

Interferences in ICP-MS Analysis and How to Deal With Them

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Abstract

In the analysis of trace metals in water samples by inductively coupled plasma-mass spectrometry (ICP-MS), there exist many polyatomic interferences, such as ³⁵Cl¹⁶O on ⁵²Cr, ³⁵Cl⁴⁰Ar on ⁷⁵As, ⁴⁰Ar⁴⁰Ar on ⁸⁵Se and many more. Three approaches are commonly employed to overcome such interferences: 1) selection of interference-free isotopes for analysis; 2) use of the correction equation to correct for interferences; and 3) more recently the advancement of the 'collision/reaction' technique. The actual application of these approaches, however, depends critically on the sample matrices and detailed knowledge of the samples. For example, for the analysis of selenium in drinking water under standard ICP-MS operation, ⁸²Se, the major isotope at 49.7% relative abundance, cannot be used for quantification due to the interference from ⁴⁰Ar⁴⁰Ar which is one of the major species in the plasma. Accordingly, it has been a common practice to select either ⁷⁸Se (still suffers ⁴⁰Ar⁴⁰Ar interference, but much less) or ⁸²Se (provided that argon used is free of krypton). For typical drinking water sample matrices, ⁸²Se (9.2% relative abundance) works very well for the quantification of selenium at sub-parts per billion concentration levels. However, if samples contain high concentrations of bromine (with two isotopes, ⁷⁹Br and ⁸¹Br), there will be a high level of ⁸¹Br¹H in the plasma which interferes with ⁸²Se, resulting an erroneous selenium quantification. Under such a sample matrix, ⁷⁸Se would be preferred for selenium quantification. The bromine may be present naturally or be added as part of a treatment process.

In modern ICP-MS instruments, many correction equations are built into the instrument software to facilitate automatic correction of certain isobaric or polyatomic interferences. The most common example is the quantification of ⁷⁵As. All ICP-MS instruments currently in use have a correction equation built into the software to correct for ³⁶Cl⁴⁰Ar interference on ⁷⁵As. The equation takes the following form: a corrected ⁷⁵As signal = total signal in mass 75 - (3.127 x (signal in mass 77 - (0.815 x signal in mass 82))). There are two assumptions in this equation: 1) all signals in mass 82 are from Se and 2) after subtraction of the ⁷⁷Se contribution on mass 77, the remaining signals on mass 77 are due to ⁷⁷Cl⁴⁰Ar. However, if samples contain high bromine as described above, signals in mass 82 are a combination of ⁸²Se and ⁸¹Br¹H. As a result, the built-in correction equation for ⁷⁵As quantification would produce erroneous results for arsenic. There are other examples of matrix-dependent correction equations. This underscores the importance of understanding the correction equations used and detailed knowledge of sample matrices. In conclusion, there is no single universal method in dealing with interferences in ICP-MS analysis. A successful strategy requires a full understanding of the technique used and detailed knowledge of the sample matrices.

Introduction

The ICP-MS is an analytical technique used in the determination of trace metals in the sub parts per trillion ranges. It is a simultaneous multi-element analytical tool where samples are decomposed to ions in high temperature argon plasma and analyzed based on the mass-to-charge ratio. The ICP-MS is used for many different applications including the analysis of trace metals in drinking water, surface water, waste water, soils, vegetation and fish.

There are many polyatomic interferences in ICP-MS that are produced by the combination of two or more atomic ions. Many spectral overlaps such as ⁴⁰Ar⁴⁰Cl on ⁷⁵As, ⁴⁰Ar⁴⁰Ar on ⁸⁵Se, ⁴⁰Ar ¹²C on ⁵²Cr are caused by plasma gas ions or the combination of plasma gas ions with other species. Other spectral overlaps such as ³⁷Cl¹⁶O on ⁵³Cr and ⁸¹Br¹H on ⁸²Se may be caused by matrix components in the sample. There are several different ways to compensate for polyatomic interferences in ICP-MS. Three approaches commonly used to overcome such interferences: selection of interference-free isotopes for analysis, the use of correction equations and the use of collision/reaction cells to eliminate the interference. (R. Thomas, 2008, Practical Guide to ICP-MS, second edition)

