

Simplifying Correction of Doubly Charged Ion Interferences with Agilent ICP-MS MassHunter

Fast, automated M^{2+} correction routine improves data accuracy for Zn, As, and Se



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Introduction

Almost all current quadrupole based ICP-MS systems use collision/reaction cell (CRC) methodology to control polyatomic interferences, with helium collision mode (He mode) one of the most widely used techniques. He mode uses Kinetic Energy Discrimination (KED) to resolve common polyatomic ion interferences on many analyte ions in the CRC. But KED cannot address the doubly charged ion interferences (M^{2+}) that affect several important elements, so a reactive cell gas such as hydrogen (H_2) is often used instead. However, to maintain a high level of sample throughput, many laboratories prefer to avoid using a second cell gas if possible. Also, some facilities may be restricted in the choice of gases allowed in the lab because of safety concerns associated with reactive gases.

Barium (Ba) and the Rare Earth Elements (REEs) have relatively low second ionization potentials, so readily form doubly charged ions in the plasma. As a quadrupole mass filter separates ions based on their mass to charge ratio (m/z), these M^{2+} ions appear at half their true mass. This means that Ba^{2+} and the REE $^{2+}$ ions of neodymium (Nd), samarium (Sm), gadolinium (Gd), and dysprosium (Dy) appear between m/z 65 and 82 where they can overlap the singly charged ions of

zinc (Zn), arsenic (As), and selenium (Se). For example, $^{150}\text{Nd}^{2+}$ and $^{150}\text{Sm}^{2+}$ can interfere with $^{75}\text{As}^+$, $^{156}\text{Gd}^{2+}$ and $^{156}\text{Dy}^{2+}$ can interfere with $^{78}\text{Se}^+$, and $^{132}\text{Ba}^{2+}$ can interfere with $^{66}\text{Zn}^+$.

Most M^{2+} ions are relatively low intensity, so are not problematic. But if a sample contains a high concentration of Ba or REEs, doubly charged ion interferences will contribute a significant number of counts, leading to false positive results. By monitoring the isotopes of Ba, Nd, Sm, Gd, and Dy, the potential interference from M^{2+} ions on Zn, As, and Se can be estimated and corrected using an equation. But this type of doubly charged ion correction requires multiple steps and is time consuming to set up. Using the singly charged ions to estimate the formation rate for doubly charged ions is also prone to errors if the ionization conditions change, for example due to different sample matrices. An automated approach based on monitoring the doubly charged ions directly could therefore streamline analysis and improve accuracy.

Interference correction equations

The quadrupole mass filters used in ICP-MS instruments separate ions according to their mass-to-charge ratio (m/z). Since $^{66}\text{Zn}^+$ and $^{132}\text{Ba}^{2+}$ have the same m/z of 66, a quadrupole mass filter is unable to distinguish between them. The mode is not effective for the removal of $^{132}\text{Ba}^{2+}$, but it is possible to calculate the intensity of the $^{132}\text{Ba}^{2+}$ contribution at m/z 66. Ba has several isotopes (^{130}Ba , ^{132}Ba , ^{134}Ba , ^{135}Ba , ^{136}Ba , ^{137}Ba , and ^{138}Ba) and they all form doubly charged ions in the plasma.

As the production rate of doubly charged ions is constant for all isotopes, the M^{2+} ions should form with the same natural isotopic abundance ratio as the singly charged M^+ ions. $^{135}\text{Ba}^{2+}$ appears at m/z 67.5 and it is therefore free from direct overlap by any singly charged ions. Based on the isotopic abundance ratio ($^{132}\text{Ba} : ^{135}\text{Ba} = 0.1 : 6.59$), $^{132}\text{Ba}^{2+}$ should produce 0.0152 times fewer counts than $^{135}\text{Ba}^{2+}$. Using this information, a correction equation can be used to calculate the counts of $^{132}\text{Ba}^{2+}$ based on the counts of $^{135}\text{Ba}^{2+}$ and the known isotope abundance ratio, as shown in Figure 1a. The equation can then be applied to subtract the contribution of $^{132}\text{Ba}^{2+}$ on $^{66}\text{Zn}^+$.

