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

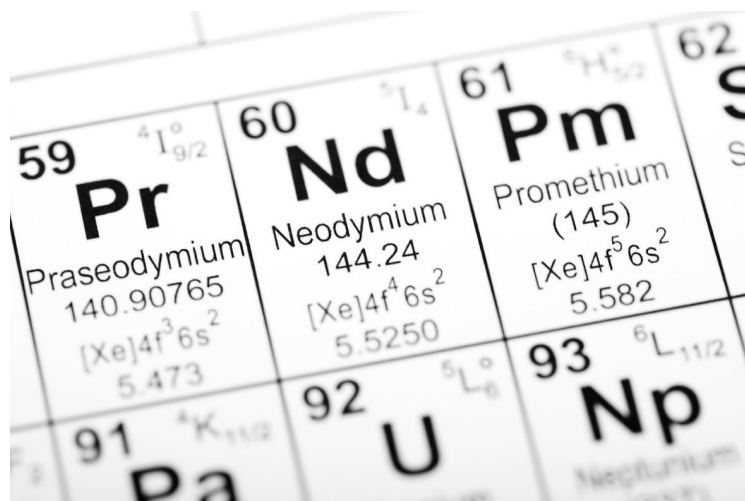## Application note

Materials

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Introduction

Rare earth elements (REE) are widely used in advanced technology. Praseodymium (Pr), neodymium (Nd), samarium (Sm) and dysprosium (Dy) are used in high-power permanent magnets. Ytterbium (Yb), erbium (Er) and holmium (Ho) are used in lasers. Lanthanum (La), gadolinium (Gd), terbium (Tb), europium (Eu) and Yb are components of luminescent and fluorescent phosphors, used in fluorescent lamps, radar screens and plasma displays. REEs are also used in auto exhaust absorption catalysts and in high-technology glasses. It is clear from these examples that REEs play a key role in many types of materials used in high-technology industries. However, the presence of other REEs as contaminants in the pure single-element material often impacts the functionality of the final product, so impurities in the REE oxide raw material must therefore be carefully controlled.

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ICP-MS is the most commonly used atomic spectroscopy technique used for the trace measurement of REEs due to its simple REE spectra — particularly when compared to emission techniques. The trace measurement of higher-mass REEs in a low-mass REE matrix is, however, very challenging. This is because REEs have among the highest metal-oxide (M-O) bond strengths of any element, and the oxide ions of the low mass REE interfere with the mid-mass and high-mass REEs in the ICP-MS spectrum. For example in analysis of trace REEs in high-purity Sm_2O_3, $^{147}Sm^{16}O^+$ overlaps the preferred isotope of Dy ($^{163}Dy^+$) and $^{149}Sm^{16}O^+$ overlaps the only isotope of Ho ($^{165}Ho^+$). Separation of the trace REE analytes from the REE matrix can be performed using either off-line or on-line matrix removal utilizing a chelating resin, but this technique is time-consuming and the method needs to be customized according to the matrix element being separated. The direct analysis of trace REEs in a variety of high-purity REE matrices is desired.

In this work, an Agilent 8800 Triple Quadrupole ICP-MS (commonly abbreviated to ICP-QQQ) was used for the determination of trace REE contaminants in high-purity REE materials. Compared to conventional quadrupole ICP-MS (or ICP-QMS), the 8800 features an additional quadrupole mass filter (Q1), situated in front of the Octopole Reaction System (ORS[3]) cell and quadrupole mass filter (now called Q2). In this tandem MS (MS/MS) configuration, Q1 operates as a 1 amu mass filter, allowing only the target analyte mass to enter the cell, and rejecting all other masses. Because plasma and matrix ions are eliminated by Q1, this ensures that the reaction processes in the ORS[3] are precisely controlled and so accurate measurements can be performed even in complex, high-matrix samples.

