APPLICATION NOTE

ICP-Mass Spectrometry

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Direct Determination of Trace Rare Earth Impurities in High-Purity Europium Oxide Using the NexION 5000 ICP-MS

Introduction

Because rare earth elements exhibit many optical, electrical, and magnetic properties, they play an irreplaceable role in high-tech photoelectromagnetic materials. They are known as the "treasure house" of new materials in the twenty-first century. At present, the widely used color TV phosphors, Ni-H batteries, high-performance magnetic materials, etc., are all examples of rare earth elements in high-tech applications. The application of high-purity rare earth elements is mainly concentrated in luminescent materials, such as phosphors, luminescent powders, crystal materials, optical fiber materials, optical glass, etc., as well as high-tech fields of electronic materials, and giant magnetostrictive materials. With the rapid development of optoelectronic communication technology, the requirements of optoelectronic materials are increasing, especially as the demand for high-purity rare earths is rising, and the development prospects are very bright.

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High-purity europium oxide is used to make color powder, energy-saving lamp powder, self-luminous powder, etc., for displays. The high-definition display (HDP) currently being developed and used requires higher purity and particle size, and its demand is also greater. Therefore, high-purity rare earth analysis and detection technology is also facing technological innovation as the application demand increases.

Chemical pre-concentration with ICP-OES and ICP-MS measurements can be used to determine ultra-trace rare earth elements (REEs) in high-purity rare earth matrix (4N-6N) and requires complicated sample preprocessing. For ultra-trace REE analysis in europium oxide (Eu_2O_3), direct determination of Tm (a mono-isotopic element at m/z 169) by ICP-MS is exceptionally challenging due to the interference of $^{153}Eu^{16}O^+$.[1-3]

In this application note, PerkinElmer's NexION® 5000 Multi-Quadrupole ICP-MS is used for the direct determination of trace rare earth impurities in high-purity europium oxide by eliminating matrix-based interferences. Fourteen rare earth elements were analyzed using Multi Quad mode.

Experimental

Samples and Standards Preparation

Approximately 0.100 g (accurate to 0.0001 g) of europium oxide (99.999%, Quannan New Resources Rare Earth Co., Ltd., Jiangxi, China) was weighed into a 100 mL PFA bottle, 2% HNO_3 (TAMAPURE-AA-10, 55%, Tama Chemicals, Japan) was added to dissolve it at room temperature and then diluted to a volume of 50 mL.

The method of standard additions (MSA) was used for the analysis of fourteen rare earth elements in the high-purity europium oxide sample solution. MSA calibration standards were prepared from a 10 ppm multi-element rare earth standard (PerkinElmer Inc., Shelton, Connecticut, USA). Standards were prepared by pipetting 10 mL of the europium oxide solution into a 50 mL PFA bottle, followed by the additions of different volumes of the rare earth multi-element solution to produce REE standards of 20, 100, and 500 ng/L when diluted to a final volume of 40 mL and final Eu_2O_3 concentration of 500 ppm.

Since there was no rhodium in the sample solution, and rhodium is stable in Reaction mode with NH_3 and O_2, rhodium was used as an internal standard. The internal standard was prepared from 1000 ppm Rh (PerkinElmer Inc., Shelton, Connecticut, USA) and added on-line to all standards and samples, eliminating the need for manual addition.

Instrumentation

PerkinElmer's NexION 5000 Multi-Quadrupole ICP-MS, described in detail in the NexION 5000 product note, represents a truly significant advancement in ICP mass spectrometry and the removal of spectral interference in trace elemental analyses.[4]

The instrument's analytical performance, sensitivity, and stability are elevated through the novel second-generation Triple Cone Interface (TCI) with OmniRing™ technology and the patented plasma RF generator with LumiCoil™ RF coil.[5]

The balanced and free-running RF generator design delivers improved robustness, high efficiency, wide power range, and ensures fast power-switching between Cold and Hot Plasma modes. Multi-mode methods can now leverage these technologies in combination with a cell-based Reaction mode (in the quadrupole Universal Cell) and multi-quadrupole technology, yielding superior polyatomic interference removal that can further improve detection limits (DLs) and lower background equivalent concentrations (BECs).

The NexION 5000's Universal Cell is a dedicated quadrupole reaction cell that controls reaction chemistry within the cell. This is achieved by applying dynamic bandpass tuning within the cell, preventing by-products of the original reaction from forming new interferences within the cell gas or cell gas impurities that may have been introduced into the cell. The reaction cell's bandpass allows predictable and reproducible interference removal using either 100% pure or a mixture of highly reactive gases in the cell. Plus, the NexION 5000 ICP-MS provides four gas channels, which allows on-the-fly gas mixing of reaction and/or collision gases within the same analytical method, delivering ultimate flexibility in removing interferences.

