Reaction Cell Frontier: Removing oxide polyatomic ion interferences using an innovative reaction cell ICP-MS

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Introduction

ICP-MS is an analytical technique capable of achieving detection limits in the part per trillion (ppt) or sub-ppt range for most elements. However, its excellent detection capability is often limited in real applications by two major factors: contamination and spectral interference. Collision/reaction cell technology, which had been routine in LC/MS, was applied to ICP-MS and proved effective at resolving most interference problems. This technology relies on one of two types of cells in ICP-MS: collision cells or reaction cells. Collision cells remove interfering polyatomic ions using the size difference between the analyte ion and interfering polyatomic ion and so are effective on all interferences caused by polyatomic ions. Since collision cells do not sacrifice the multi-element capability of ICP-MS, they have been widely accepted for many applications. However, for some interferences, the effectiveness of collision cells is limited. Interference by metal oxide ions is a common example. In this work, we applied novel reaction cell technology based on a triple quadrupole configuration to ICP-MS in order to remove interferences due to oxide ions such as **$^{59}Co^{16}O^+$ on $^{75}As^+$** with excellent results.

Experimental

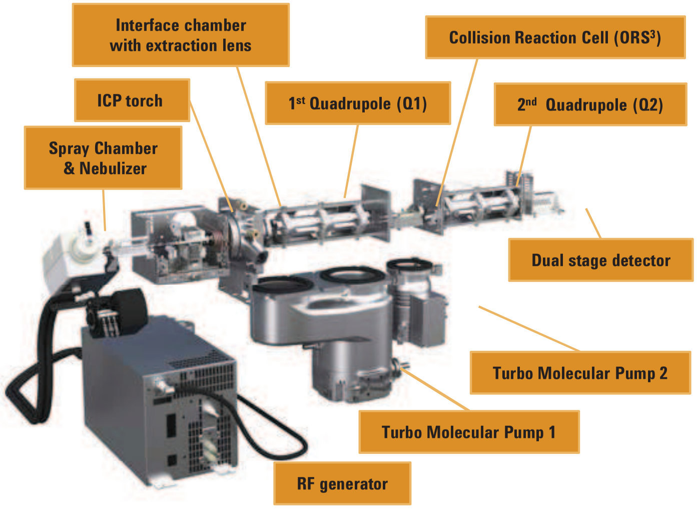
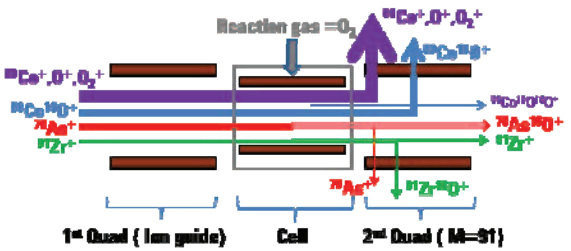


Figure 1. Configuration of Agilent ICP-QQQ

Agilent ICP-QQQ

Agilent Technologies has developed a new high-end, Triple Quadrupole ICP-MS (ICP-QQQ). As shown in Figure 1, it has two quadrupoles, one before and one after the Collision/Reaction Cell. The 1st quadrupole selects ions to enter the cell, providing consistent reaction conditions to changing sample composition (Figure 2 (2) MS/MS mode). It solves the problem of current cell technologies using reaction gas, allowing analysts to use reaction mode for more elements/applications, more effectively. Figure 2 illustrates the principle of two different modes for ICP-QQQ. One is (1) Single-Quad mode and the other is (2) MS/MS mode. The comparison of the two modes is discussed in this paper. In both cases, standard plasma conditions (CeO^+/Ce^+=0.9%) were employed.

(1) Single-Quad mode (Q1 as an ion guide)



(2) MS/MS mode (Q1 as 1amu-window (*m/z* 75) band pass)

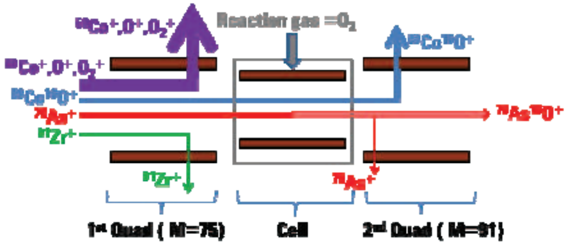


Figure 2. Illustration of the O_2 mass shift method of ICP-QQQ using two different modes (^{75}As as $^{75}As^{16}O^+$ at *m/z* 91)

(1) Single-Quad mode: allows all ions through to the collision/reaction cell (as an ion guide), with the system acting as a single-quad ICP-MS (functioning like the octopole-based cell of the current Agilent 7700 series ICP-MS)

(2) MS/MS mode: operates the 1st Quad as **1 amu-window band pass mass filter**, selecting ions entering the reaction cell.