Experimental

Instrumentation
An Agilent 8800 ICP-QQQ was used for all measurements. The instrument configuration was standard, including Ni interface cones, standard ion lens and sample introduction system consisting 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.

Cell gas mode investigation
The 8800 can be operated in two reaction modes using MS/MS: direct ('on-mass') mode, or indirect ('mass-shift') mode. On-mass mode is used when interferences are removed by reaction with the chosen cell gas but the analyte does not react; the analyte is measured directly at its original mass. Mass-shift mode is used when the analyte itself reacts with the chosen cell gas and is measured as a reaction product ion at a new mass — 'shifted' away from the original interference. Both modes are applicable to the analysis of some of the REEs, and a single pre-defined method can include fast sequential measurement of different analytes in either or both modes. A great advantage of the 8800 is that the product ion spectra generated by MS/MS are far simpler than those generated by traditional ICP-QMS, because MS/MS mode ensures that any co-existing analyte or matrix ions that might overlap the original analyte mass or new analyte product ion mass are rejected by Q1. This means that mass-shift mode is much more accurate and more widely applicable and little or no method development is required when an existing method is applied to a new sample type.

The performance of the 8800 utilizing mass-shift mode using oxygen cell gas (O_2) and on-mass measurement using ammonia cell gas (10% NH_3 in He) for the measurement of REE impurities in single element REE oxides was evaluated. For all cell modes, the 8800 was operated with the built-in 'general purpose' preset plasma conditions, giving CeO^+/Ce^+ <0.8% (in no gas mode). Cell-related tuning parameters are summarized in Table 1.

Table 1. Agilent 8800 Triple Quadrupole ICP-MS ORS[3] cell-related tuning parameters

Cell mode	No gas	O_2	NH_3
Scan mode	MS/MS	MS/MS	MS/MS
Octopole bias (V)	−8	−5	−18
Octopole RF (V)	180	180	180
KED (V)	5	−8	−8
Cell gas	N/A	O_2	NH_3/He
Cell gas flow rate (mL/min)	N/A	0.35	9.0
Cell entrance (V)	−80	−90	−110
Cell exit (V)	−80	−90	−110
Deflect (V)	20	10	−3
Plate bias (V)	−80	−90	−110

Figure 1. Measured REE oxide formation ratio and enthalpy of oxide formation reaction. MO^+ formation ratio is calculated from $MO^+/(M^+ + MO^+)$, for each analyte mass number M.

Mass-shift mode using O_2

The reaction efficiency of each REE with O_2 cell gas was investigated, and the results are shown in Figure 1, together with the calculated reaction enthalpy. As can be seen, all of the REEs except for Eu and Yb form oxide ions efficiently (conversion of M^+ to MO^+ with O_2 cell gas was close to 100%). For the remaining two elements, Eu and Yb, the $M^+ \rightarrow MO^+$ reaction is endothermic, so these elements react to form oxide ions with much lower efficiencies (10–20%). Even so, Eu and Yb can still be detected as MO^+ with detection limits (DLs) of <1 ppt. Assuming the REE reacts with the O_2 cell gas more efficiently than the interfering REE-oxide ion, this reaction mode approach could be utilized to avoid the original oxide interference.

On-mass measurement using NH_3

Since NH_3 is a highly reactive gas, it might be expected to react with both the target REE analyte ion and any corresponding REE-oxide interference, but most likely at different reaction rates. If the interfering REE-oxide ion reacts more efficiently with NH_3 than the analyte ion, this should allow the REE-oxide overlap to be removed, allowing the target REE analyte to be detected at its original mass.