In this work, reaction gases (NH_3, O_2) were used to remove spectral interferences by changing them into atoms or ions of a different mass or creating a cluster ion with an analyte (Mass Shift). In MS/MS mode, Q1 and Q3 are set up at the same mass, while in Mass Shift mode, an analyte is measured as an ion product with a reaction gas at a higher mass. Some elements that do not have spectral interferences were measured in Standard mode without any gases entering the cell. All instrumental parameters are listed in Table 1.

Although various modes are used in this work, the optimization procedure can be easily achieved on the intuitive Syngistix™ for ICP-MS software through the SmartTune wizard. This simplified optimization procedure aids in attaining the most optimized conditions for interference removal while maintaining maximum sensitivity for the analytes.

Table 1. NexION 5000 ICP-MS Instrumental Parameters.

Parameter	Value
Plasma Gas Flow (L/min)	16
Aux Flow (L/min)	1.2
Nebulizer Gas Flow (L/min)	0.94
RF Power (W)	1600
Nebulizer	MEINHARD® plus Glass Type C
Spray Chamber	Cyclonic Spray Chamber (Standard)
Torch and Injector	One-piece Quartz Torch with 2.0 mm ID Injector
Pump Tubing - Sample	Yellow/Green (0.28 mL/min)
Pump Tubing - IS	Yellow/Green (0.28 mL/min)
Scan Type	Focusing (MS/MS)
Reaction Gas	Ammonia (100%), Oxygen

Results and Discussion

By using 100% pure ammonia and oxygen as cell gases with the MS/MS and Mass Shift modes, interferences are removed by either reacting with the gas, or the reactive gas reacts with the analyte, creating a reaction product at a higher mass.

For the analysis of trace rare earth impurities in high-purity europium oxide, the most challenging REE to measure is Tm. It has only one isotope at m/z 169, which has a direct interference from $^{153}Eu^{16}O^+$.

In this application note, the matrix is 500 ppm Eu_2O_3. Mass Shift mode with O_2 was not effective for the removal of the EuO^+ interference on Tm^+. Tm does not create clusters with NH_3 effectively, but MS/MS mode with NH_3 was used to remove spectral interferences on Tm. Gd in Eu_2O_3 was also investigated in this application note. Since Gd can react with NH_3 but not so efficiently, MS/MS mode was used for Gd analysis in Eu_2O_3 solution.

The REEs were investigated in Standard mode and Mass Shift mode with O_2 simultaneously except Tm in Standard mode only. In the Mass Shift mode with O_2, the Q3 mass is set 16 amu higher than the Q1 mass. All the REEs can react with the oxygen but with variable efficiency forming MO^+. Yb reacts with O_2 less efficiently than others, and the reaction efficiency is about 18% for Yb^+ to form YbO^+, even though all the REEs can be detected with Mass Shift mode in O_2 cell gas. The measured values are shown in Figure 1.

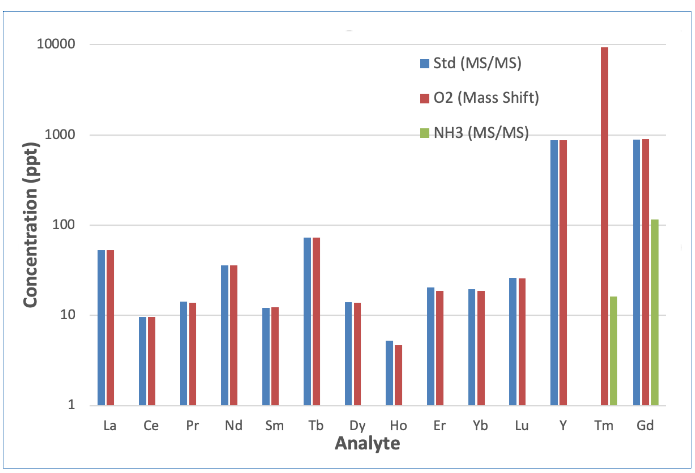

Figure 1. Determined concentration of REE impurities in 500 ppm Eu_2O_3.

According to the results shown in Figure 1, the values of Tm and Gd by MS/MS mode with NH_3 gas were lower than the Mass Shift mode with O_2. Other REE values were equivalent to Standard mode and Mass Shift mode with O_2; therefore, in the final analysis, they were measured in Standard mode. It also confirmed that the other REEs had no interferences in the 500 ppm Eu_2O_3. The result of fourteen REE impurities in high-purity europium oxide are listed in Table 2. The total REE concentration of solid is 2.5 µg/g, less than 10 µg/g, meeting the 99.999% content requirement.

