APPLICATION NOTE

ICP - Mass Spectrometry

AUTHOR

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Direct Determination of Rare Earth Impurities in High-Purity Cerium Oxide with the NexION 5000 ICP-MS in Accordance with Chinese Method GB/T 18115.2-2020

Introduction

The collective term “rare earth elements” (REEs) includes the lanthanides (atomic number between 57 and 71) and yttrium, since it shares the same properties, including charge and ionic radius as the heavier lanthanides and, as a result, behaves similarly. REEs have similar physical and chemical properties and are generally divided into light (from La to Sm) and heavy (from Eu to Lu) REEs.

The application of REEs is mainly concentrated in the field of luminescent high-purity materials, such as phosphors, luminescent powders, crystal materials, optical fiber materials, optical glass, electronic materials, etc. With the development of optoelectronic communication technology, the demand for radio and television materials is increasing, especially that of high-purity rare earths. As such, REEs are often referred to as “industrial vitamins”. In these applications, the purity of the REE materials is of the utmost importance, as this can have a direct impact upon the end-product quality, performance and yields.

Cerium oxide (CeO_2), for example, is used as an additive in the glass industry, as an abrasive material for plate glass, and in the grinding of spectacle glass, optical lens, and picture tubes. CeO_2 helps with decolorization, clarification, and absorption of ultraviolet rays and electron rays in the glass, as well as being used as an anti-ultraviolet component in cosmetics. The purity of cerium oxide is usually required to be as high as possible, mandating the accurate determination of REE impurities in CeO_2 at ultralow levels.[1]

One of the biggest challenges in the analysis of impurities in purified REE compounds, such as CeO_2, is that the impurities are often present as spectral interferences. An example, the analysis of 6N purity CeO_2 by ICP-MS was reported by *Li et al.*[2], where mathematical corrections were needed for the elimination of interferences. Another option for measuring impurities is to separate them by solvent extraction. However, this is a time-consuming and labor-intensive process.

Instead of physical separation and measurement of impurities or mathematical corrections, another approach is to remove the interferences on REE impurities in the mass spectrometer. This can be accomplished by placing an additional full-sized quadrupole before a collision-reaction cell such that only the mass of interest is allowed to enter the reaction cell while all other masses are ejected, a design unique to triple- and multi-quadrupole ICP-MS instruments.

The interferences on REE impurities come from polyatomic ions (MO^+, MOH^+, MH^+, MOH_2^+) which form in the high-temperature plasma. By using ICP-MS with triple-quadrupole or multi-quadrupole functionality, other ions residing on the mass of interest are not allowed to enter the collision-reaction cell. In order to address these interferences to the levels required for ultra-trace analysis, reaction gases, such as NH_3, can be used to react with either the interference or the analyte ions in the cell such that the interference is removed.[3] Therefore, having an instrument which is capable of running pure reaction gases, such as pure ammonia, for an extended period of time is highly advantageous. This interference removal can further benefit from having an ICP-MS with a true quadrupole cell which is able to control the reaction to ensure that no new interferences form, further delivering on the low BEC and DL requirements of these challenging applications.

The third method of the latest Chinese standard GB/T 18115.2-2020 is the first method certified for the determination of lanthanum, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium and yttrium content in cerium metal and oxide by triple/multi-quadrupole ICP-MS. In this application note, PerkinElmer's NexION® 5000 Multi-Quadrupole ICP-MS was used for the direct determination of trace rare earth element impurities in a high-purity cerium oxide matrix. Fourteen rare earth element impurities were analyzed in 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 cerium oxide (99.999%, Changchun Institute of Applied Chemistry, Jilin, China) was weighed into a 50 mL PFA bottle followed by the addition of 2 mL 55% HNO_3 (TAMAPURE-AA-10, 55%, Tama Chemicals, Japan) and 5 mL 30% H_2O_2 (Suzhou JINGRUI Chemical Co. Ltd., Suzhou, Jiangsu, China). The mixture was heated at 120 °C for 20 minutes and cooled to room temperature. This solution was then brought to a final volume of 50 mL with ultrapure water for a final CeO_2 concentration of 500 ppm.

An external standard calibration method was used for the analysis of fourteen REEs in the high-purity CeO_2 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 µg/L in solutions of 1% HNO_3.

Since there were no cesium (Cs) and 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 internal standard addition.