Interference correction equation for ^{66}Zn

$$\text{Mc}(66) = \text{M}(66) - \text{M}(67.5) \times 0.0152$$

(Mc(X) is the corrected count of mass X and M(X) is the measured count of mass X)

Similarly, doubly charged ion interferences that affect $^{75}\text{As}^+$ and $^{78}\text{Se}^+$ can be calculated and corrected using the information given in Figures 1b and 1c. For $^{75}\text{As}^+$, $^{145}\text{Nd}^{2+}$ and $^{147}\text{Sm}^{2+}$ are measured at m/z 72.5 and 73.5, respectively. For $^{78}\text{Se}^+$, $^{155}\text{Gd}^{2+}$ and $^{163}\text{Dy}^{2+}$ are measured at m/z 77.5 and 81.5, respectively.

Interference correction equation for ^{75}As

$$\text{Mc}(75) = \text{M}(75) - \text{M}(72.5) \times 0.6747 - \text{M}(73.5) \times 0.4923$$

Interference correction equation for ^{78}Se

$$\text{Mc}(78) = \text{M}(78) - \text{M}(77.5) \times 1.3841 - \text{M}(81.5) \times 0.0024$$

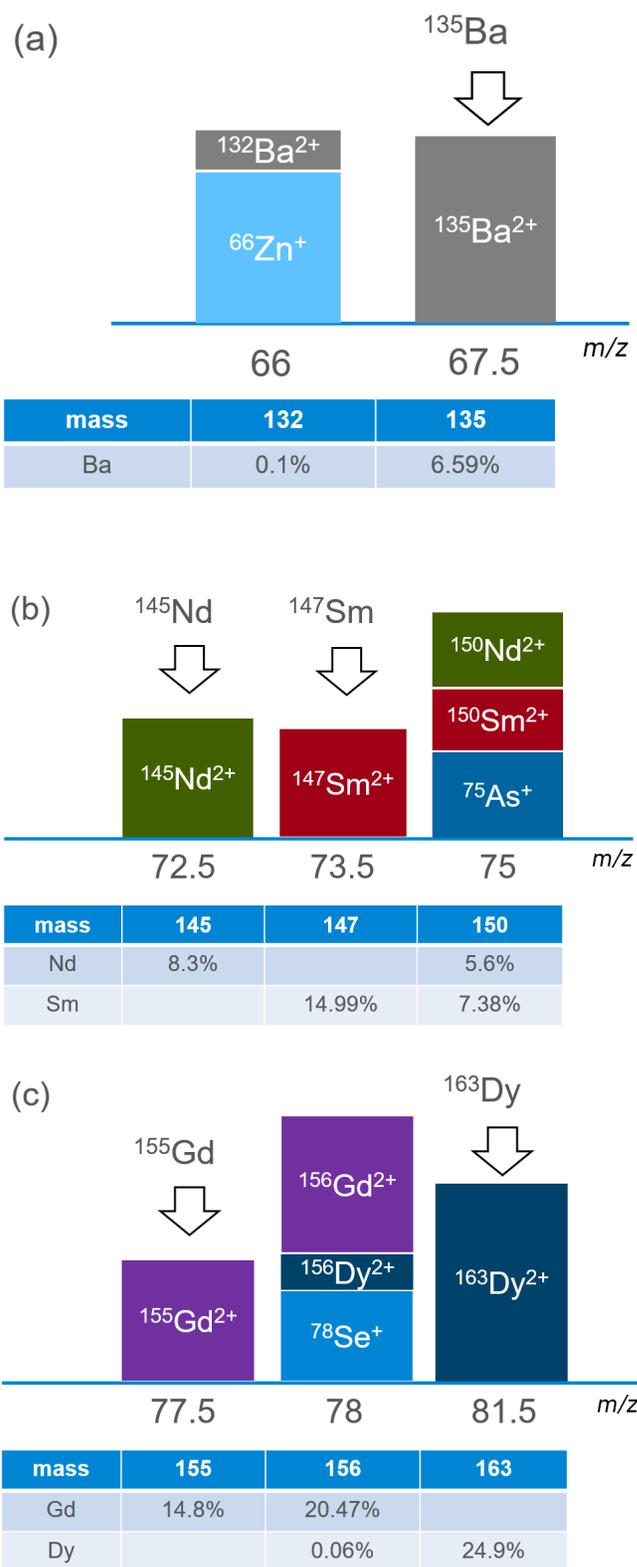


Figure 1. Doubly charged ion interferences on (a) ^{66}Zn , (b) ^{75}As , and (c) ^{78}Se and relative isotopic abundance tables for (a) Ba, (b) Nd and Sm, and (c) Gd and Dy.

