the presence of other REEs as contaminants in a purified single-element REE material may affect the functionality of the final product, so impurities in the REE oxide raw material must be carefully controlled.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is the most commonly used atomic spectrometry technique for the measurement of trace REEs. This is partly because the mass spectrum of the REEs is relatively simple, particularly when compared to the complex REE optical emission spectrum produced by techniques such as ICP-OES. The measurement of mid- and high-mass REEs in a low-mass REE matrix is, however, very challenging for ICP-MS because REEs have high metal-oxide (M-O) bond strengths, and the oxide ions of the low mass REEs overlap the preferred isotopes of the mid-mass and high-mass REEs. For example, in the analysis of trace REEs in high-purity Nd_2O_3, $^{145}Nd^{16}OH_2^+$ and $^{146}Nd^{16}OH^+$ overlap the preferred isotope of dysprosium ($^{163}Dy^+$), $^{143}Nd^{16}O^+$ overlaps the only isotope of terbium ($^{159}Tb^+$) and $^{148}Nd^{16}OH^+$ overlaps the sole isotope of holmium ($^{165}Ho^+$). While separation of the trace REEs from the REE matrix can be performed using a chelating resin, this technique is time-consuming and needs to be customized to the particular analyte and matrix under investigation. Clearly there is a requirement for a method capable of the direct analysis of trace REEs in a variety of high purity REE matrices.

In this study, an Agilent 8800 Triple Quadrupole ICP-MS (ICP-QQQ) was used for the direct analysis of trace REEs in a high-purity Nd_2O_3 sample. In MS/MS reaction mode, the Nd-based interferences were all removed effectively, enabling the 8800 ICP-QQQ to determine all 13 REE impurities at trace levels in the high purity REE-matrix material.

Experimental

A standard configuration Agilent 8800 ICP-QQQ (G3663A #100) with nickel interface cones was used. The sample introduction system consisted of a MicroMist glass concentric nebulizer, a Peltier-cooled quartz double-pass Scott-type spray chamber, and a quartz torch with 2.5 mm injector. The 8800 ICP-QQQ features High Matrix Introduction (HMI) aerosol dilution technology, which reduces the total sample load introduced to the plasma by accurately and reproducibly diluting the sample aerosol using an additional argon gas flow. A preset plasma condition (HMI-Low) was selected in the MassHunter software to achieve a robust plasma to permit the routine (long-term) analysis of samples containing a 500 ppm Nd_2O_3 matrix. To compare the efficiency of removing Nd-based polyatomic ions, five different collision/reaction cell (CRC) modes (no gas, He, O_2 mass-shift, NH_3 on-mass and NH_3 mass-shift) were tested. Table 1 summarizes the tuning conditions used in the study.

Table 1. Agilent 8800 ICP-QQQ tuning parameters (NH_3 as 10% NH_3 in He)

Parameter		No gas	He	O_2 mass shift	NH_3 on mass	NH_3 mass shift
Scan mode		SQ		MS/MS		
RF power	W	1550				
Sampling depth	mm	8				
Carrier gas	L/min	0.6				
Dilution gas	L/min	0.5				
Octopole bias	V	-8	-18	-4	-18	
Octopole RF	V	190		150	190	
Cell entrance	V	-30	-40	-50	-120	
Cell exit	V	-50	-60	-70	-120	
Deflect	V	10	0	4	-5	
Plate bias	V	-50	-40	-70	-120	
KED	V	5	3	-7	-15	
He	mL/min	-	5	-	1	
O_2	mL/min	-	-	0.3	-	
NH_3	mL/min	-	-	-	8	3

Five calibration standards [0, 0.1, 0.5, 2.0 and 5.0 µg/kg (ppb)] were prepared from an Agilent REE mixed standard (Part no. 8500-6944). Rhodium (Rh) and rhenium (Re) were used as internal standards (ISTD). High purity (99.999%) Nd_2O_3 (Baotou Research Institute of Rare Earths, China) was dissolved gently in semiconductor grade HNO_3, diluted to 500 ppm as Nd_2O_3 and analyzed for 13 REE impurities by ICP-QQQ.