Instrumentation

PerkinElmer's NexION 5000 Multi-Quadrupole ICP-MS (cleanroom model), described in detail in the NexION 5000 product note[4], 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 to remove interferences and dynamic bandpass tuning applied to the cell to actively prevent new interferences from forming in the cell, a feature unique to true quadrupole reaction cells. 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	16 L/min
Aux Flow	1.2 L/min
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(s)	MS/MS and Mass Shift
Reaction Gas	Ammonia (100%), Oxygen (100%)

** Used with MEINHARD® Nebulizer Internal Standard Tee*

Results and Discussion

In a 500 ppm CeO_2 solution, the main interfered elements are Pr, Gd and Tb. Pr and Tb are monoisotopic, having only one isotope at *m/z* 141 for Pr and 159 for Tb, which have direct interferences from $^{140}CeH^+$ and $^{142}Ce^{16}OH^+$. Although there are many different masses of Gd, each has an interference from the CeO_2 matrix. All the interfered elements and their CeO_2 interferences are listed in Table 2.

Table 2. Interfered Elements in 500 ppm CeO_2.

Element	**La**	**Pr**	**Gd**							**Tb**	**Lu**
Mass	**139**	**141**	**152**	**154**	**155**	**156**	**157**	**158**	**160**	**159**	**175**
Matrix Interference	^{138}CeH	^{140}CeH	^{136}CeO	^{138}CeO	$^{138}CeOH$	^{140}CeO	$^{140}CeOH$	^{142}CeO	$^{142}CeOH_2$	$^{142}CeOH$	$^{142}CeO_2H$

The method detection limits (MDLs) can be seen in Figure 1 and were all found to be below 0.5 ppt. They were determined by measuring seven blanks of 1% nitric acid (using the external calibration) and their standard deviations multiplied by 3.14 utilizing different modes of operation and with different reaction gases. As shown in Figure 2, the concentrations measured in Standard mode and Mass Shift mode with O_2 were similar for Y, Nd, Eu, Er, Tm and Yb. The concentrations measured in Standard mode and Mass Shift mode with O_2 for Sm, Dy, and Ho were all lower than the detection limits of the instrument and so were not displayed. Since both modes produced comparable results, it was concluded that there were no significant interferences from 500 ppm of the CeO_2 matrix on these elements, so Standard mode was used for their analysis.

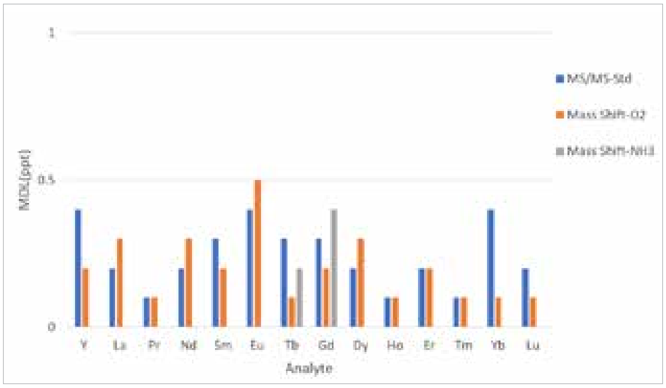

Figure 1. MDLs determined in 1% HNO_3 utilizing different modes of operation and different reaction gases.

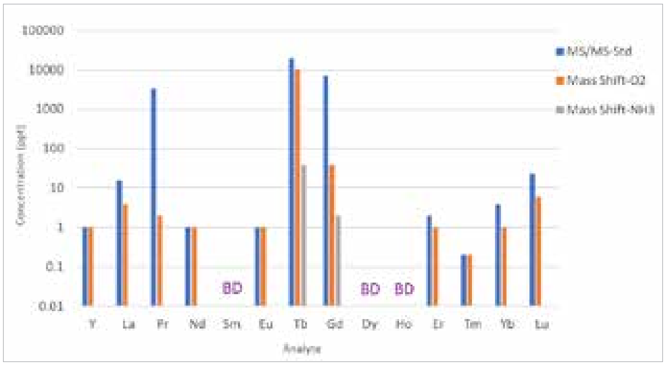

Figure 2. Concentration of REE impurities (ppt) in 500 ppm CeO_2 utilizing different modes of operation and different reaction gases where BD indicates "below detection".