Narrow peak mode

Normally in ICP-MS measurements, the quadrupole is operated with a peak width of about 0.7 u, so peaks at half masses (such as $^{135}\text{Ba}^{2+}$ at m/z 67.5) are overlapped by the "tails" of the adjacent peaks (at m/z 67 and 68). The high performance hyperbolic quadrupole used in Agilent ICP-MS systems enables analysts to use "narrow peak mode" and select "+0.5 u" in the software. These settings support the measurement of ions at $m/z = 67.5, 72.5, 73.5, 77.5,$ and 81.5 without any peak overlap.

Agilent ICP-MS systems use a hyperbolic quadrupole that delivers high ion transmission under increased resolution conditions. The quadrupole performance combines with an automated "doubly charged ion correction" tool for Agilent ICP-MS MassHunter software. This tool allows analysts to routinely monitor the M^{2+} interference level and automatically correct the data.

Experimental

Instrumentation and batch setup

Doubly charged ion correction is suitable for the Agilent 7800 ICP-MS and Agilent 7900 ICP-MS operating with ICP-MS MassHunter version 4.5 (or later) software and the Advanced Acquisition module. To set up a new analytical method in ICP-MS MassHunter, analysts can use a Method Wizard, which simplifies the process by guiding the user through a series of questions and options.

In this study, a 7800 ICP-MS fitted with the standard sample introduction system was used. All method batch parameters and settings for M^{2+} correction were set automatically by selecting "REE $^{2+}$ Correction" in the Method Wizard. The software automatically applied narrow peak mode, +0.5 u, and correction equations, as shown in Figures 2 and 3.

Tune Mode		#1: No Gas	#2: He
Quick Scan		<input type="radio"/>	<input checked="" type="radio"/>
Stabilization Time [sec]		0	5
Resolution		Standard	Narrow Peak

Mass	Element Name	Monitor	+0.5 u	IntegTime /Mass [sec]	+0.5 u	IntegTime /Mass [sec]
66	Zn	<input type="checkbox"/>	<input type="checkbox"/>	N/A	<input type="checkbox"/>	1.0000
67		<input type="checkbox"/>	<input type="checkbox"/>	N/A	<input checked="" type="checkbox"/>	1.0000
72	Ge	<input type="checkbox"/>	<input type="checkbox"/>	0.5000	<input checked="" type="checkbox"/>	1.0000
73		<input type="checkbox"/>	<input type="checkbox"/>	N/A	<input checked="" type="checkbox"/>	1.0000
75	As	<input type="checkbox"/>	<input type="checkbox"/>	N/A	<input type="checkbox"/>	1.0000
77		<input type="checkbox"/>	<input type="checkbox"/>	N/A	<input checked="" type="checkbox"/>	3.0000
78	Se	<input type="checkbox"/>	<input type="checkbox"/>	N/A	<input type="checkbox"/>	3.0000
81		<input type="checkbox"/>	<input type="checkbox"/>	N/A	<input checked="" type="checkbox"/>	3.0000

Figure 2. ICP-MS MassHunter screenshot showing automatic setting of narrow peak mode and +0.5 u.

After data acquisition, the correction equations relating to Zn, As, and Se were automatically applied to the batch results.

Batch Table: FullQuant							
Sample:		Sample Type:	Analyte:				
Sample:		<All>	78 Se [He]				
Correction Equation(s) 66 Zn [He]: $Mc(66) = M(66) * 1.0000 - M(67.5) * 0.0152$ 75 As [He]: $Mc(75) = M(75) * 1.0000 - M(72.5) * 0.6747 - M(73.5) * 0.4923$ 78 Se [He]: $Mc(78) = M(78) * 1.0000 - M(77.5) * 1.3831 - M(81.5) * 0.0024$							
	Rjct	Type	Sample Name	CPS	CPS RSD	CPS	CPS RSD
1	<input type="checkbox"/>	Sample	water1	8005.11	0.2	266.67	0.0
2	<input type="checkbox"/>	Sample	water2	8008.78	0.2	266.67	0.0

Figure 3. ICP-MS MassHunter screenshot showing automatic application of correction equations for Zn, As, and Se.

