Practical benefits of abundance sensitivity using a MS/MS capable ICP-MS

Glenn D. Woods[1], Amir Liba[2], Yasuyuki Shikamori[3]

[1] Agilent Technologies LDA UK Ltd., 5500 Lakeside, Cheadle Royal Business Park, Stockport. SK8 3GR United Kingdom
[2] Agilent Technologies, Inc., 2850 Centerville Road, Wilmington, DE 19808-1610,United States of America
[3] Agilent Technologies Japan Ltd., 9-1 Takakura-Machi, Hachioji-shi, Tokyo-To 192-8510,Japan

Agilent Technologies

Introduction

Abundance Sensitivity (AS) is the term given in mass spectrometry to the undesired signal contribution from an adjacent mass peak. Not to be confused with resolution, AS can be good at low resolution or poor at high resolution as it is simply a measure of peak tailing at the low and high mass side. A worst case scenario would be to have a trace analyte peak adjacent to a major, matrix peak.

Modern quadrupoles can offer extremely low (good) AS but when a very low intensity signal needs to be measured close to an intense matrix peak, tailing can still occur and cause incorrectly high results on the analyte(s) either side of the matrix peak.

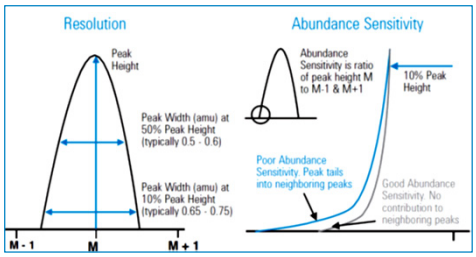

Fig.1 Difference between Abundance Sensitivity and Resolution

To improve AS performance quadrupoles need to possess a hyperbolic cross-section and operate at high frequency, and these can typically give AS performance in the region of $<10^{-7}$ however if two mass separations can be performed in tandem then the AS performance is a function of both separations combined and multiplied producing AS factors of $<<10^{-10}$.

The second generation Agilent 8900 ICP-QQQ (or tandem MS/MS) instrument uniquely has two quadrupoles either side of a Collision/Reaction Cell (CRC), both capable of unit mass resolution enabling advanced reaction chemistry but also the ability to run in MS/MS mode to greatly improve AS.

Experimental

Performance was tested using analytes from low to high mass in matrices that would provide interference problems due to peak overlap.

Fig 2. Agilent 8900 ICP-QQQ

Matrices selected are listed in table 1 below and typical instrument parameters in table 2.

Element	Matrix	Overlap
Boron (B)	Kerosene	^{12}C on ^{11}B (possibly ^{10}B)
Manganese (Mn)	Blood & Steel	^{54}Fe & ^{56}Fe on ^{55}Mn
Neptunium (Np)	Uranium	^{238}U on ^{237}Np

Table 1. Matrix and analytes used to test Abundance Sensitivity performance, note the blood sample was diluted 10x in a basic medium

The sample introduction system was standard Quartz with concentric nebuliser, oxygen was added to the plasma for the kerosene matrix.

Parameter	Value
Forward Power	1550W
Carrier Gas	0.85~1.07 l min^{-1}
Oxygen (20% in Ar)	0.0~0.2 l min^{-1}
Helium Cell Gas	0.0 or 5.0 ml min^{-1}
Acquisition Modes	Single Quad & MS/MS

Table 2. Typical instrument parameters, oxygen was only needed for the kerosene matrix to avoid carbon deposition on the cones and Helium Collision Gas was only needed for Mn determination

Results and Discussion

Boron in an Organic Matrix

Boron can suffer an overlap from the adjacent ^{12}C isotope when appreciable quantities of carbon are present within the sample matrix. Hydrocarbons such as kerosene can challenge the AS performance of any mass spectrometer particularly if access to both Boron isotopes is desired. The figures below display the benefits of using MS/MS (ICP-QQQ) mode contrasted to Single Quad (ICP-MS).

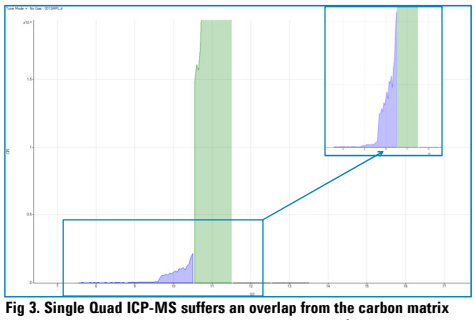

Fig 3. Single Quad ICP-MS suffers an overlap from the carbon matrix when trying to measure boron (B spike at 5.77µg Kg^{-1})

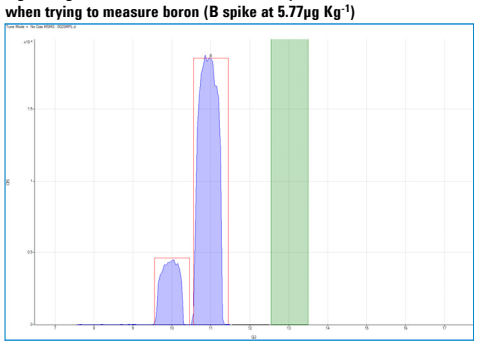

Fig 4. Same spiked kerosene sample measured under MS/MS mode – both isotopes are clearly visible and accessible with no ^{12}C peak tailing

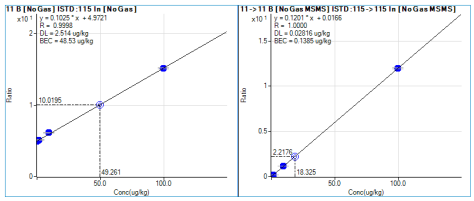

Fig 5. Calibration under SQ (left) and MS/MS (right) modes, note improvement in BEC under MS/MS mode from ~49µg Kg^{-1} to ~0.14µg Kg^{-1}

The improvement in AS clearly allows access to the boron isotopes even with this very intense carbon interference.