As expected, the apparent concentration of ^{141}Pr in Standard mode was higher than that observed in Mass Shift mode with O_2 due to the presence of the $^{140}CeH^+$ interference on ^{141}Pr in Standard mode. Figure 3 shows a product ion scan of the mass range 141-285 which demonstrates the effective removal of the hydride interference via mass-shifting of the analyte. Figure 3a shows how CeH^+ (m/z 141) reacts with O_2 to form $^{140}Ce^{16}O^+$ and $^{140}CeOO^+$. The peak at mass 141 almost disappeared, which means $^{140}CeH^+$ completely reacts with O_2 and does not have an apparent peak at mass 157. In Figure 3b, when 500 ppm CeO_2 solution was spiked with 1 ppb Pr, a strong peak at mass 157 appears, corresponding to the ion $^{141}Pr^{16}O^+$. This was confirmed by observing that a 1 ppb Pr standard run under the same conditions produces a peak at *m/z* 157.

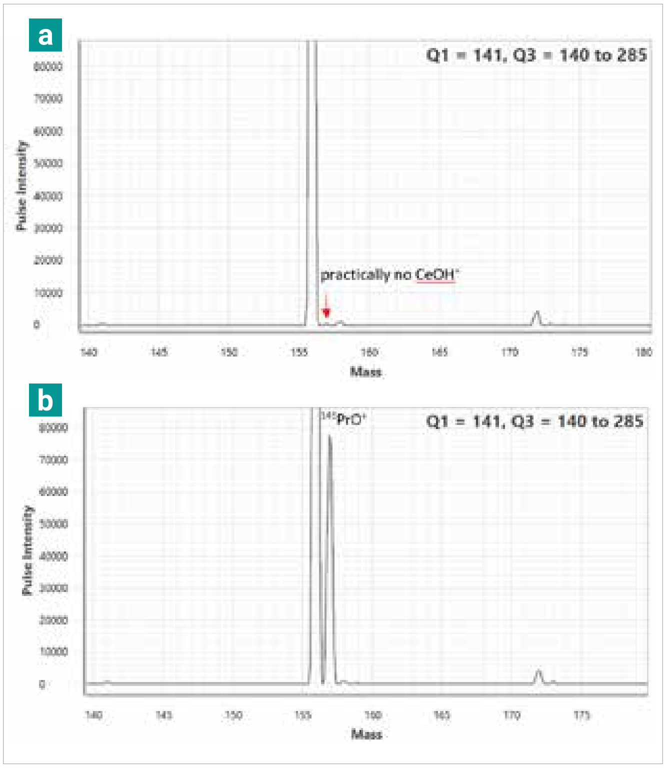

Figure 3. Mass spectrum for (a) 500 ppm CeO_2 and (b) 500 ppm CeO_2 spiked with 1 ppb Pr with both a) and b) analyzed in Mass Shift mode with O_2.

Meanwhile, the apparent concentrations of ^{139}La measured in Standard mode and Mass Shift mode with O_2 were 16 and 4 ppt respectively, indicating an interference on $^{139}La^+$. Ba was not detected in the Ce matrix, so BaH^+ would not exist, therefore the interference was most likely from $^{138}CeH^+$. As demonstrated earlier, $^{138}CeH^+$ reacts with O_2, creating CeO^+ on mass 154 not interfering with LaO at mass 155, allowing La to be measured at *m/z* 155.

The apparent concentration of ^{159}Tb in Standard mode was higher than that observed in Mass Shift mode with O_2 and NH_3 due to the presence of $^{142}CeOH^+$. By clustering with NH_3, Tb^+ can be measured at higher masses where the $CeOH^+$ interference does not exist. A product ion scan mass spectrum was used to display the removal of $CeOH^+$ with NH_3, as shown in Figure 4. Tb reacts quickly with ammonia to produce $TbNH^+$ and $TbNH(NH_3)_x^+$ (Figure 4b), corresponding to masses 174 , 191 and 208 at 0.3 mL/min NH_3 flow rate. The TBNH cluster at mass 179 has the smallest BEC value, so the 159/174 ion pair is used for analysis.

