



Removal of hydride ion interferences (MH^+) on Rare Earth Elements using the Agilent 8800 Triple Quadrupole ICP-MS

Application note

Geochemistry, mining and materials science

Authors

Naoki Sugiyama

Agilent Technologies, Tokyo, Japan



Introduction

The Agilent 8800 Triple Quadrupole ICP-MS, also referred to as ICP-QQQ, delivers excellent reaction cell performance due to its MS/MS reaction mode, which is unique to ICP-QQQ. The first quadrupole (Q1), before the Octopole Reaction System (ORS³) cell, operates as a 1 amu mass filter, strictly controlling the ions that enter the reaction cell. Only ions with the target analyte mass enter the cell; all other masses are rejected. Because plasma and matrix ions are eliminated by Q1, reaction processes in the cell become far simpler and more predictable, allowing the Agilent 8800 ICP-QQQ to be applied to a wide range of difficult interference problems [1]. This note describes the removal of MH^+ interferences on rare earth elements (REEs).

The measurement of REEs is of great importance in geochemistry, mining and materials science. The manufacturers of high purity REE materials need a technique to quantify REE impurities in refined, single element REE



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materials. ICP-MS is the technique of choice for the trace measurement of REEs, but most REEs suffer from interference by polyatomic species (predominantly hydride ions (MH^+) and oxide ions (MO^+)) derived from other REE elements. While MH^+ interferences are lower in intensity than MO^+ interferences, they are a more challenging problem for ICP-MS, since they cannot be mass-resolved even by high-resolution magnetic-sector ICP-MS. The mass resolution required to resolve the analyte ion from an interfering MH^+ peak exceeds the capability of commercial high resolution ICP-MS [2]. Figure 1 shows the spectrum of 10 ppm La. The peaks at m/z 138 and 139 are $^{138}La^+$ and $^{139}La^+$ respectively, and the peak at m/z 140 is $^{139}LaH^+$. The contribution of $^{138}LaH^+$ to the 139 peak is insignificantly small due to the very low relative abundance of ^{138}La (0.09%). The most abundant Ce isotope, and the only one not overlapped by another element is $^{140}Ce^+$. When La is present at a significant concentration, it can cause positive bias on the Ce measurement. To remove the

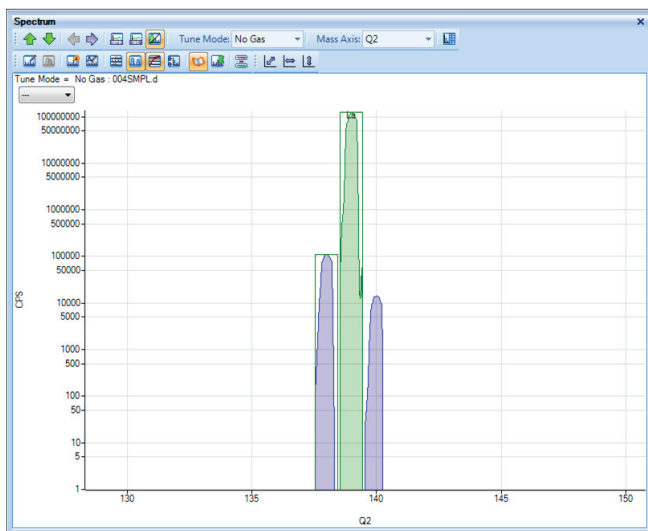


Figure 1. Spectrum of 10 ppm lanthanum obtained using an Agilent 8800 ICP-QQQ (note log scale)

$^{139}LaH^+$ interference, the Agilent 8800 ICP-QQQ was used in MS/MS mass-shift mode, using oxygen as a reaction gas. This technique was also applied to the trace determination of Tb in a Gd matrix.

Experimental

An Agilent 8800 Triple Quadrupole ICP-MS (G3663A #100) was used in standard configuration, featuring an x-lens and Ni cones. A pumped PFA nebulizer was used in place of the Micromist nebulizer, for faster washout. A preset method, "general purpose generic method" provided in the ICP-MS MassHunter software was used, with minimal modifications. This preset method contains tuning parameters for oxygen reaction gas. Figure 2 illustrates the theory of the mass-shift method using oxygen gas. The REE to be measured is converted to the oxide ion and detected at the product (oxide) ion mass. With the exception of Eu and Yb, all REEs react with oxygen and are efficiently converted to the oxide ion [3]. Provided the interfering molecular ion does not also react with oxygen, the interference is removed. Table 1 summarizes the conditions used for the experiment.

