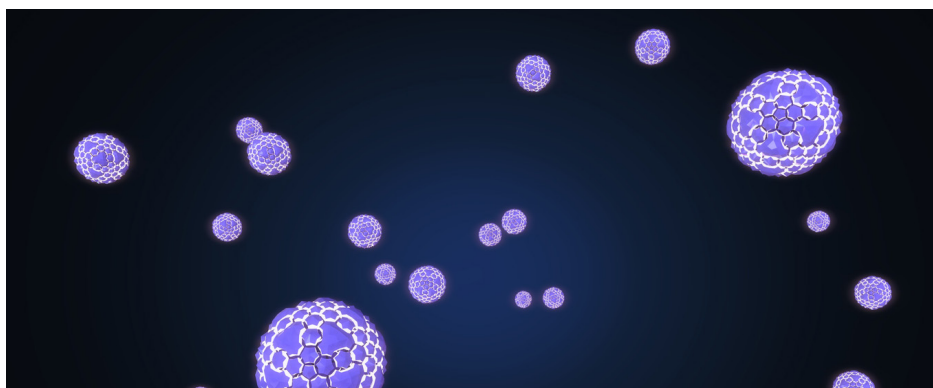


# Solving Doubly Charged Ion Interferences using an Agilent 8900 ICP-QQQ

Improved data quality using MS/MS oxygen mass-shift method to resolve common  $M^{++}$  ion interferences



## Author

Naoki Sugiyama,  
Agilent Technologies Inc.

## Introduction

Most ICP-MS instruments use collision/reaction cell (CRC) technology to control spectral interferences, greatly improving data accuracy for many elements in routine applications. Helium collision cell mode (He mode) is the most widely used CRC technique for the trace element analysis of many commonly analyzed samples. It is especially effective at resolving spectral interferences that arise from overlapping matrix or plasma-based ions such as metal oxide ions or argide ions. He mode uses Kinetic Energy Discrimination (KED) to reduce the transmission of all common matrix-based polyatomic interferences under a single set of cell conditions.

A different approach is needed to remove doubly charged ion interferences ( $M^{++}$ ) though, since He mode enhances the interference. While  $M^{++}$  interferences are not as common as polyatomic ion interferences in most general applications, it is useful for analysts to be aware of the potential for their formation. It is also useful for analysts to have a method to correct for  $M^{++}$  interferences should they arise. A quadrupole mass spectrometer separates ions based on their mass-to-charge ratio ( $m/z$ ), so  $M^{++}$  ions appear at half their true mass, overlapping any singly charged analyte

ions with the same  $m/z$ .  $M^{++}$  interferences can be corrected using mathematical interference correction equations. This approach is often used to compensate for doubly charged ion interferences from rare earth elements ( $REE^{++}$ ) on arsenic (As) and selenium (Se). But accurate results can only be obtained using correction equations when the interference and analyte signal are of the same order of magnitude. Otherwise, the correction provides an inaccurate value. With the development of samples with more complex matrices, there is an increasing need for more reliable, reproducible, and higher-quality data.

Triple quadrupole ICP-MS (ICP-QQQ) with its double mass selection (MS/MS) can remove  $M^{++}$  interferences using controlled reaction chemistry in the CRC. ICP-MS/MS methods enable reactive cell gases such as hydrogen, oxygen, and ammonia to be used effectively (1, 2).

In this study, an ICP-MS/MS reaction cell method using  $O_2$  was used to remove  $M^{++}$  interferences on various analytes. Many elemental ions react with  $O_2$  to form an oxide ion while the  $M^{++}$  interference remains unreactive or is much less reactive. This allows the element of interest to be quantified by measuring the oxide ion at + 16 u, away from the spectral interference (1, 2). This “mass-shift” methodology was used to remove doubly charged ion interferences on Ca, Sc, Zn, As, and Se.

## Experimental

### Instrumentation

An Agilent 8900 Triple Quadrupole ICP-MS (ICP-QQQ #100 for Advanced applications) was used. The instrument was fitted with the standard sample introduction system comprising a glass concentric nebulizer, quartz double-pass spray chamber, quartz torch with 2.5 mm id injector, and Ni interface cones. The ICP-QQQ was operated in single quadrupole (SQ) no gas mode, in SQ He mode, and with  $O_2$  cell gas in MS/MS mass-shift mode. The 8900 is fitted with a four cell gas channels, allowing different cell gases to be used in the same method if needed. Robust “general purpose” plasma conditions were set automatically using the ICP-MS MassHunter software. The main operating conditions and tuning parameters are shown in Table 1.