Objectives

- To illustrate the effects of polyatomic interference of bromine and chlorine on arsenic and selenium
- To demonstrate that the use of correction equations to eliminate spectral interferences may result in biased results
- To demonstrate that there is no universal method in dealing with interferences in ICP-MS
- To deal with interferences, the analyst needs a full understanding of the sample matrices and techniques used to correct them

Methodology

Two matrix studies containing 1) 200 ppm of chlorine and varying concentrations of bromine and 2) 500 ppm of chlorine with varying concentrations of bromine were analyzed using a Perkin Elmer Elan DRC II ICP-MS.

In both of our matrix studies there was a 1% HNO₃ blank with either 200 ppm or 500 ppm chlorine with varying concentrations of bromide as shown in Table 1. Both matrix study 1 and 2 include a 1% HNO₃ blank spiked with a known concentration of 5 µg/L arsenic and selenium for analysis. These samples were analyzed to determine the effect on the analysis of selenium and arsenic by ICP-MS.

Selenium

It is important to monitor multiple isotopes for the determination of low level selenium in water samples. In our laboratory we monitor ⁷⁸Se, ⁸²Se, and ⁸⁵Se including sample matrix ions such as ³⁵Cl and ⁷⁹Br. By monitoring the matrix composition it is possible to determine potential matrix related interferences on the different selenium isotopes. For ⁷⁸Se the major interference in water samples is ⁴⁰Ar⁴⁰Cl, for ⁷⁸Se it is ³⁶Cl⁴⁰Ar, and for ⁸²Se it is ⁸¹Kr or ⁸¹Br¹H.

To illustrate the effect of chlorine and bromine interferences on selenium isotopes a matrix study was conducted as shown in Table 1.

Table 1: 1% HNO₃ blank with chlorine and bromine as interferences

Matrix Study 1	Expected	Se77-CH4	Se77	Se78-CH4	Se78	Se80-CH4	Se82
	ppb	ppb	ppb	ppb	ppb	ppb	ppb
250 ppb Br, 200 ppm Cl	0	0.1	2.0	0.0	1.7	0.7	1.4
500 ppb Br, 200 ppm Cl	0	0.0	2.0	0.0	1.9	1.5	2.8
1000 ppb Br, 200 ppm Cl	0	0.0	2.2	0.0	2.1	2.9	5.0
2500 ppb Br, 200 ppm Cl	0	0.0	2.1	0.0	2.0	7.0	12.3
5000 ppb Br, 200 ppm Cl	0	0.0	2.2	0.0	2.3	14.0	24.8
10000 ppb Br, 200 ppm Cl	0	0.0	2.3	0.0	2.5	28.4	51.0
Matrix Study 2							
250 ppb Br, 500 ppm Cl	0	0.0	5.0	0.0	2.4	0.8	1.3
500 ppb Br, 500 ppm Cl	0	0.0	5.1	0.0	2.7	1.6	2.7
1000 ppb Br, 500 ppm Cl	0	0.0	5.2	0.0	3.0	3.0	5.2
2500 ppb Br, 500 ppm Cl	0	0.1	5.1	0.1	2.9	7.2	13.3
5000 ppb Br, 500 ppm Cl	0	0.0	5.4	0.1	3.1	14.5	25.9
10000 ppb Br, 500 ppm Cl	0	0.0	5.5	0.1	3.3	28.1	52.2

The Ontario Ministry of the Environment participated in an inter-laboratory study in December 2009 as shown in Table 2 and Table 3. The first sample was a blank with a relatively complex matrix containing approximately 200 ppm chlorine and 2.5 ppm bromine. The second sample contained the same sample matrix spiked with 7.5 ppb selenium and 9.35 ppb arsenic.