In preliminary tests, we found that REEs can be categorized into two groups: The first group includes the REEs that don't react efficiently with NH_3, namely Eu, Ho, Tm and Yb. These REEs can be measured at their original masses with excellent sensitivity in NH_3 cell gas mode.
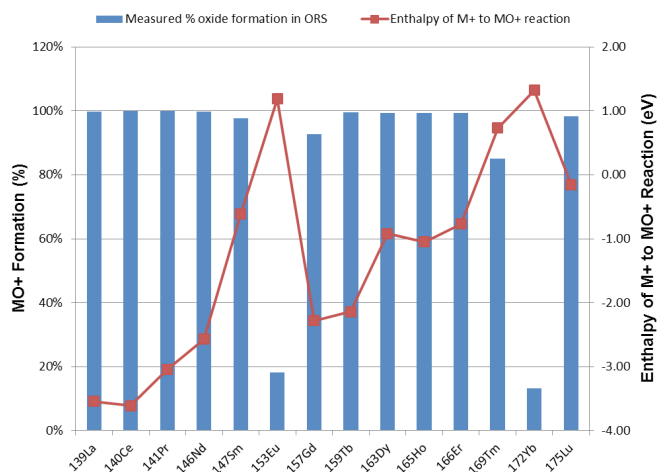
The second group of REEs includes those that react efficiently with NH_3 under the test conditions summarized in Table 1, namely La, Ce, Nd, Sm, Gd, Tb and Lu. For these analytes, the reduced sensitivity in NH_3 mode means that it would be difficult to achieve a DL of better than 1 ppt by on-mass measurement, even if the REE-oxide interference (where present) was removed effectively. The sensitivity of each element in the three cell modes (no gas, O_2 and NH_3) is summarized in Figure 2.
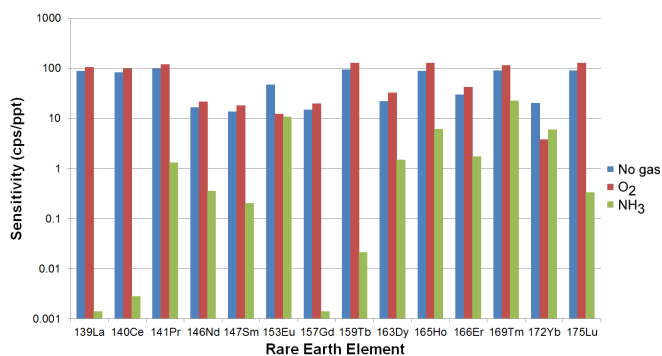

Figure 2. Sensitivity of the preferred isotope of each REE in three cell modes: no gas, O_2 mass-shift and NH_3 on-mass. In O_2 mass-shift mode, analyte ions are measured as their oxide product ions at the original mass + 16 (Q1 is set to the original mass and Q2 is set to the original mass + 16).

As stated, La, Ce, Nd, Sm, Gd, Tb and Lu react efficiently with NH_3, resulting in reduced sensitivity for these analyte ions in this cell gas mode. However, if the oxide ions of these elements also react efficiently with NH_3, this mode might provide a means to reduce the

interferences due to the oxide ions of these elements on higher mass REEs. The signal response of $^{156}GdO^+$ was investigated with changing NH_3/He cell gas flow. At the same time, the response of $^{172}Yb^+$ was monitored, as this isotope is overlapped by $^{156}GdO^+$. Figure 3 shows the calculated background equivalent concentration (BEC) of Yb in 1 ppm Gd solution, indicating more than three orders of magnitude improvement in BEC of Yb in the Gd matrix at the optimum cell gas flow rate of 9.0 mL/min.
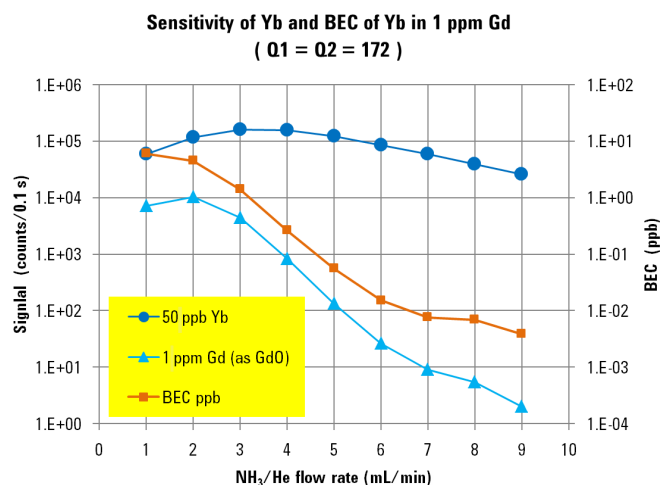