### Calibration standards and sample preparation

Calibration standards were prepared from Agilent Environmental Calibration Standards (p/n 5183-4688) via sequential dilution using de-ionized water. Fe, Sc, and Sr calibration standards were prepared separately from single elements standards (Kanto Chemical Co Inc., Japan). A Rare Earth Element (REE) mixed solution was bought from SPEX CertiPrep Inc. National Institute of Standards and Technology (NIST) 1640a Trace Elements in Natural Water Standard Reference Material (Gaithersburg MD, USA) was used to evaluate the method. The SRM was also spiked with 1 ppm of each of Sr, Zr, Ba, Sm, Gd, Nd, and Dy to simulate a more challenging sample matrix for the evaluation. Also, since no Sc is present in NIST 1640a, a 10 ppb spike was added to the SRM to represent the analyte.

**Table 1.** ICP-QQQ operating conditions and tuning parameters.

	No Gas	He	$O_2$
Acquisition mode	Single quad	Single quad	MS/MS
RF power (W)	1550		
Sampling depth (mm)	10		
Nebulizer gas flow rate (mL/min)	1.05		
Make up gas flow rate	0.0		
Octopole bias (V)	-8	-18	-10
Axial acceleration (V)	2		
KED (V)	5		-8
Cell gas flow rate (mL/min)	-	4.5	0.6 (40% full scale)
Deflection lens (V)	20	4	2

*Shaded parameters are predefined by selecting general-purpose plasma settings.*

## Results and discussion

### Attenuation of doubly charged ion interferences

To study the effectiveness of the method for the removal of  $M^{++}$  interferences,  $Sr^{++}$  interference on  $Ca^+$ ,  $Zr^{++}$  on Sc,  $Ba^{++}$  on  $Zn^+$ , and  $REE^{++}$  interferences on  $As^+$  and  $Se^+$  were investigated. The background equivalent concentrations (BECs) of Ca, Sc, and Zn were determined in a solution containing 10 ppm of Sr, Zr, and Ba. As and Se were measured in a solution containing 10 ppm each of 16 REEs.

The results, which were obtained using no gas mode, He mode, and  $O_2$  mass-shift mode, are shown in Figure 1. The graphs show that the lowest BECs for all elements were obtained using  $O_2$  mass-shift mode. The higher results obtained in no gas mode highlight the effect of the doubly charged ion spectral interferences that arise from the matrix elements on all five analytes. The results also show that He mode is ineffective for the removal of  $M^{++}$  ion interferences, even enhancing the interference slightly compared to no gas mode.

### Natural water SRM analysis

Matrix spiked and unspiked samples of the NIST 1640a natural water SRM were analyzed using ICP-QQQ. All elements were measured in He mode. For comparison purposes, the five analyte elements (Ca, Sc, Zn, As, and Se) that potentially suffer  $M^{++}$  interferences arising from the Sr, Zr, Ba, Sm, Gd, Nd, and Dy matrix spikes were also measured in MS/MS mass-shift mode with  $O_2$  cell gas. Quantitative results are given in Tables 2 and 3.

As can be seen in Table 2, He mode provided accurate results for all elements in the non-matrix spiked SRM sample. All isotopes were within  $\pm 10\%$  of the certified values apart from  $^{43}Ca$  (111%), which suffered interference from a  $Sr^{++}$  overlap (the SRM contains 126 ppb Sr).

There was a large deviation from the certified concentrations for some isotopes of Ca, Sc, Zn, As, and Se in the 1 ppm

matrix spiked SRM due to M++ ion interferences, as indicated by the shaded cells in Table 2.