Table 1. Agilent 8800 ICP-QQQ tuning conditions

	Parameter	Value
Plasma conditions	Preset plasma	General purpose
Ion lens voltages	Extract 1	0 V
	Extract 2	-180 V
	Omega bias	-50 V
	Omega	+10 V
	Cell exit	-90
	Deflect lens	+16
Cell conditions	Octopole bias voltage	-5 V
	Cell gas	Oxygen
	Cell gas flow rate	0.3 mL/min (30% of full scale)
	KED	-8 V

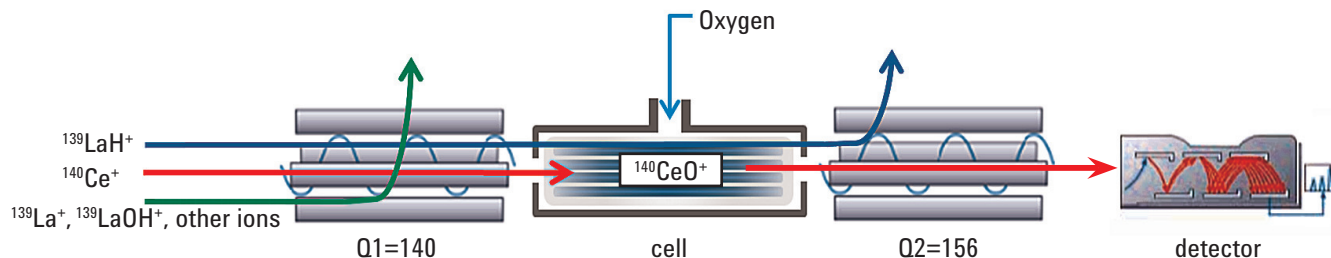


Figure 2. MS/MS mass-shift mode using oxygen cell gas for the measurement of Ce in a La matrix. Q1 is set to m/z 140, allowing $^{140}Ce^+$ and any other ions at m/z 140 to pass through to the cell. All other ions are rejected. In the cell, Ce reacts with oxygen to form CeO^+ at m/z 156. Q2 is set to m/z 156, allowing CeO^+ to pass to the detector. Since $^{139}LaH^+$ does not react with oxygen, it is rejected by Q2.

Results

The measurement of La in a 50 ppm Ba matrix, Ce in a 50 ppm La matrix sample and Tb in a 50 ppm Gd matrix was performed. The separate La, Ce and Gd (all 99.999% purity, Alfa Aesar, MA USA) matrix solutions were prepared in 1% HNO₃ (TAMAPURE-AA-100, Tama Chemicals Co. Kanagawa, Japan). They were analyzed using the Method of Standard Additions (MSA), each with a single element standard of La, Ce and Tb at 50, 100, 150 and 200 ppt. For comparison, data was acquired using MS/MS in mass-shift mode as described above, but also using the single quad scan mode of the Agilent 8800. In this case, Q1 acts as an ion guide (strictly speaking a wide bandpass mass filter), emulating mass-shift mode with a conventional single quadrupole ICP-MS (ICP-QMS).

The calibration plots are shown in Figure 3, and the results can be summarized as follows:

- Mass-shift mode with single quad scan generates interferences that prevent the measurement of the analyte in these three analyte/matrix pairs.
- Mass-shift mode with MS/MS scan can successfully perform the trace quantitation of La in a Ba matrix, Ce in a La matrix and Tb in a Gd matrix. The BECs achieved were 8.5 ppt, 10.6 ppt and 24.8 ppt for La, Ce and Tb respectively. DLs were 2.5 ppt, 0.8 ppt and 2.0 ppt for La, Ce and Tb respectively.

This clearly shows the advantage of the MS/MS mode of operation of the ICP-QQQ over conventional ICP-QMS. With conventional ICP-QMS, non-target mass matrix ions enter the cell and can form new reaction products which interfere with the analyte, even though the analyte is itself reacted and measured at a new mass.