Results and discussion

All thirteen trace REEs were measured in the Nd_2O_3 sample using the no gas, He and O_2 cell modes. The results are summarized in Table 2. Pr and Sm were evidently present as impurities but, as expected, the Background Equivalent Concentration (BEC) of the other low- and mid-mass REEs, La, Ce, Pr, Sm, Eu and Gd, were comparable in all modes, as these elements are free from interferences due to Nd. In contrast, the BECs for the high-mass REEs were lower in He mode than in no gas mode, suggesting that the high-mass REEs suffer interferences from Nd-derived polyatomic ions.

O_2 mass-shift mode

All 13 trace REEs react with O_2 efficiently to form REE-oxide ions, as shown below:

$$REE^+ + O_2 \rightarrow REE\text{-}O^+ + O$$

This reaction pathway, combined with the MS/MS capability of the 8800 ICP-QQQ, allows spectral interferences on the REEs to be avoided by using "mass-shift" mode. In O_2 mass-shift mode, all 13 REEs can be detected as their REE-O^+ reaction product ions at 16 amu higher than the original elemental mass (M+16). This mode can be used in the CRC of a conventional quadrupole ICP-MS (ICP-QMS), but in practice the reaction chemistry is not consistent enough for routine analysis of real samples. In ICP-QMS, all of the ions produced in the plasma are able to enter the reaction cell, so other analyte ions or cell-formed reaction product ions may overlap the analyte ion of interest. For example, in the case of Dy measured as $^{163}Dy^{16}O^+$ using O_2 mass-shift mode, $^{146}Nd^+$ also reacts with the O_2 cell gas to form $^{146}Nd^{16}O_2H^+$ that would overlap the $^{163}Dy^{16}O^+$ product ion at *m/z* 179. Furthermore, hafnium has a natural isotope at *m/z* 179 which could also overlap the target product ion. To avoid the formation of the overlapping $NdOH^+$ product ion, the precursor ion $^{146}Nd^+$ (and any native ions such as Hf^+ that would appear at the analyte product ion mass) must be removed before they enter the reaction cell; this can only be achieved with MS/MS mode on the ICP-QQQ. In MS/MS mode, the first quadrupole (Q1) operates as a single amu mass filter so that only ions with the targeted *m/z* enter the reaction cell and can react with the cell gas. All other masses are rejected by Q1, so they are not able to pass through the cell or undergo the reactions that would lead to interfering product ions.

In addition to the significant improvement in the analysis of the elements Tb, Dy and Ho, that suffer intense interference from NdO^+, O_2 mass-shift mode also delivers improved BECs for the other high-mass REEs Er, Tm, Yb and Lu, indicating that these elements were also affected by interferences from Nd-based polyatomic ions in no gas mode. Likely overlaps are $^{150}NdOH_3^+$ on $^{169}Tm^+$; $^{142}NdN_2^+$, $^{142}NdCO^+$ and $^{144}NdCN^+$ on $^{170}Er^+$; $^{142}NdO_2^+$ on $^{174}Yb^+$; $^{143}NdO_2^+$, $^{144}NdONH^+$ and $^{150}NdC_2H^+$ on $^{175}Lu^+$. The Nd-based interferences on Er, Tm, Yb and Lu are not very significant (less than 0.2 µg/kg in the Nd_2O_3 matrix), but nevertheless O_2 mass-shift mode was shown to be an effective approach for the removal of all the polyatomic ion interferences, typically providing around a 5-10x lower BEC compared to no gas mode and He mode.

Table 2. BECs of 13 REEs in 500 ppm Nd_2O_3. All units are ppb.

Element	Isotope	No gas	He	O_2 mass shift	NH_3 on mass	NH_3 mass shift
La	139	0.143	0.127	0.143	-	-
Ce	140	0.018	0.012	0.011	-	-
Pr	141	1.376	1.202	1.056	-	-
Sm	152	1.061	0.950	0.999	-	-
Eu	153	0.032	0.026	0.028	-	-
Gd	155	0.035	0.046	0.033	-	-
Tb	159	442.6	74.6	1.258	-	0.022
Dy	163	250.3	196	1.161	0.040	-
Ho	165	20.43	16.2	0.101	0.004	-
Er	170	0.065	0.020	0.013	-	-
Tm	169	0.084	0.031	0.003	-	-
Yb	174	0.251	0.120	0.058	-	-
Lu	175	0.014	0.006	0.004	-	-