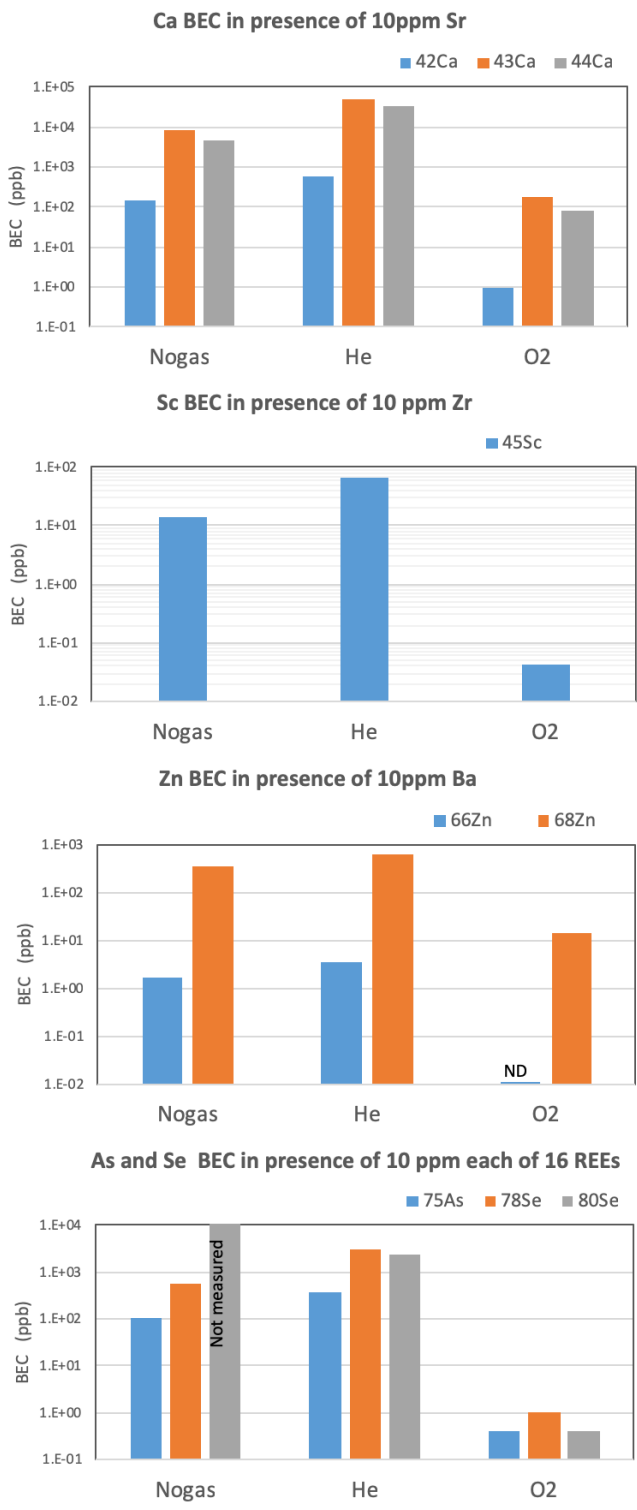


Figure 1. BEC results of the matrix spectroscopic interference study.

Table 2. Analytical results for NIST 1640a Trace Elements in Natural Water SRM with and without matrix element spikes. All data was acquired using the 8900 ICP-QQQ operating in He mode.

Element	Integration Time (s)	MDL** n=9 (µg/L)	SRM 1640a	SRM 1640a		SRM 1640a + 1 ppm Matrix	
			Certified (µg/L)	Average n=3 (µg/L)	Recovery (%)	Average n=3 (µg/L)	Recovery (%)
<sup>9</sup> Be	0.5	0.06	3.026	3.15	104	3.15	104
<sup>23</sup> Na	0.5	0.54	3137	3195	102	3200	102
<sup>24</sup> Mg	0.5	0.35	1058.6	1056	100	1028	97
<sup>27</sup> Al	0.5	0.07	53.0	54.2	102	52.0	98
<sup>39</sup> K	0.5	2.8	579.9	595	103	568	98
<sup>42</sup> Ca	0.5	58	5615	5598	100	5376	96
<sup>43</sup> Ca	0.5	5.8	5615	6257	111	11120	198
<sup>44</sup> Ca	0.5	1.0	5615	5767	103	9085	162
<sup>45</sup> Sc	0.5	0.02	10*	10.6	106	13.7	137
<sup>51</sup> V	0.5	0.01	15.05	14.9	99	14.3	95
<sup>52</sup> Cr	0.5	0.01	40.54	40.4	100	38.9	96
<sup>53</sup> Cr	0.5	0.02	40.54	41.3	102	39.8	98
<sup>55</sup> Mn	0.5	0.01	40.39	39.9	99	38.1	94
<sup>56</sup> Fe	0.5	0.03	36.8	34.7	94	33.4	91
<sup>59</sup> Co	0.5	0.01	20.24	20.9	103	20.2	100
<sup>60</sup> Ni	0.5	0.02	25.32	26.3	104	25.4	101
<sup>66</sup> Zn	1.0	0.01	55.64	55.6	100	54.0	97
<sup>68</sup> Zn	1.0	0.01	55.64	59.3	107	107	192
<sup>75</sup> As	1.0	0.02	8.075	8.1	100	40.9	506
<sup>78</sup> Se	1.0	0.14	20.13	19.7	98	320	1588
<sup>80</sup> Se	1.0	8.6	20.13	19.3	96	165	819
<sup>88</sup> Sr	0.5	0.01	126	127.1	101	1130.2	100
<sup>95</sup> Mo	0.5	0.01	45.6	44.8	98	43.3	95
<sup>107</sup> Ag	0.5	0.01	8.081	8.47	105	8.52	105
<sup>111</sup> Cd	0.5	0.01	3.992	4.03	101	4.01	101
<sup>121</sup> Sb	0.5	0.01	5.105	4.99	98	4.77	93
<sup>137</sup> Ba	0.5	0.02	151.8	151	100	1165	101
<sup>205</sup> Tl	0.5	0.00	1.619	1.51	93	1.47	91
<sup>208</sup> Pb	0.5	0.01	12.101	11.5	95	11.1	92
<sup>238</sup> U	0.5	0.00	25.35	27.1	107	26.5	104

