ICP - Mass Spectrometry

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Direct Determination of Rare Earth Impurities in High-Purity Neodymium Oxide with the NexION 5000 ICP-MS

Introduction

Rare earth elements (REEs) include the lanthanide series (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) as well as Sc and Y.

Currently, these metals have become critical to several modern technologies ranging from cellular phones and televisions, to LED light bulbs and wind turbines. Since the purity of the REEs govern their efficacy and the price, it is of great interest to produce ultra-high purity rare earth oxides.

Neodymium oxide (Nd_2O_3) is one such REE and is mainly used as a colorant for glass and ceramics, a raw material for the manufacture of metallic neodymium as well as a raw material for a strong magnetic alloy of neodymium-iron-boron. Adding 1.5%-2.5% nano-neodymium oxide to a magnesium alloy or aluminum alloy can improve the high temperature performance, air resistance and corrosion resistance of the alloy, and as such is widely used in aerospace materials. Moreover, Nd is extensively applied in super-magnets for disk drives, where high purities of the Nd and Nd₂O₃ are crucial. Therefore, the detection of impurities for these applications is vitally important. For this reason, inductively coupled plasma mass spectrometry (ICP-MS) has long been valued as the technique of choice for the measurement of impurities in high-purity REE compounds because of the low detection capabilities of this technology.

However, the main challenge analyzing trace concentrations of rare earth elements in high-purity rare earth oxides by ICP-MS is overcoming polyatomic spectral interferences from the matrix (MO^+ , MOH^+ , MH^+ , MOH_2^+).



The most common approach to eliminate molecular interferences is to separate the matrix element from the analytes. Such separation has been traditionally done by liquid-liquid extraction, off-line chromatographic separation, or utilizing high-performance liquid chromatography (HPLC) as a sample introduction technique to the ICP-MS, but these approaches tend to be both time-consuming and labor-intensive.

An alternate solution is to separate the analyte from the matrix in the ICP-MS which is best achieved by placing an additional full-sized quadrupole before the reaction cell. The size of the quadrupole is important as this governs the ability of the instrument to meet < 1 amu mass resolution without the need to increase the frequency on the guads which would otherwise contribute to long-term drift. With an additional quadrupole before the cell, only the mass of interest is allowed to proceed to the cell and all other masses are ejected, a design unique to triple- and multi-guadrupole instruments. In order to address polyatomic ion interferences, reaction gases, such as pure ammonia (NH_2) , oxygen (0_2) , or hydrogen (H_2) can be used to react with either the interference or the analyte ions in the collision/reaction cell such that the effect of the interference is removed. Therefore, having an instrument which is capable of running pure, highly reactive gases, such as ammonia, for an extended period of time is highly advantageous. This interference removal can be further enhanced by having an ICP-MS with a true-quadrupole cell which is able to control the reaction in the cell and ensure that no new interferences are formed from the reaction gases themselves, delivering on the low background equivalent concentration (BEC) and detection limit (DL) requirements of these challenging applications.

In this application note, PerkinElmer's NexION® 5000 Multi-Quadrupole ICP-MS was used for the direct determination of rare earth element impurities in a high-purity neodymium oxide matrix. Fourteen rare earth element impurities were analyzed using Multi Quad mode and pure reaction gases were used to facilitate the removal of interferences and aid the detection of ultra-trace concentrations of impurities.

Experimental

Samples and Standard Preparation

Approximately 0.200 g (accurate to 0.0001 g) of neodymium oxide (99.999%, Changchun Institute of Applied Chemistry, Jilin, China) was weighed into a 50 mL PFA bottle followed by 3 mL 55% HNO₃ (TAMAPURE-AA-10, 55%, Tama Chemicals, Japan) to aid the dissolution. This solution was then brought to a volume of 50 mL with ultrapure water. The above solution was diluted for a final Nd_2O_3 concentration of 500 ppm before analysis.

The external calibration method was used for the analysis of 14 rare earth elements in the high-purity neodymium oxide sample solution. Calibration standards were prepared from a 10 ppm

Multi-Element Rare Earth Element Standard (PerkinElmer Inc., Shelton, Connecticut, USA) at concentrations of 0.02, 0.1, 1, 10, 20 and 50 μ g/L with a final acid composition of 1% HNO₃. 500 ppm Nd₂O₃ matrix solution spiked with 1 ppb REEs was used for quality control.

Since there were no cesium (Cs) or rhenium (Re) impurities in the sample, and neither Cs nor Re reacts with either NH_3 or O_2 , Cs and Re were used as internal standards. The internal standards were prepared from 1000 ppm Cs and Re stock standards (PerkinElmer Inc.) and added on-line to all standards and samples, eliminating the need for manual addition.

Instrumentation

PerkinElmer's NexION 5000 Multi-Quadrupole ICP-MS (cleanroom model), described in detail in the NexION 5000 product note,¹ was used for all analyses, utilizing Standard, MS/MS and Mass Shift modes.