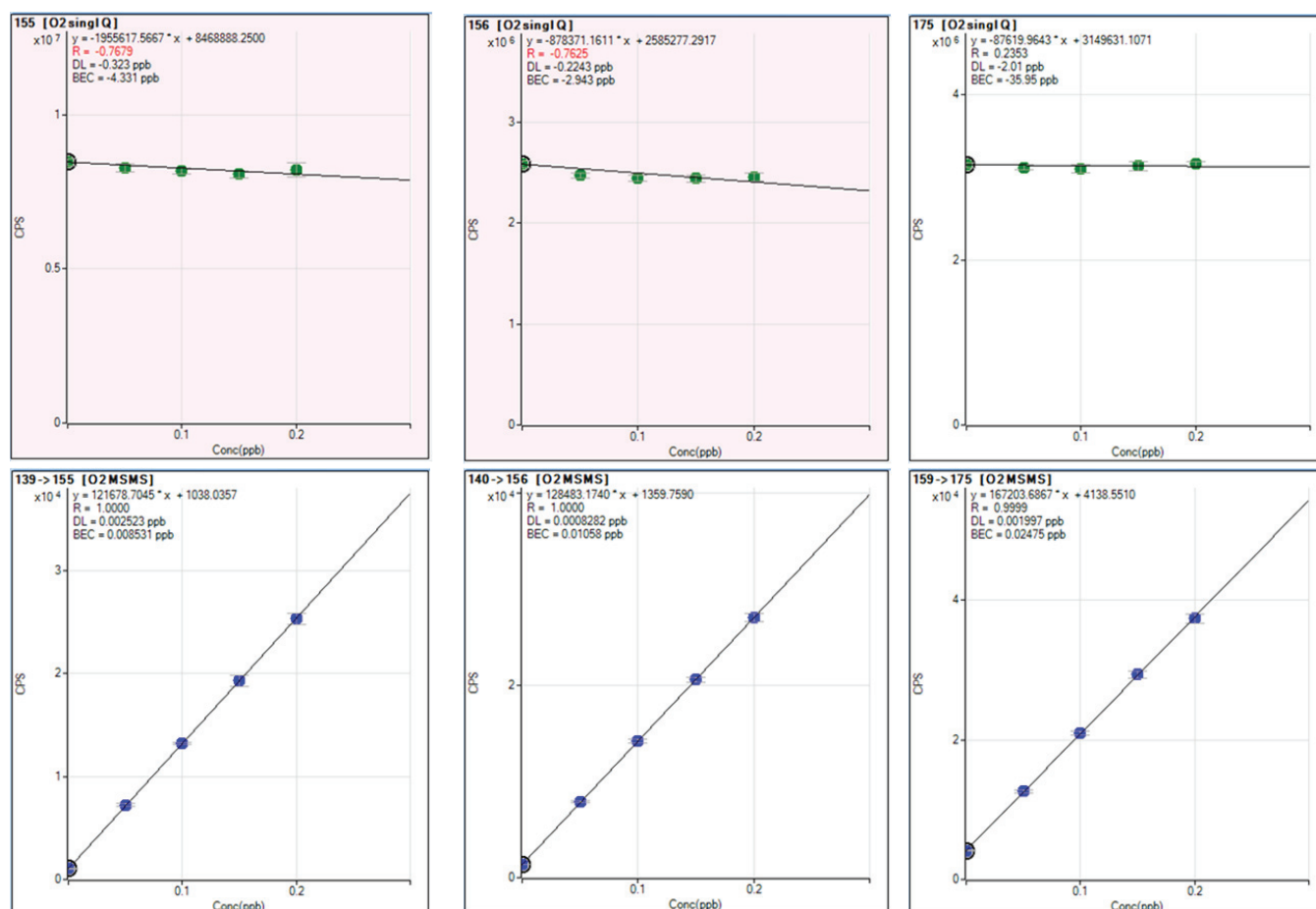


Figure 3. Calibration plots with oxygen mass-shift method for La in 50 ppm Ba matrix (left), Ce in 50 ppm La matrix (center) and Tb in 50 ppm Gd matrix (right). The upper calibration plots were acquired in single quad scan and the lower calibration plots were acquired using MS/MS scan mode.

Discussion

As the results show, with mass-shift mode, using single quad scan (emulating ICP-QMS) it was not possible to generate a calibration curve at this concentration level for these analyte/matrix pairs. The BEC was determined separately at 10s of ppb, which is even worse than the BEC achieved using a no cell gas method. It implies that unexpected reactions occurred in the cell with single quad scan. The Agilent 8800 has a “precursor scan” function which is a useful tool to investigate cell reaction processes. To investigate Ce measurement in La matrix, Q2 was fixed at m/z 156, while Q1 was scanned from m/z 2 to m/z 260 to allow us to identify what ions (i.e. precursor ions) entering the cell, would generate product ions at m/z 156. The precursor scan spectrum for m/z 156 is shown in Figure 4. From this, we can see that $^{138}\text{La}^+$, $^{139}\text{La}^+$, $^{139}\text{LaO}^+$ and $^{139}\text{LaOH}^+$ all form species at m/z 156, interfering with the measurement of Ce as CeO^+ . The reaction pathways of $^{139}\text{La}^+$ and $^{139}\text{LaO}^+$ to product ions, probably both producing $^{139}\text{LaOH}^+$, on m/z 156 are not clear. It is reasonable to think, however, that water impurities

in the cell gas, or water vapor or H_2 entrained in the plasma play a role in the reaction. Clearly, for the effective application of mass-shift mode with oxygen to the measurement of Ce in a La matrix, precursor ions $^{139}\text{La}^+$, $^{139}\text{LaO}^+$ and $^{139}\text{LaOH}^+$ must be rejected before the reaction cell. This work demonstrates that a 1 amu bandwidth filter prior to the cell (i.e. MS/MS mode with an ICP-QQQ) is an effective approach.