Table 2: no selenium or arsenic in the sample

Se Isotopes	Expected µg/L	Results µg/L	Matrix Ion mg/L	Correction Equation Applied
Se77	0	2.6		
Se78	0	0.5		78 - 0.030461 x Kr83
Se82	0	12.7	2.5 ppm Br	82 - 0.007833 x Kr83
Se82-1	0	-0.3		82 - 0.007833 x Kr83 - 0.00187 x Br79
Se78-CH4	0	0.03	230 ppm Cl	
Se80-CH4	0	12.2		
As75	0	4.3		75 - 3.127 x (ArCl77 - (0.815 x Se82))
As75-1	0	-0.2		75 - 0.000249 x Cl35
As75-2	0	0.8		
As75-CH4	0	0.3		

Table 3: the same sample matrix spiked with 7.5 ppb selenium and 9.35 ppb arsenic

Se Isotopes	Expected µg/L	Results µg/L	Matrix Ion mg/L	Correction Equation Applied
Se77	7.5	10.0		
Se78	7.5	0.7	2.5 ppm Br	78 - 0.030461 x Kr83
Se82	7.5	18.8		82 - 0.007833 x Kr83
Se82-1	7.5	7.1	230 ppm Cl	82 - 0.007833 x Kr83 - 0.00187 x Br79
Se78-CH4	7.5	7.7		
Se80-CH4	7.5	17.8		
As75	9.35	14.0		75 - 3.127 x (ArCl77 - (0.815 x Se82))
As75-1	9.35	9.8		75 - 0.000249 x Cl35
As75-2	9.35	10.8		
As75-CH4	9.35	9.8		

As illustrated in Tables 2 and 3, different selenium isotopes produce different analytical results. The ⁸²Se isotope has a false positive bias. This is due to the high concentration of bromine in the sample which results in the ⁸¹Br¹H interference on ⁸²Se. There is also a false positive bias on ⁷⁸Se due to the ³⁷Cl⁴⁰Ar interference.

There are three different ways to overcome the interferences on selenium: select an interference-free isotope such as ⁷⁸Se; use a reaction cell to eliminate the interference Se78-CH4; or apply a correction equation/correction factor to correct for the bromine interference. This is done by modifying the correction equation to include a correction factor for bromine as shown in tables 2 and 3 for Se82-1.

To calculate the bromine correction factor for ⁸²Se measure ⁸²Se counts/sec and ⁷⁹Br counts/sec in a 1% HNO₃ blank solution and 1 ppm bromine solution.

Calculate the correction factor as follows:

$$\text{Correction Factor: } \frac{Se82c / (s(ppmBr) - Se82c / (s(Blank)))}{Br79c / (s(ppmBr) - Br79c / (s(Blank)))}$$

It is important to monitor and calculate the correction factor daily as it is dependant on the instrument condition.

Arsenic

The determination of low level arsenic in drinking water samples by conventional ICP-MS is typically hampered by the ⁴⁰Ar³⁶Cl interference at mass 75. The most common way to deal with spectral interferences on mono-isotopic elements such as arsenic is the use of correction equations. The correction equation typically used by instrument manufacturers to correct for the ⁴⁰Ar³⁶Cl interference on ⁷⁵As is ⁷⁵As signal = total signal in mass 75 - (3.127 x (signal in mass 77 - (0.815 x signal in mass 82))).

Correction equations are based on the principle of measuring the intensity of the interfering isotope or interfering species at another mass, which is ideally free of any interference (R. Thomas, 2008, Practical Guide to ICP-MS, second edition). This correction equation works well for most Ontario drinking water samples in the absence of bromine. However, this equation may produce positive biased results for samples containing bromine due to the false signal of ⁸¹Br¹H on mass 82. When using correction equations you must ensure that there is no interference from another species.