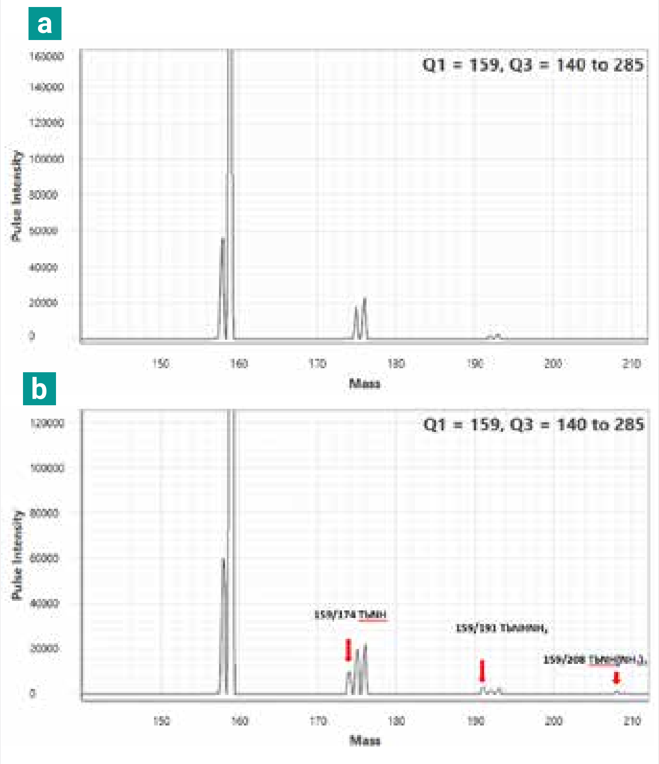

Figure 4. Mass spectrum for (a) 500 ppm CeO_2 and (b) 500 ppm CeO_2 spiked with 1 ppb Tb with both a) and b) analyzed in Mass Shift mode with NH_3.

There are many different masses of Gd that can be used for analysis, but each mass of Gd in Table 1 corresponds to a Ce matrix interference. ^{160}Gd was chosen for analysis since the interference on ^{160}Gd is the smallest and the abundance of ^{160}Gd is 21.86%. ^{160}Gd has a direct interference from $^{142}Ce^{16}OH_2^+$, resulting in an apparent concentration of 7028 ppt Tb in 500 ppm CeO_2 when measured in Standard mode (Figure 2). The effect of the interference can be reduced dramatically via Mass Shift mode using O_2 or NH_3, corresponding to 38 ppt and 2 ppt respectively, with the lower values being achieved when using NH_3 as a reaction gas at mass 175 for $^{160}GdNH^+$. This interference removal effect is consistent with a previously released application note[5] and points to the benefit of being able to use pure reaction gases in the NexION ICP-MS series of instruments.

The use of the reaction gas O_2 in Mass Shift mode was found to improve the measurement of ^{175}Lu in a Ce matrix when compared to the analysis in Standard mode. This was due to the presence of a small $^{142}Ce^{16}O_2H^+$ interference that can be resolved by measuring Lu as LuO^+ at mass 191, demonstrating that ^{175}Lu can be measured interference-free.

The results for the 14 REE impurities in the high-purity CeO_2 sample are listed in Table 3, where the pure nature of the material is proven by the results.

Table 3. REE Impurities Results in CeO_2.

Element	Q1	Q3	Mode	Concentration in Solution (ng/L)	Content (µg/g)
Y	89	89	Standard	1.0	0.002
La	139	155	O_2 Mass Shift	4.0	0.008
Pr	141	157	O_2 Mass Shift	2.0	0.004
Nd	144	144	Standard	1.0	0.002
Sm	147	147	Standard	<DL	<DL
Eu	151	151	Standard	1.0	0.002
Tb	159	174	NH_3 Mass Shift	38.0	0.076
Gd	160	175	NH_3 Mass Shift	2.0	0.004
Dy	163	163	Standard	<DL	<DL
Ho	165	165	Standard	<DL	<DL
Er	166	166	Standard	1.0	0.002
Tm	169	169	Standard	0.2	0.0004
Yb	171	171	Standard	1.0	0.002
Lu	175	191	O_2 Mass Shift	6.0	0.012

Spike recoveries of 100 ppt and 1 ppb in a 500 ppm CeO_2 solution (Figure 5) were within ±10% of the spiked value for all analytes, further validating the method and proving its accuracy in the sample matrix.

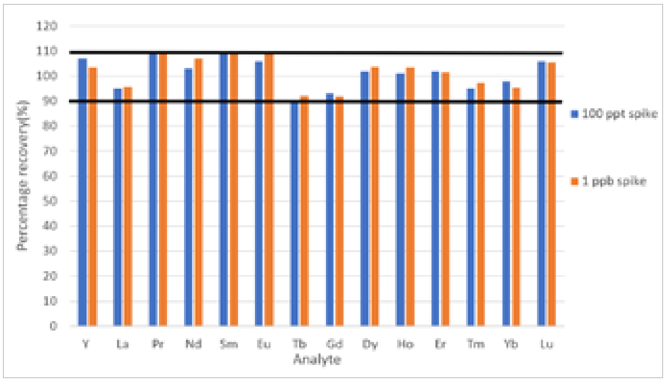

Figure 5. Spike recoveries (%) for 100 ppt and 1 ppb in 500 ppm CeO_2.