NH_3 on-mass mode for Dy and Ho

A previous study [1] showed that NH_3 cell gas reacts with many of the polyatomic ions that interfere with the REEs. However, NH_3 also reacts quickly with some of the REE ions, leading to reduced sensitivity of < 1 cps/ppt for La, Ce, Nd, Sm, Gd, Tb and Lu. For the remaining REEs that react less quickly (or not at all) with NH_3, i.e. Pr, Eu, Dy, Ho, Er, Tm and Yb, on-mass measurement with NH_3 cell gas could therefore be a valuable approach for avoiding the Nd-based overlaps. The results in Table 2 show that NH_3 on-mass mode gave excellent results for Dy and Ho in the Nd_2O_3 matrix, with an improvement in BECs of 20x compared to O_2 mass-shift mode.

NH_3 mass-shift mode for Tb

For the REEs that react efficiently with NH_3 (La, Ce, Nd, Sm, Gd, Tb and Lu), NH_3 cell gas can be used in combination with mass-shift mode, where the target REE element is measured as its reaction product ion.

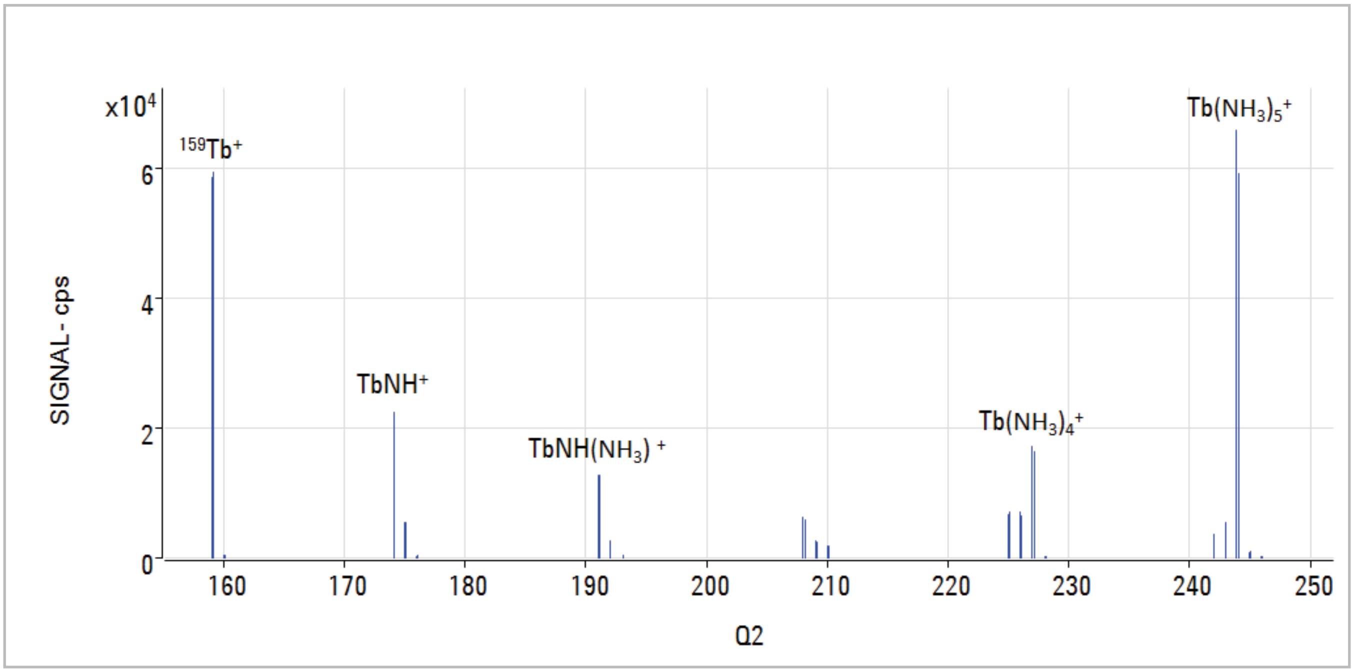

Figure 1. Product ion scan for ^{159}Tb in NH_3 mode

In this study, NH_3 mass-shift mode was investigated for the determination of Tb. In order to find the most appropriate ammonia-cluster product ion for Tb, a 10 ppb Tb solution was introduced and a product ion scan was performed. Q1 was set at *m/z* 159, allowing only ions at the mass of the target precursor ion (^{159}Tb) to enter the cell. Q2 was scanned over a selected mass range to measure all of the product ions formed in the cell via NH_3 reaction with ^{159}Tb (Figure 1). The scan revealed the