Peak resolution in narrow peak mode

As shown in Figure 4, there is clear separation between the peaks at whole and half mass values in narrow peak mode. The excellent peak resolution enables the measurement of ions at all required m/z settings without any peak overlap.

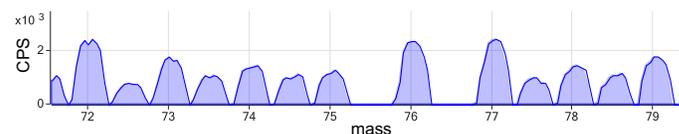


Figure 4. ICP-MS mass spectrum showing the shape and separation of peaks in narrow peak mode.

Evaluation of doubly charged ion correction mode

To test the performance of doubly charged ion correction mode for the analysis of Zn, As, and Se in the presence of M^{2+} ions, data was acquired with and without correction. The 7800 ICP-MS operating parameters are shown in Table 1.

Table 1. ICP-MS operating parameters.

Parameter	No M^{2+} Correction	With M^{2+} Correction
Plasma Mode	General purpose	
Lenses (V)	Autotune	
Helium Cell Gas Flow Rate (mL/min)	4.3	
Resolution	Standard	Narrow peak

Sample preparation

Electronic (EL) grade HNO_3 and 1,000 mg/L single element standards of Zn, As, Se, Ba, Nd, Sm, Gd, and Dy were bought from Kanto Chemicals, Japan. Five point calibration standards were prepared for Zn, As, and Se at 0, 0.1, 1, 5, and 10 ppb. Three sets of spiked samples were prepared to represent the relative concentrations of analytes and matrix elements in typical samples types where M^{2+} overlaps occur. Ba was spiked into the 5 ppb Zn standard solution at 0, 50, 500, and 5000 ppb. The 5 ppb As standard was spiked with Nd and Sm at 0, 0.5, 5, and 50 ppb. Gd and Dy were added to the 5 ppb Se standard solution at 0, 0.5, 1, and 5 ppb. Agilent internal standard (ISTD) mix (p/n 5183-4681) containing 10 ppm ^6Li , Sc, Ge, Y, In, Tb, and Bi was diluted to 1 ppm. The ISTD solution was mixed with the spiked samples using an online mixing connector. All the blanks, standards, and samples contained 1% HNO_3 .

Results and discussion

M^{2+} interferences on Zn, As, and Se

Zn, As, and Se were measured in the spiked samples containing Ba and the REEs, with and without doubly charged ion correction. The spike recovery results for Zn, As, and Se are shown in Figures 5 to 7, respectively.

Figure 5 shows that good recoveries were achieved for Zn ($\pm 10\%$) in the presence of Ba up to 500 ppb, with and without doubly charged ion correction. These results suggest that few doubly charged Ba ions were formed in the plasma at these concentration levels. However, without correction, the 5000 ppb Ba spike level caused a significant interference on ^{66}Zn due to $^{132}\text{Ba}^{2+}$, as indicated by the spike recovery result for Zn of 130%. Using the automated doubly charged ion correction routine, good accuracy was achieved for Zn in the 5000 ppb Ba matrix. The 96% recovery result shows the effectiveness of the correction method.

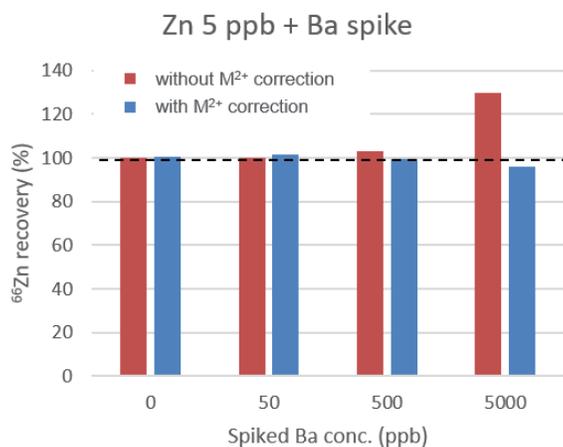


Figure 5. ^{66}Zn recovery without doubly charged ion correction (red bars) and with doubly charged ion correction (blue bars).

As shown in Figure 6, without correction, the 50 ppb spike of Nd and Sm caused an interference on As, leading to a higher than expected result (148%). Accurate As measurement was obtained (106% recovery) by applying doubly charged ion correction.

