Dramatically Improved Performance of Arsenic and Selenium Determination using the Thermo Scientific iCAP Q ICP-MS with Methane Addition

Tomoko Vincent, Shona McSheehy Ducos, Julian D. Wills, Torsten Lindemann
Thermo Fisher Scientific, Bremen, Germany

Application Brief 43250

Key Words
Arsenic, CCT, High Sensitivity, Methane Addition, Selenium

Goal
To determine ultratrace concentration of As and Se using the Thermo Scientific iCAP Q ICP-MS and to demonstrate the use of CCT mode with CH_4 addition to improve analytical performance.

Application Challenge
Arsenic and selenium ultratrace analysis is generally one of the most challenging using ICP-MS due to complicated polyatomic interferences arising from the argon plasma source and the inherent lower sensitivity of these analytes due to the high 1st ionization potential (IP).

While collision/reaction cell technology or high mass resolution enable increased performance, there is still room for improvement with regards to lowering detection limits and increasing sensitivity.

A hydrogen based reaction gas is known to improve the performance for Se analysis at *m/z* 78. However, this method has the disadvantage of producing side reaction components such as $^{38}Ar^{40}ArH_2^+$, and therefore results in better BEC and LoD for ^{78}Se compared to ^{80}Se, despite the fact that ^{80}Se is the more abundant isotope.

To further increase performance, an approach known as carbon loading has been used with the Thermo Scientific™ iCAP™ Q ICP-MS (Figure 1). Carbon loading is a technique known to improve the ionization efficiency of high IP analytes such as arsenic and selenium through what is thought to be a charge transfer process in the plasma. An approach using methane as the carbon source[1-3] has been used as it has been found in previous applications (data not shown) to be more effective than the addition of organic solvents.

Through the combination of sensitivity enhancement and interference removal, a method has been developed, which provides a significant increase in signal to noise performance enabling ultra low quantification limits for As and Se in various applications.

Figure 1. The Thermo Scientific iCAP Q ICP-MS.

Sample Preparation
As and Se standards at concentrations of 1, 2, 3, 4 and 10 ng·L^{-1} were prepared by diluting single stocks of SPEX CertiPrep solutions, directly in 2% HNO_3 prepared with Fisher Chemicals Optima grade nitric acid.

Table 1. Polyatomic interferences from an ICP source.

Isotope	Abundance (%)	Interference
^{75}As	100	$^{36}Ar^{38}Ar^{1}H^+$, $^{40}Ar^{35}Cl$
^{74}Se	0.87	$^{36}Ar^{38}Ar$
^{76}Se	9.02	$^{40}Ar^{36}Ar$
^{77}Se	7.58	$^{36}Ar^{40}Ar^{1}H^+$, $^{40}Ar^{37}Cl$
^{78}Se	23.52	$^{40}Ar^{38}Ar^+$
^{80}Se	49.82	$^{40}Ar_2^+$
^{82}Se	9.19	$^{40}Ar_2{}^{1}H_2^+$

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Instrument Configuration

A Thermo Scientific iCAP Qs ICP-MS was configured with a quartz, cyclonic spray chamber cooled to 2 °C and a self aspirating microflow PFA-400 nebulizer. The ICP-MS was used in CCT mode with 7% H_2 in He gas at 9 mL·min^{-1}. 1% CH_4 in Ar gas was added to the plasma via an additional gas port on the spray chamber elbow at 120 mL·min^{-1}. (Please note, the iCAP Qs ICP-MS was not setup in a cleanroom).