four most abundant cluster ions: $TbNH^+$ (at Q1 + 15 amu), $TbNH(NH_3)^+$ (at Q1 + 32 amu), $Tb(NH_3)_4^+$ (at Q1 + 68 amu) and $Tb(NH_3)_5^+$ (at Q1 + 85 amu). For each of the four candidate cluster ions, the BEC of Tb in the Nd matrix was studied and $TbNH^+$ (*m/z* 174) was found to give the lowest BEC of 22 ppt for Tb in a 500 ppm Nd_2O_3 solution. This BEC is 50x lower than the result achieved in O_2 mass-shift mode, indicating the effective avoidance of the NdO^+ overlap.

Spike recoveries and long term stability

To validate the method, a spike-recovery test was carried out by analyzing a spiked solution containing 0.5 ppb mixed REE standard in a 500 ppm Nd_2O_3 sample. NH_3 on-mass mode was used for the determination of Dy and Ho, NH_3 mass-shift mode was used for Tb, and O_2 mass-shift mode for the remaining REEs. The results, which are shown in Figure 2, indicate that the recoveries for all elements were good, demonstrating the sensitivity and effectiveness of the method.

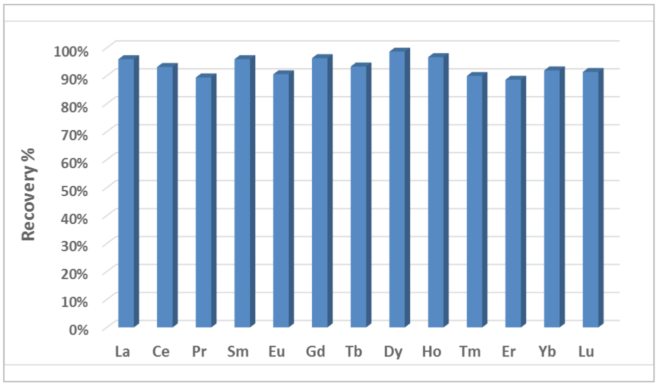

Figure 2. Recovery of 0.5 ppb REE spike added to 500 ppm Nd_2O_3 sample solution.

Long term stability over 2 hours was also measured using the same spiked sample. The stability of each REE signal is illustrated in Figure 3 and the average signal and RSD of each signal over the test period is summarized in Table 3. The data shows excellent stability (<5% RSD), demonstrating the applicability of the method for the routine analysis of high purity REE materials using the Agilent 8800 ICP-QQQ.