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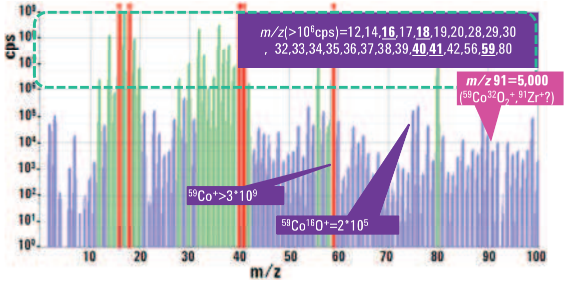
Results and Discussion

(1) **Single-Quad mode** (Q1 as an ion guide)



(2) **MS/MS mode** (Q1 as 1amu-window (*m/z* 75) band pass)

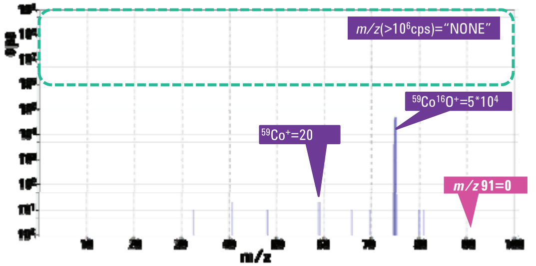


Figure 3. ICP-QQQ mass spectra for 100ppm (mg L^{-1}) Co in 1% HNO_3 by no gas mode (Octopole bias:- 8 V, Q2 bias: -5 V)

(1) Single-Quad mode: Red color spectrum (*m/z* 16,18,40,41,59) was measured as "EM protection (> $3*10^9$ cps)

(2) MS/MS mode: Q1 rejected all masses except target mass (*m/z*75). Only target-mass ions (m/z 75) entered the cell

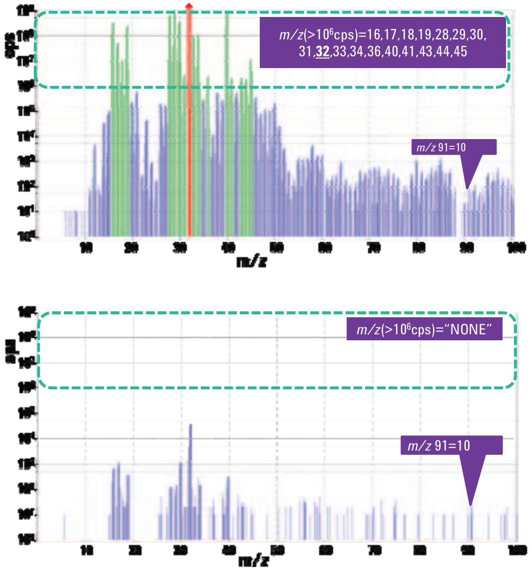


Figure 4. ICP-QQQ mass spectra for 1% HNO_3 by O_2 mode (Octopole bias: -16 V, Q2 bias:- 26 V)

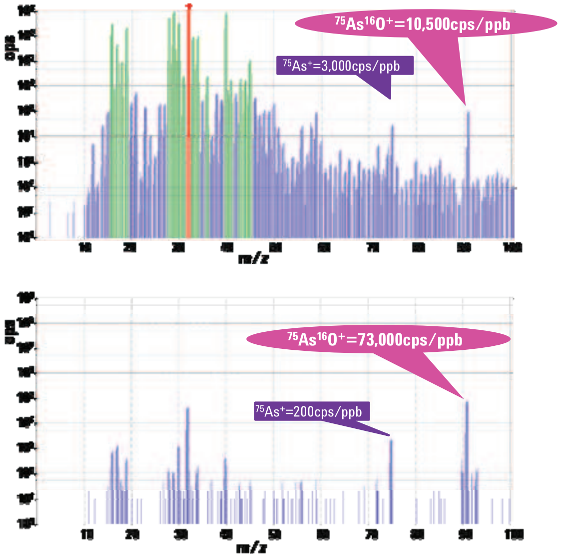


Figure 5. ICP-QQQ mass spectra for 10 ppb (µg L^{-1}) As in 1%HNO_3 by O_2 mode (Octopole bias: -16 V, Q2 bias: -26 V)