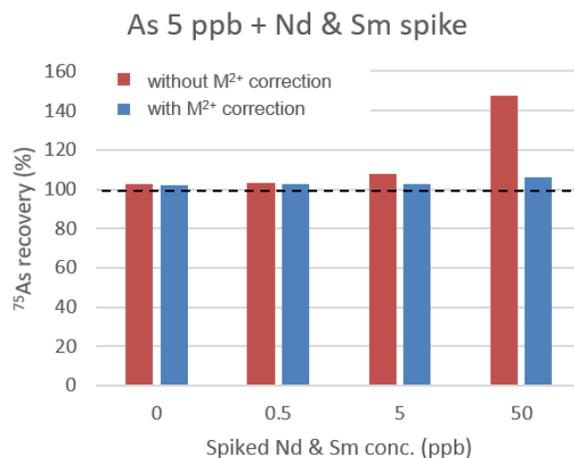


Figure 6. ^{75}As recovery without doubly charged ion correction (red bars) and with doubly charged ion correction (blue bars).

The accuracy of Se measurements is affected by a relatively low concentration of Gd and Dy, as shown in Figure 7. Without correction, poor accuracy (215% recovery) was achieved for 5 ppb Se in the presence of 5 ppb of Gd and Dy. However, good accuracy was achieved for Se (107% recovery) by applying doubly charged ion correction.

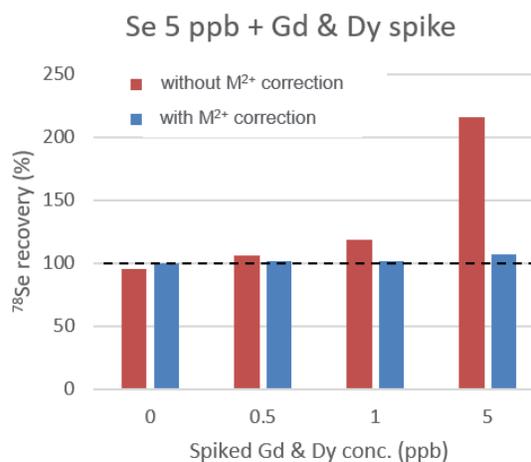


Figure 7. ^{78}Se recovery without doubly charged ion correction (red bars) and with doubly charged ion correction (blue bars).

Excellent spike recoveries were obtained for Zn, As, and Se in the presence of the Ba/REE matrix elements. This clearly demonstrates the capability of the doubly charged ion correction function of ICP-MS MassHunter to improve the accuracy of these measurements. The study also shows that the concentration of each matrix element that led to a significant M^{2+} contribution was different for Ba (5000 ppb), Nd and Sm (50 ppb), and Gd and Dy (5 ppb). The impact of doubly charged interferences depends on the isotopic abundance ratio and the difference of sensitivities between the singly charged analyte and the doubly charged interferent.

Conclusion

The study outlined a simple way to correct doubly charged ion interferences using an Agilent 7800 or 7900 ICP-MS and ICP-MS MassHunter software. M^{2+} ion interferences arising from Ba or REEs can affect the accurate measurement of Zn, As and Se, leading to errors in the reported results. Selecting "REE²⁺ Correction" in the ICP-MS MassHunter Method Wizard enables real-time correction of unknown samples that may contain enough Ba or REEs to cause M^{2+} interferences.

A 7800 ICP-MS was used to measure Zn, As and Se in a series of samples containing different concentrations of potential interferents. The doubly charged ion correction method measures the M^{2+} interference level and corrects the data automatically. The effectiveness of the method was demonstrated by the excellent recoveries for Zn, As and Se in all matrix samples.

Instead of carrying out a series of manual steps to define and update standard correction equations, Agilent ICP-MS users can simply use the ICP-MS MassHunter doubly charged ion correction tool. By fully automating the M^{2+} interference correction process, doubly charged ion correction saves operator time and improves data quality by reducing any potential method errors.

More information

Doubly charged ion correction requires the following options:

- Agilent 7800 ICP-MS or Agilent 7900 ICP-MS
- ICP-MS MassHunter for 7800 or 7900
- Advanced Acquisition software for 7800 and 7900 (part number G5713A)

www.agilent.com/chem

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