Reaction gases (NH_3 and O_2) were used in the Universal Cell in combination with dynamic bandpass tuning to actively prevent new interferences from forming in the cell and to address the interferences. Since most of the REEs readily react with the oxygen to form MO⁺, oxygen was used as the reaction gas in many cases, whereas some analytes were measured with pure ammonia for improved performance. Both MS/MS and Mass Shift modes were used. In MS/MS mode, Q1 and Q3 are set to the same mass, and the interference reacts with the reaction gas. In Mass Shift mode, Q1 and Q3 are set to different masses where the analyte is measured as the product ion from the reaction with a reaction gas. Some elements that do not have spectral interferences were measured in Standard mode without any gases in the cell. All instrumental parameters are listed in Table 1.

Table 1: NexION 5000 ICP-MS Instrumental Parameters

Parameter	Value
Plasma Gas Flow (L/min)	16
Aux Flow (L/min)	1.2
Nebulizer	MEINHARD® plus Glass Type C*
Spray Chamber	Glass Cyclonic High Sensitivity Spray Chamber⁺
Torch and Injector	One-piece SilQ Quartz Torch with 2.5 mm ID Injector
Analyzer Mode	MS/MS and Mass Shift
Reaction Gas	Ammonia (100%), Oxygen (100%)

* Used with MEINHARD® Nebulizer Internal Standard Tee

⁺ Glass Cyclonic High Sensitivity Spray Chamber for high matrix

Results and Discussion

In the 500 ppm Nd_2O_3 solution, analytes with potential spectral interferences from the Nd_2O_3 matrix are Tb, Dy and Ho. Tb and Ho are monoisotopic, having only one isotope at mass 159 for Tb and 165 for Ho which have direct interferences

from $^{142}Nd^{16}OH^+,\,^{143}Nd^{16}O^+$ and $^{148}Nd^{16}OH^+.$ Although there are many different isotopes of Dy, each has an interference from the Nd_2O_3 matrix. Nd_2O_3 interferences on Tb, Dy and Ho are listed in Table 2.

Table 2. Interfered Elements in 500 ppm Nd₂O₃

Element	Tb	Dy					Но		
Mass	159	156	158	160	161	162	163	164	165
Matrix Interference	¹⁴² NdOH, ¹⁴³ NdO	¹⁴² NdN	¹⁴² NdO	¹⁴⁴ NdOH, ¹⁴³ NdOH, ¹⁴² NdOH ₂	¹⁴⁵ NdO, ¹⁴⁴ NdOH, ¹⁴³ NdOH ₂	¹⁴⁶ NdO, ¹⁴⁵ NdOH, ¹⁴⁴ NdOH ₂	¹⁴⁶ NdOH, ¹⁴⁵ NdOH ₂	¹⁴⁸ NdO, ¹⁴⁶ NdOH ₂	¹⁴⁸ NdOH

As shown in Figure 1, the concentrations measured in Standard MS/MS mode and Mass Shift mode with O_2 were similar for Y, La, Ce, Pr, Sm, Eu, Gd, Er, Tm, Yb and Lu. Since both modes produced comparable results, it was concluded that there were no significant interferences from 500 ppm of the Nd₂O₃ matrix on these elements, so Standard MS/MS mode was used for their analysis.



Figure 1. Apparent concentration of REE impurities (ppt) in 500 ppm Nd₂O₃ utilizing different modes of operation and with different reaction gases, where Tb, Dy and Ho were found best suited to NH₂.

As expected, the apparent concentration of ¹⁵⁹Tb in Standard mode was higher than that observed in Mass Shift mode with O_2 and NH₃ due to the presence of ¹⁴²NdOH and ¹⁴³NdO. By clustering with NH₃, Tb⁺ can be measured at higher masses where ¹⁴²NdOH⁺ and ¹⁴³NdO⁺ interference does not exist. A product ion scan spectrum was used to display the removal of ¹⁴²NdOH⁺ and ¹⁴³NdO⁺ with NH₃, as shown in Figure 2. Tb reacts quickly with ammonia to produce TbNH⁺ and TbNH(NH₃)_x⁺ in Figure 2b, corresponding to masses 174 and 191 at 0.3 mL/min NH₃ flow rate. The TBNH cluster at mass 174 has the smallest BEC value, so the 159/174 ion pair is used for analysis.



Figure 2. Mass spectrum for (a) 500 ppm $\rm Nd_2O_3$ and (b) 500 ppm $\rm Nd_2O_3$ spike 1 ppb Tb in Mass Shift mode with $\rm NH_3$

There are many different masses of Dy that can be used for analysis, but each isotope of Dy in Table 2 has a Nd matrix interference. ¹⁶³Dy was chosen for analysis since the interference on ¹⁶³Dy was the smallest and the abundance of ¹⁶³Dy is 24.90%. ¹⁶³Dy has a direct interference from ¹⁴⁶NdOH and ¹⁴⁵NdOH₂, resulting in an apparent concentration of 29,258 ppt in 500 ppm Nd₂O₃ when measured in Standard mode (Figure 1). The effect of the interference can be reduced dramatically with Mass Shift mode using O_2 or MS/MS mode using NH₃, corresponding to 308 ppt and 119 ppt, with the lower values being achieved when using NH₃ as a reaction gas at mass 163 for ¹⁶³Dy. Figure 3 shows a composite product ion scan spectrum, displaying the removal of ¹⁴⁶NdOH⁺ and ¹⁴⁵NdOH₂⁺ with NH₃. 119 ppt of Dy in Nd₂O₃ indicates that the majority or all of the interference was removed and some Dy contamination might be present in the matrix.