Manganese in Whole Blood and Steel Digest

The manganese concentration in blood averages around 10µg l^{-1} with iron around 500000µg l^{-1} (500ppm); ^{55}Mn is the only natural Mn isotope so there is no alternative and as this sits between the ^{54}Fe and ^{56}Fe isotopes, can suffer AS interferences from both low mass and high mass sides. In the case of the digested steel sample, Fe concentration is even higher at 1000ppm. Manganese can also suffer from polyatomic interferences so in this instance it was measured under Helium Collision Mode.

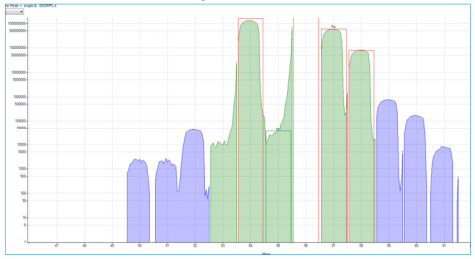

Fig 6. Iron overlap on Mn in a 1000ppm Fe matrix – SQ Mode

The large Fe overlap is clearly visible in SQ mode (figure 6) whilst being eliminated under MS/MS measurement mode (figure 7).

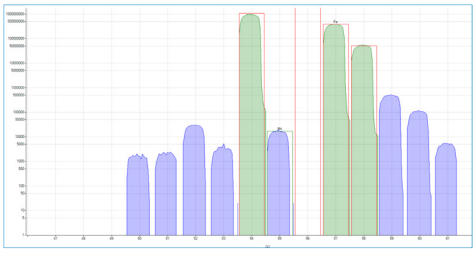

Fig 7. Same 1000ppm Fe measured under MS/MS mode

Accuracy was checked with spiked blood and steel CRM samples and results are displayed in table 3 below.

Sample	Cert./Spike	Found	Recovery
Blood	0.5	0.492µg/l	98%
JSS 001-6	*0.03**	*0.036mg/Kg*	*120%*
JSS 003-6	3.2 (+/- 0.2)	3.432mg/Kg	101%

Table 3. Spike recovery for blood (original sample 0.432ppb) and values for steel CRM. **JSS 001-6 data is non-certified.*

Recoveries were acceptable even in the presence of such intense interferences leading to reliable Mn data.

Neptunium in a Uranium Matrix

Neptunium is produced by neutron bombardment of uranium and can occur naturally at trace to ultratrace levels in U ores and from bomb testing or as a decay product of ^{241}Am used in some smoke detectors. However around 50000Kg p/a are produced in nuclear waste. ^{237}Np is the longest lived isotope ($t_{1/2}$=2.14MY) but suffers from overlap from the neighbouring ^{238}U isotope.

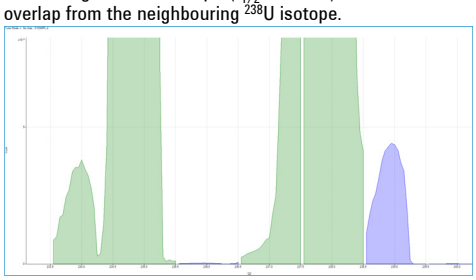

Fig 7. 0.1µg/l Np in 10mg/l U matrix in SQ mode note large overlap from the uranium matrix

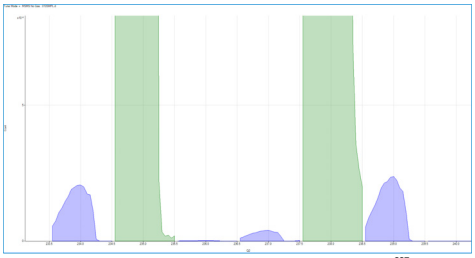

Fig 8. 0.1µg/l Np in 10mg/l U matrix under MS/MS mode – ^{237}Np is clearly separated from the uranium matrix peak

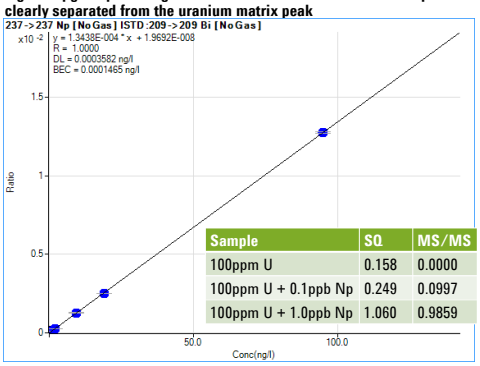

Fig 9. ^{237}Np calibration (DL<0.4ppq, BEC<0.2ppq) with comparative data for a 100ppm U matrix with and without Np spikes measured under SQ and MS/MS modes

Conclusions

Performing two separate mass separations in series (MS/MS) significantly improves the Abundance Sensitivity in quadrupole ICP-MS. This unique feature gives access to analytes and applications that would otherwise require extensive sample preparation or lead to compromised data.