Figure 3. Sensitivity of GdO and Yb at m/z 172, plus Yb BEC as a function of NH_3/He flow rate

Results

High-purity REE oxide materials
Two high-purity REE oxide materials, Sm_2O_3 and Gd_2O_3 were gently dissolved in semiconductor grade HNO_3 and diluted to a concentration of 1 ppm (as the REE). All of the other REE elements were measured in each matrix solution, using the three cell gas modes described above. The contribution of the oxide interferences from the matrix element on the other REEs was compared by measuring the apparent concentration of each trace REE in each matrix. La, Ce, Nd, Sm, Gd, Tb and Lu were not measured using NH_3, because the response of those elements was too low to allow reliable measurement.

Figure 4a shows the BEC of each REE impurity in the 1 ppm Sm solution. In no gas mode, the BECs for ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm and ^{172}Yb were high due to the interferences from SmO^+, $SmOH^+$ and $SmOH_2^+$ polyatomic ions formed from various Sm isotopes. O_2 mass-shift mode improved the BECs for these elements

by nearly two orders of magnitude, but on-mass measurement using NH_3 further improved the BEC to below 1 ppt for each interfered element demonstrating that NH_3 on-mass mode effectively removed the Sm-based polyatomic interferences.

Figure 4b shows the BECs of each REE impurity in the 1 ppm Gd solution. ^{159}Tb, ^{172}Yb and ^{175}Lu showed increased BECs due to interferences from Gd polyatomic ions. $^{158}GdH^+$ interferes with ^{159}Tb, $^{156}GdO^+$ interferes with $^{172}Yb^+$ and $^{158}GdOH^+$ interferes with $^{175}Lu^+$. Since Tb and Lu cannot be measured in NH_3 on-mass mode due to reduced sensitivity, O_2 mass-shift mode is the preferred approach.