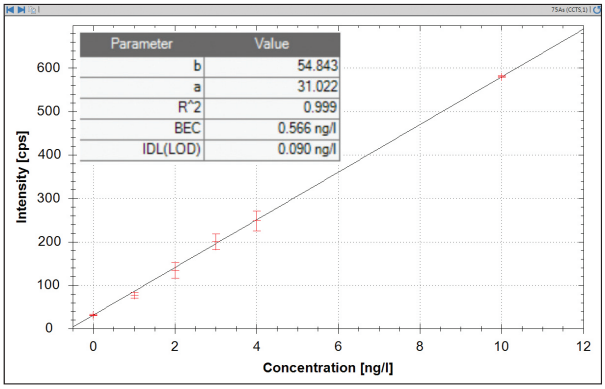

Figure 2a. Calibration curve for ^{75}As with CCT using CH_4 addition.

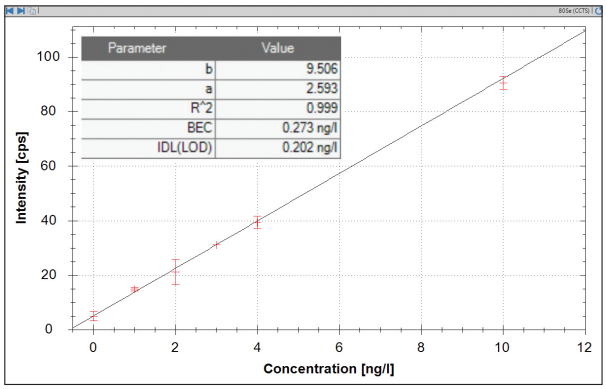

Figure 2b. Calibration curve for ^{80}Se with CCT using CH_4 addition.

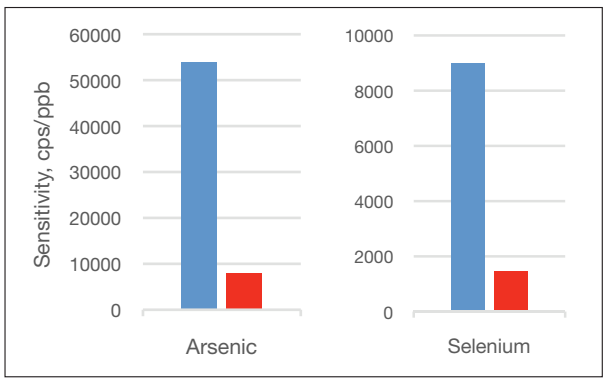

Figure 3. Sensitivity of As and Se without (red) and with (blue) the addition of methane to the plasma.

Results

Linear calibration curves in sub ng·L^{-1} concentration range with correlation coefficients better than 0.999 for both analytes (Figure 2a and 2b).

A dramatic improvement in sensitivity: ^{75}As 54 kcps·ppb^{-1}, ^{80}Se 9 kcps·ppb^{-1}, equivalent to a seven-fold increase in sensitivity compared to the same method without CH_4 addition (Figure 3).

Excellent LoD and BEC using a single CCT measurement mode with CH_4 addition.

Accurate spike recoveries from 95% to 107% for both elements at 1 ng·L^{-1}.

Table 2. iCAP Qs ICP-MS performance data for As and Se in a 2% HNO_3 matrix. Recovery values are shown as the percentage recovery for a 1 ng·L-1 spike.

Analyte	LoD (ng·L^{-1})	BEC (ng·L^{-1})	Recovery (%)
^{75}As	0.1	0.6	107
^{80}Se	0.2	0.3	95

Conclusions

The benefit of carbon loading to improve sensitivity of high IP analytes has been shown. The use of methane gas in the plasma is especially effective and has shown to give a sensitivity increase of seven fold for arsenic and selenium. Although the method has been developed with the Thermo Scientific iCAP Qs ICP-MS, the use of methane would be of equal advantage with the Thermo Scientific iCAP Qc ICP-MS and the Thermo Scientific™ ELEMENT 2 and Thermo Scientific™ ELEMENT XR. These instruments offer accurate and extremely low level quantification of arsenic and selenium with both BEC and LoD in the sub-ppt range. Methane addition is a simple technique that can be easily implemented for trace elemental analysis in various markets and matrices where ultra low detection capabilities are required.

References

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