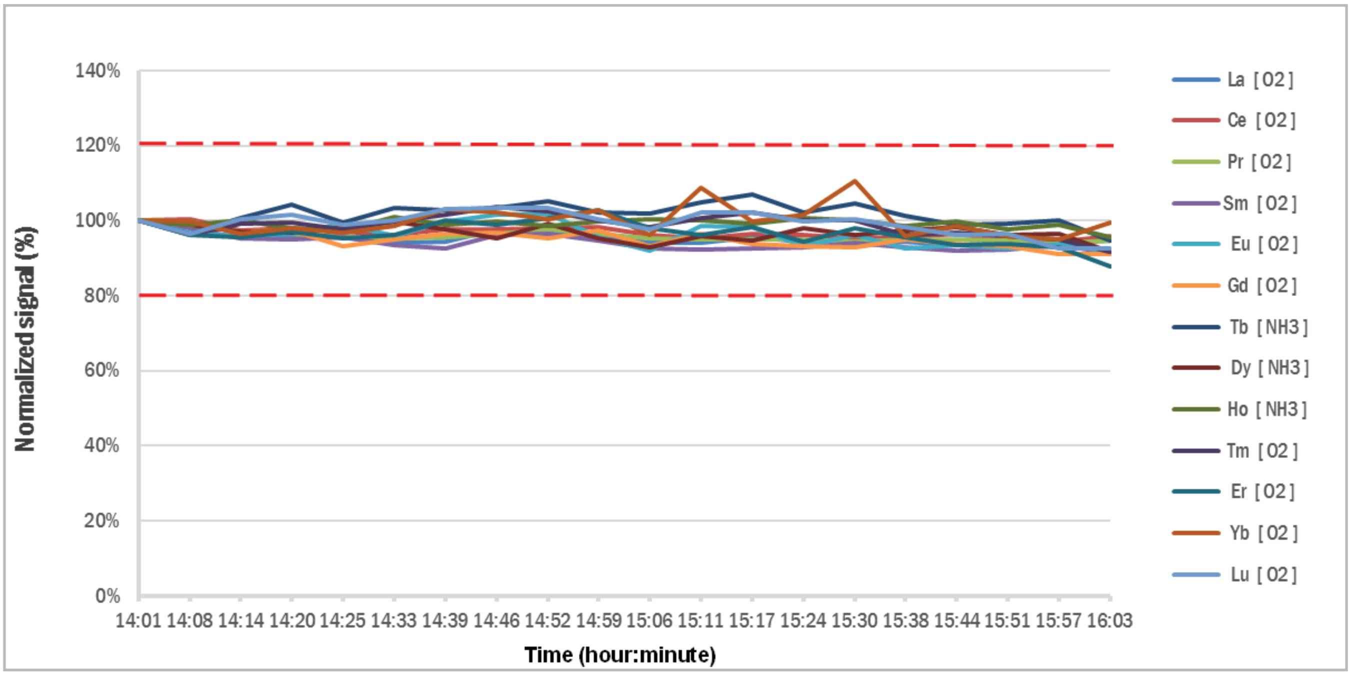

Figure 3. Long-term (2 hour) stability of 13 trace REEs spiked at 0.5 ppb in 500 ppm Nd_2O_3 solution

Table 3. Long-term (2 hour) %RSD for 13 trace REEs spiked at 0.5 ppb in 500 pm Nd_2O_3 solution

Element	Mass pair	Reaction gas	CPS		Concentration (ppb)	
	Q1 -> Q2		Mean	RSD%	Mean	RSD%
La	139->155	O_2	33443	2.0	0.625	1.1
Ce	140->156	O_2	24217	1.7	0.480	1.4
Pr	141->157	O_2	93453	1.7	1.512	1.2
Sm	152->168	O_2	24081	2.4	1.483	1.2
Eu	153->169	O_2	2171	3.3	0.485	3.2
Gd	155->171	O_2	4268	2.6	0.517	1.9
Tb	159->174	NH_3	1549	3.0	0.495	2.4
Dy	163->163	NH_3	939	2.3	0.530	3.1
Ho	165->165	NH_3	3508	1.3	0.484	2.3
Er	170->186	O_2	3735	3.4	0.463	3.7
Tm	169->185	O_2	18649	2.9	0.452	3.8
Yb	174->190	O_2	548	4.1	0.529	5.2
Lu	175->191	O_2	20623	3.2	0.470	4.0

Conclusion

The Agilent 8800 ICP-QQQ with MS/MS capability was used to successfully measure 13 REE impurities in a high-purity Nd_2O_3 sample solution. Oxygen mass-shift mode was effective at removing all of the polyatomic interferences from the Nd_2O_3 matrix. However, NH_3 on-mass mode further improved the BECs for Dy and Ho, and NH_3 mass-shift mode improved the BEC of Tb. Using NH_3 reaction mode, overlaps from NdO^+, $NdOH^+$, $NdOH_2^+$ on Dy, Tb and Ho respectively were reduced by around two orders of magnitude compared to O_2 mass shift mode, allowing the trace (ppt) measurement of Dy, Tb and Ho in a 500 ppm Nd_2O_3 matrix.

With the combination of Agilent's HMI and MS/MS reaction cell mode, the 8800 ICP-QQQ provided good long term stability over 2 hours for all trace REEs present in the 500 ppm Nd_2O_3 sample, demonstrating the validity of the analytical method for the direct analysis of high purity Nd_2O_3.

Reference

1. Naoki Sugiyama and Glenn Woods, Direct measurement of trace rare earth elements (REEs) in high-purity REE oxide using the Agilent 8800 Triple Quadrupole ICP-MS with MS/MS mode, Agilent publication 5991-0892EN (2012).

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