\*SRM was spiked with 10 ppb Sc analyte  
 \*\* MDL was calculated as 3 sigma of quantified value of 9 replicates of the solution which contains 1/10 of the concentration of the lowest level of calibration standards; 1 ppb for Na, Mg, Ca, K and 0.1 ppb for other elements.

In contrast to the He mode data, accurate results were obtained for Ca, Sc, Zn, As, and Se in both the matrix spiked and matrix unspiked SRM using O<sub>2</sub> mass-shift mode (Table 3). The results demonstrate the effective interference removal capability of O<sub>2</sub> reaction cell mode to handle M<sup>++</sup> ion overlaps.

**Table 3.** Analytical results for NIST 1640a Trace Elements in Natural Water SRM with and without matrix element spikes. All data was acquired using the 8900 ICP-QQQ operating in MS/MS mass-shift mode with O<sub>2</sub> cell gas.

Element	Integration Time (s)	MDL** n=9 (µg/L)	SRM 1640a		SRM 1640a + 1 ppm Matrix		
			Certified (µg/L)	Average n=3 (µg/L)	Recovery (%)	Average n=3 (µg/L)	Recovery (%)
<sup>42</sup> Ca	0.5	2.48	5615	5671.2	101	5739.5	102
<sup>43</sup> Ca	0.5	9.72	5615	5731.7	102	5839.4	104
<sup>44</sup> Ca	0.5	1.36	5615	5721.5	102	5774.5	103
<sup>45</sup> Sc	0.5	0.001	10*	10.4	104	10.5	105
<sup>66</sup> Zn	1.0	0.09	55.64	54.2	97	52.8	95
<sup>68</sup> Zn	1.0	0.07	55.64	54.9	99	53.9	97
<sup>75</sup> As	1.0	0.01	8.075	8.4	104	8.6	106
<sup>78</sup> Se	1.0	0.05	20.13	20.4	101	20.7	103
<sup>80</sup> Se	1.0	0.03	20.13	20.4	101	20.8	103

\*SRM was spiked with 10 ppb Sc analyte

\*\* MDL was calculated as 3 sigma of quantified value of 9 replicates of the solution which contains 1/10 of the concentration of the lowest level of calibration standards; 1 ppb for Na, Mg, Ca, K and 0.1 ppb for other elements.

## Conclusion

The Agilent 8900 ICP-QQQ operating in MS/MS mode with O<sub>2</sub> cell gas is highly effective for the removal of doubly charged ion interferences on different isotopes.

A natural water SRM was spiked with Sr, Zr, Ba, and REEs to cause M<sup>++</sup> interferences on Ca, Sc, Zn, As, and Se. Accurate results were obtained for all elements in the SRM apart from Ca, Sc, Zn, As, and Se using helium mode. Although He mode is a proven approach used to reduce common polyatomic interferences in ICP-MS, it isn't effective for the removal of M<sup>++</sup> interferences – as confirmed by the results in this study. However, M<sup>++</sup> interferences were successfully resolved using a MS/MS mass-shift method with O<sub>2</sub> cell gas, providing accurate results for Ca, Sc, Zn, As, and Se.

Agilent ICP-QQQ instruments combine the versatile, almost universal He mode (using KED) with controlled reactive cell gas modes (using MS/MS). This combination of methods enables ICP-QQQ to generate the most accurate results for environmental and food sample analysis, without sacrificing instrument ease-of-use. It also allows the analytical results to be checked across multiple isotopes, providing extra confidence in the final data.

## References

1. Reaction data for 70 elements using O<sub>2</sub>, NH<sub>3</sub> and H<sub>2</sub> with the Agilent 8800 Triple Quadrupole ICP-MS, Agilent publication, [5991-4585EN](#)
2. Agilent 8800 Triple Quadrupole ICP-MS: Understanding oxygen reaction mode in ICP-MS/MS, Agilent publication, [5991-1708EN](#)

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