The measurement of different analytes in different reaction modes is simple to set up and run using a multi-tune method on the 8800. In the acquisition method, the cell gases and measurement modes are switched automatically during the analysis, giving a fast and automated analysis using the optimum mode for each analyte. With the O_2 mass-shift mode, the BECs of Tb and Lu were reduced to approximately 1 ppt. For Yb^+ the O_2 mass-shift method was not effective, but NH_3 on-mass mode dramatically improved the BEC for Yb in the Gd matrix to less than 1 ppt, as seen in Figure 4b.
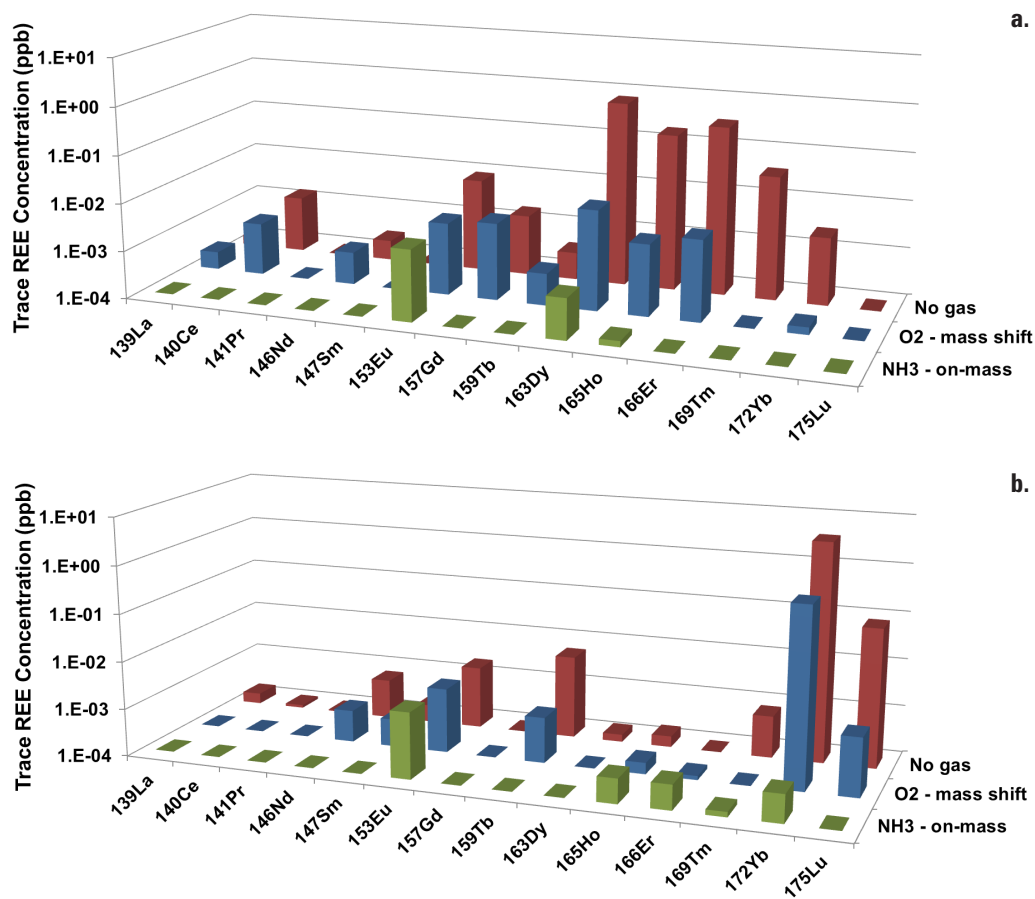
Figure 4. a) Determined concentration of REE impurities in 1 ppm Sm in three modes. b) Determined concentration of REE impurities in 1 ppm Gd in three modes. Note: La, Ce, Nd , Sm, Gd, Tb and Lu were not measured in NH_3 on-mass mode.

Conclusions

The Agilent 8800 Triple Quadrupole ICP-MS was operated using a single acquisition method that included both O_2 mass-shift mode and NH_3 on-mass mode to successfully measure all REE impurities in high-purity REE materials. The cell gas modes were effective in removing REE matrix-based hydride, oxide and hydroxide polyatomic interferences.

In a 1 ppm Sm matrix, overlaps from SmO^+, $SmOH^+$ and $SmOH_2^+$ on Dy, Ho, Er, Tm and Yb were reduced by around two orders of magnitude using O_2 mass-shift mode. The method allowed DLs of less than 0.1 ppt to be achieved. However O_2 mass-shift mode was not as effective for the removal of the GdO^+ interference on Yb^+.

On-mass measurement using NH_3 further improved BECs of trace REEs that suffer interferences from

matrix-based polyatomic ions in Sm and Gd matrices. NH_3 on-mass mode was also effective in reducing the interference of GdO^+ on Yb^+, improving the BEC of Yb to approximately 1 ppt in a matrix of 1 ppm Gd. However some REE elements such as La, Ce, Sm, Gd, Tb and Lu react with NH_3 so efficiently that this cell gas mode could not be used for the on-mass measurement of those analytes.

With the combination of the two reaction modes, all of the trace REE impurities can be measured at levels of less than 1 ppt in a 1 ppm solution of the interfering matrix material (Sm or Gd). The combined cell gas modes give an optimized routine method that can be applied to the accurate determination of trace REEs, not only in high-purity REE materials, but also in natural samples such as rock digests, because in nature, low-mass REEs are almost always present at higher concentrations than high-mass REEs.

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