With the accuracy of the methodology established, the stability was verified over a two-hour continuous analysis of 500 ppm CeO_2 spiked with a 1 ppb REE mixture. Over two hours, the %RSD for this solution was well within 2.5% (Figure 6), demonstrating the outstanding stability of the NexION 5000 ICP-MS system, despite the challenging and complex matrix. It is important to note that this data was acquired without recalibration or excessive rinsing between samples and therefore mimics a typical run in a commercial lab.

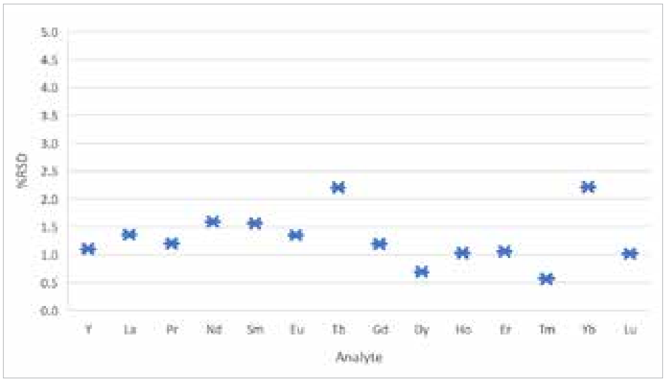

Figure 6. %RSD for 1 ppb REEs spiked in 500 ppm CeO_2 over a two-hour analysis.

Conclusion

The results presented in this work demonstrate the ability of the NexION 5000 Multi-Quadrupole ICP-MS to accurately and directly measure 14 ultra-trace REE impurities in a high concentration, high-purity cerium oxide matrix, proving that the NexION 5000 can be used to satisfy Chinese standard GB/T 18115.2-2020 and other similar standards. Using a combination of the true quadrupole Universal Cell, multi-quadrupole technology and the ability to use pure ammonia and oxygen reaction gases, with dynamic bandpass tuning to create controlled reactions in the cell, the Ce polyatomic interferences on La, Pr, Gd, Tb and Lu were eliminated, ensuring accurate results.

During the analysis, elements which were not thought to have an interference on them were analyzed in Standard mode. These assumptions were validated by analyzing the element in Mass Shift mode with O_2. Since no significant differences in the concentrations between Standard and Mass Shift modes were observed, Y, Nd, Sm, Eu, Dy, Ho, Er, Tm and Yb were analyzed in Standard mode.

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

- The quadrupole Universal Cell with the ability to use 100% pure reactive gases to eliminate spectral interference.
- Multi Quad mode, which allows active control over the reactions in the cell for improved performance and repeatability of the reaction.
- The robust instrumental design of the NexION 5000 ICP-MS, which allows the analysis of concentrated and challenging matrices, such as high-purity Ce.

References

1. Shi T. et al, "Ytterbium-doped large-mode-area silica fiber fabricated by using chelate precursor doping technique", Applied Optics, Vol. (53) 3191-3195, 2014.
2. Li B., "Determination of Trace Amounts of Rare Earth Elements in High-purity Cerium Oxide by Inductively Coupled Plasma Mass Spectrometry After Separation by Solvent Extraction", Analyst, Vol. (122) 543-547, 1997.
3. Pedreira W.R., "Determination of trace amounts of rare earth elements in highly pure praseodymium oxide by double focusing inductively coupled plasma mass spectrometry and high-performance liquid chromatography", Journal of Alloys and Compounds, Vol. 323-324, 2001.
4. "NexION 5000 Multi-Quadrupole ICP-MS", PerkinElmer Product Note, 2020.
5. Ma X., "Direct Determination of Trace Rare Earth Impurities in High Purity Praseodymium Oxide with the NexION 5000 ICP-MS", PerkinElmer Application Note, 2021.

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: Orange/Green (0.38 mm i.d.)	N8145197
MEINHARD® Nebulizer Internal Standard Tee	N8152386
Carrier: Orange/Green (0.38 mm i.d.)	N8145197
Waste: Gray/Gray Santoprene (1.30 mm i.d.)	N8152415
1000 mg/L Cs	N9303767
1000 mg/L Re	N9303793
17-Element Solution, 5% HNO_3, 10 µg/mL, 125 mL	N9300232

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