Conclusions

The Agilent 8800 Triple Quadrupole ICP-MS operated in MS/MS mass-shift mode was able to remove hydride interferences on REEs — a feat not possible even with magnetic sector ICP-MS. The trace (ppt) measurement of La in a 50 ppm Ba matrix, Ce in a 50 ppm La matrix and Tb in a 50 ppm Gd matrix was achieved. Comparison experiments showed significant advantages of the use of ICP-QQQ over conventional ICP-QMS for this application: non-target mass rejection prior to the reaction cell is critical for effective use of the mass-shift method.

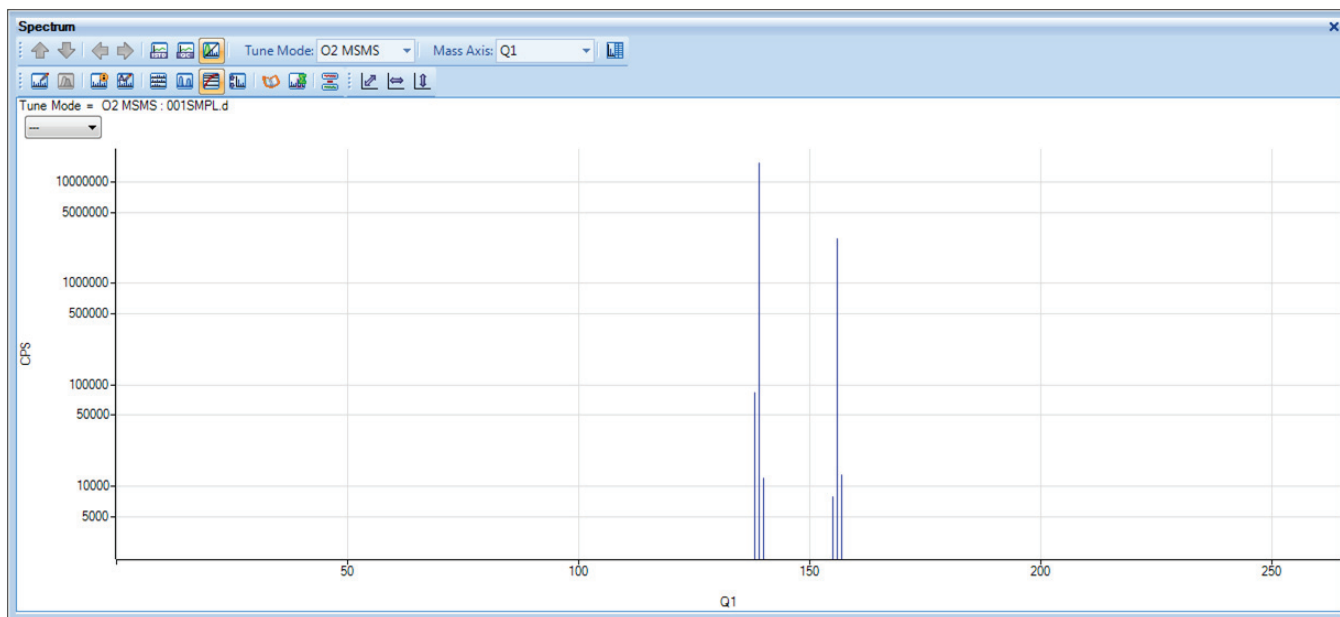


Figure 4. Precursor ion scan spectrum for a 50 ppm La matrix. Q2 was fixed at m/z 156 and Q1 was scanned from m/z 2 to m/z 260. Six peaks were found at m/z 138, 139, 140, 155, 156 and 157. These are $^{138}\text{La}^+$, $^{139}\text{La}^+$, $^{139}\text{LaH}^+$, $^{140}\text{Ce}^+$ (present as an impurity), $^{139}\text{LaO}^+$, $^{139}\text{LaOH}^+$ and $^{139}\text{LaOHH}^+$.

References

1. Agilent 8800 Triple Quadrupole ICP-MS brochure, 5991-0079EN.
2. Sabine Becker and Hans-Joachim Dietze, *Journal of Analytical Atomic Spectrometry*, 1997, vol. 12, p 881-889.
3. 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, 2012, 5991-0892EN.

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