Figure 3. Mass spectrum for 500 ppm $\rm Nd_2O_3$ and 500 ppm $\rm Nd_2O_3$ + 1 ppb Dy in $\rm NH_3$ MS/MS mode.

The apparent concentration of ¹⁶⁵Ho in Standard mode was higher than that observed in Mass Shift mode with O₂ and NH₃ due to the presence of ¹⁴⁸NdOH. The effect of the interference can be reduced dramatically with Mass Shift mode using O2 or MS/MS mode using NH2 corresponding to 43 ppt and 8 ppt respectively, indicating a significant interference reduction when NH₃ was used as a reaction gas. This can be observed in Figure 4a. Here, NdOH⁺ (mass 165) reacts with NH₃ to form higher masses. The peak at 165 was greatly reduced with a few remaining counts which can be attributed to a Ho impurity in the sample. In Figure 4b, 500 ppm Nd₂O₃ was spiked with 1 ppb Ho and a strong peak at mass 165 appeared, corresponding to the ion ¹⁶⁵Ho⁺. Ho⁺ is not expected to react with NH_{ν} and this was confirmed by the observation that running 1 ppb Ho standard under the same conditions produced a peak at mass 165.



Figure 4. Mass spectrum for (a) 500 ppm $\rm Nd_2O_3$ and (b) 500 ppm $\rm Nd_2O_3$ spike 1 ppb Ho in MS/MS mode with $\rm NH_x$

The results for the 14 REE impurities in the high-purity neodymium oxide sample are listed in Table 3.

Element	Q1	Q3	Mode	Concentration in Solution (ng/L)	Conten (µg/g)
Y	89	89	Standard	633	1.265
La	139	139	Standard	51	0.102
Ce	140	140	Standard	68	0.136
Pr	141	141	Standard	18	0.036
Sm	152	152	Standard	69	0.137
Eu	153	153	Standard	52	0.103
Tb	159	174	$\mathrm{NH_3}$ Mass Shift	22	0.044
Gd	155	155	Standard	33	0.065
Dy	163	163	$\rm NH_3$ MS/MS	119	0.238
Но	165	165	NH ₃ MS/MS	8	0.016
Er	170	170	Standard	447	0.893
Tm	169	169	Standard	5	0.01
Yb	172	172	Standard	21	0.041
Lu	175	175	Standard	5	0.01

Table 3. REE Impurities in Nd₂O₃

Spike recoveries of 1 ppb in a 500 ppm Nd_2O_3 solution (Figure 5) were within ± 10% for all analytes, further validating the method and proving its accuracy in the sample matrix.



Figure 5. Spike recoveries for 1 ppb in 500 ppm Nd₂O₃.

Conclusion

By using pure ammonia gas, the NexION 5000 Multi-Quadrupole ICP-MS was able to resolve problematic spectral interference on Tb, Dy and Ho in a 500 ppm Nd_2O_3 solution. Mass Shift mode was used in the analysis of Tb as this analyte is highly reactive with NH_3 . Since Dy and Ho have a low reactivity with NH_3 and the interfered NdOH⁺ can cluster with NH_3 to higher mass, MS/MS mode was used for the resolution of interferences on these ions.

The outstanding performance observed in the analysis was made possible thanks to:

- A true-quadrupole Universal Cell with dynamic bandpass tuning which was able to even use 100% pure reactive gases, such as ammonia, delivering superior interference removal capabilities for the analysis of Ho, Tb and Dy in a concentrated Nd matrix;
- Multi.Quad mode, which ensured active control over the reactions in the cell for improved analytical performance and controlled reactions, delivering consistent results;
- The robust instrumental design of the NexION 5000 ICP-MS, which allowed the analysis of concentrated and challenging matrices, such as high-purity Nd.

References

1. "NexION 5000 Multi-Quadrupole ICP-MS", PerkinElmer Product Note, 2022.

Consumables Used

Component	Part Number
Glass Nebulizer	N8152373
Glass Cyclonic Spray Chamber	N8152389
Fixed 2.5 mm Injector UHP Quartz Torch	N8152473
Platinum Sampler Cone	W1033614
Platinum Skimmer Cone	N8161041
Hyper-skimmer Cone	N8160120
ISTD Tubing: Orange/Green (0.38 mm i.d.)	N8145197
MEINHARD® Nebulizer Internal Standard Tee	N8152386
Carrier Tubing: Orange/Green (0.38 mm i.d.)	N8145197
Waste Tubing: Gray/Gray Santoprene (1.30 mm i.d.)	N8152415
Cesium (Cs) Pure Standard, 1000 mg/L	N9303767
Rhenium (Re) Pure Standard, 1000 mg/L	N9303793
17-Element Solution, 5% HNO ₃ , 10 µg/mL, 125 mL	N9300232

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