Yttrium (Y) has no spectral interference in high-purity europium oxide. The test value may be due to the large output of the Eu_2O_3 manufacturer's Y products, which may cause contamination to other products. When yttrium's pollution is controlled, it is easy for the NexION 5000 ICP-MS to test 99.9999% ultra-high-purity europium oxide.

Table 2. Results of REE impurities in Eu_2O_3.

Element	Q1	Q3	Mode	Concentration (ng/L)	Content (µg/g)
La	139	139	Standard	52.8	0.11
Ce	140	140	Standard	9.58	0.02
Pr	141	141	Standard	14.2	0.03
Nd	142	142	Standard	35.9	0.07
Sm	147	147	Standard	12.1	0.02
Gd	157	157	Ammonia	116	0.23
Tb	159	159	Standard	73.1	0.15
Dy	163	163	Standard	13.9	0.03
Ho	165	165	Standard	5.24	0.01
Er	166	166	Standard	20.4	0.04
Tm	169	169	Ammonia	16.2	0.03
Yb	174	174	Standard	19.4	0.04
Lu	175	175	Standard	26.0	0.03
Y*	89	89	Standard	875.4	1.7

*Y has no mass interference in high-purity europium oxide. A relatively high Y value could be the result of Y contamination in the tested Eu_2O_3 matrix.

The long-term stability of the NexION 5000 ICP-MS was evaluated by continuous measurement of fourteen REEs in Eu_2O_3 matrix solution over four hours. The plot (Figure 2) demonstrates exceptional stability for fourteen elements in all modes. RSDs were less than 10% for all elements in a four-hour analysis though the concentration of some elements is less than 10 ppt in the 500 ppm Eu_2O_3 matrix solution.

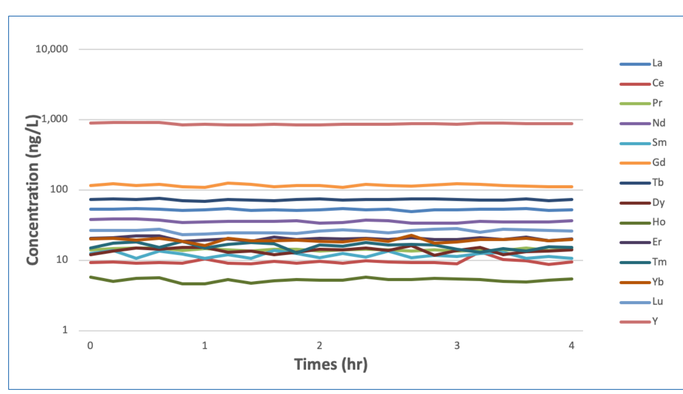

Figure 2. Determined concentration of REE impurities in 500 ppm Eu_2O_3.

Conclusion

The results presented in this work demonstrate the analysis of fourteen REEs in high-purity europium oxide. The interference of EuO^+ to single isotope Tm was dramatically reduced by using 100% NH_3. The outstanding analytical performance and stability were made possible thanks to the following features and capabilities of the NexION 5000 Multi-Quadrupole ICP-MS:

- The unique 34-MHz RF plasma generator with LumiCoil RF load coil
- The quadrupole Universal Cell with up to 100% pure reactive gas to eliminate the interference totally
- The robustness of the instrument in concentrated and challenging matrices

References

1. Anding Zhang, "Determination of rare earth impurities in high purity europium oxide by inductively coupled plasma-mass spectrometry and evaluation of concentration values for europium oxide standard material," Eur. J. Mass Spectrom. 10, 589-598, 2004.
2. Yan Zhang, "Solvent Extraction ICP-MS/MS method for the Determination of REE Impurities in Ultra-high Purity Ce Chelates," Atomic spectroscopy, Vol. 40(5), 2019.
3. Viet Hung Nguyen, "A simple separation system for elimination of molecular interferences for purity determination of europium and ytterbium oxides by HPLC-ICP-MS," J. Anal. At. Spectrom., Vol (35), 2020.
4. "NexION 5000 Multi-Quadrupole ICP-MS" PerkinElmer Product Note, 2020.
5. Badiei Hamid et al, "Advantages of a Novel Interface Design for NexION 5000 ICP-MS" PerkinElmer Technical Note, 2020.

Consumables Used

Component	Part Number
Glass Nebulizer	N8152373
Glass Cyclonic Spray Chamber	N8152389
Fixed 2.0 mm Injector UHP Quartz Torch	N8152428
Platinum Sampler Cone	W1033614
Platinum Skimmer Cone	N8161041
Hyper-Skimmer Cone	N8160120
Sample Uptake Tubing	N8145197
Rhodium (Rh) Pure Standard, 1000 mg/L	N9303794
Multi-Element Solution 2, 10 mg/L	N9300232

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