Table 4 illustrates that there is a false positive bias for arsenic as the concentration of bromine increases when the correction equation ⁷⁵As = 75As - (3.127 x (77Se - (0.815 x 82Se))) is applied due to the interference of ⁸¹Br¹H on ⁸²Se. However, if an alternate correction equation is applied that is interference free such as ⁷⁵As = 75As - (0.322 x 78Se) the concentration of arsenic is more realistic. When no correction equation is applied to correct for the ⁴⁰Ar³⁶Cl on arsenic there is a false positive bias which increases with the concentration of chlorine. However, not correcting for the ⁴⁰Ar³⁶Cl interference does not give as large a false positive bias on arsenic as the application of the ⁷⁵As = 75As - (3.127 x (77Se - (0.815 x 82Se))) correction equation. The dynamic reaction cell results using methane gas demonstrates that the ⁴⁰Ar³⁶Cl interference is eliminated as shown in Table 4.

Table 4: Matrix Study

1% HNO ₃ Blank with	Target µg/L	As75-CH4 µg/L	As75-1 µg/L	As75-2 µg/L	As75-3 µg/L	1% HNO ₃ Blank with	Target µg/L	As75-CH4 µg/L	As75-1 µg/L	As75-2 µg/L	As75-3 µg/L
250 ppb Br, 200 ppm Cl	0	0.04	0.40	0.52	0.52	0.25 ppm Br, 500 ppm Cl	0	0.04	0.37	0.47	1.4
500 ppb Br, 200 ppm Cl	0	0.05	0.85	0.51	0.56	0.5 ppm Br, 500 ppm Cl	0	0.04	0.95	0.43	1.3
1000 ppb Br, 200 ppm Cl	0	0.01	1.7	0.35	0.55	1 ppm Br, 500 ppm Cl	0	0.06	1.7	0.48	1.4
2500 ppb Br, 200 ppm Cl	0	0.02	4.1	0.31	0.56	2.5 ppm Br, 500 ppm Cl	0	0.04	4.5	0.52	1.4
5000 ppb Br, 200 ppm Cl	0	0.04	8.5	0.50	0.59	5 ppm Br, 500 ppm Cl	0	0.07	8.7	0.57	1.4
10000 ppb Br, 200 ppm Cl	0	0.03	17.7	0.46	0.57	1 ppm Br, 500 ppm Cl	0	0.02	17.9	0.66	1.4
250 ppb Br, 200 ppm Cl + 5 ppb	5	5.0	5.7	5.9	6.0	0.25 ppm Br, 500 ppm Cl + 5 ppb	5	5.5	5.8	6.0	6.8
500 ppb Br, 200 ppm Cl + 5 ppb	5	5.4	6.3	5.9	6.0	0.5 ppm Br, 500 ppm Cl + 5 ppb	5	5.3	6.4	6.0	6.8
1000 ppb Br, 200 ppm Cl + 5 ppb	5	5.2	7.1	6.0	6.0	1 ppm Br, 500 ppm Cl + 5 ppb	5	5.5	7.1	6.0	6.8
2500 ppb Br, 200 ppm Cl + 5 ppb	5	5.2	9.8	5.9	5.9	2.5 ppm Br, 500 ppm Cl + 5 ppb	5	5.1	9.7	5.8	6.8
5000 ppb Br, 200 ppm Cl + 5 ppb	5	5.8	13.9	5.9	6.0	5 ppm Br, 500 ppm Cl + 5 ppb	5	5.3	14.2	5.9	6.7
10000 ppb Br, 200 ppm Cl + 5 ppb	5	5.3	23.3	6.1	6.1	10 ppm Br, 500 ppm Cl + 5 ppb	5	5.2	23.6	6.0	6.8

$$As75-1=75As-(3.127 \times (77Se - (0.815 \times 82Se)))$$

$$As75-2=75As-(0.322 \times 78Se)$$

As75-3=No Correction Equation

Conclusion

There is no single universal method for dealing with interferences in ICP-MS analysis. The matrix of the sample should be monitored to help determine any potential interferences. Multiple isotopes must be analyzed for elements which suffer from polyatomic interferences. The application of correction equations should be closely monitored to ensure there are no interferences on the applied equation. The use of a dynamic reaction cell will minimize the effect of interferences as shown in Table 4. However, a successful strategy requires a full understanding of the technique used and detailed knowledge of sample matrices.

References

Thomas, Robert. 2008, Practical Guide to ICP-MS: A Tutorial for Beginners 2nd edition.

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