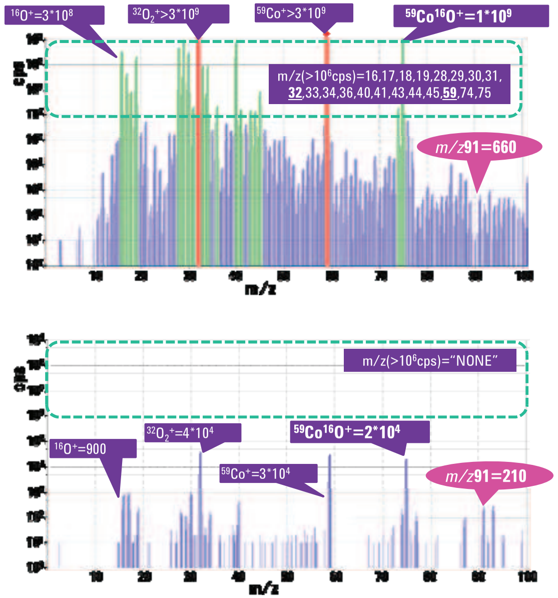


Figure 6. ICP-QQQ mass spectra for 100 ppm (mg L^{-1}) Co in 1%HNO_3 by O_2 mode (Octopole bias: -16 V, Q2 bias: -26 V)

(1) Single-Quad mode: *m/z* 91 = 660 cps (As 63 ppt as AsO)

(2) MS/MS mode: *m/z* 91= 210 cps (As 29 ppt as AsO)

1) Single-Quad mode → 34 (=63-29)ppt interference by CoO_2^+
2) MS/MS mode → The lowest BEC

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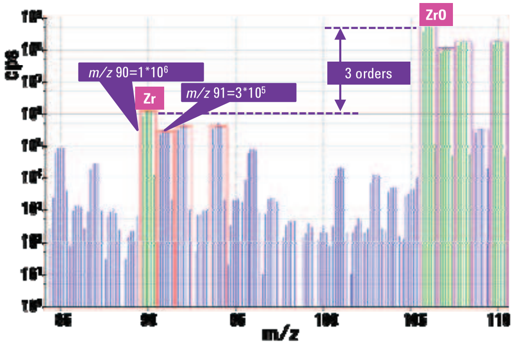
Results and Discussion

(1) Single-Quad mode (Q1 as an ion guide)



Mass	Zr Abundance(%)
90	51.45
91	11.22
92	17.15
94	17.38
96	2.80

(2) MS/MS mode (Q1 as 1amu-window (m/z 75) band pass)

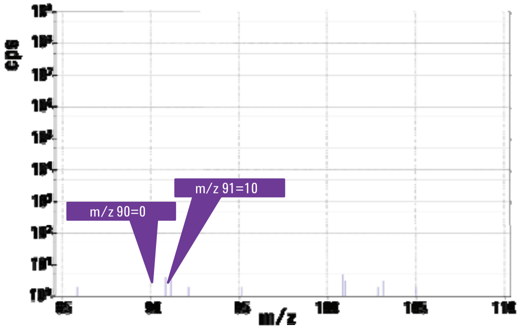


Figure 7. ICP-QQQ mass spectra for 10ppm(mg L^{-1}) Zr in 1%HNO_3 by O_2 mode (Octopole bias: -16 V, Q2 bias:- 26 V)

1. (1) Single-Quad mode: Correct match with isotopic template confirms presence of Zr and ZrO
2. (2) MS/MS mode: No Zr interference on m/z 91 (AsO^+)

Table 1. Kinetic rate constant and the enthalpy$^{(1)}$

Reaction	Kinetic Rate Constant/ cm^{3}mol^{-1}·s^{-1}	ΔH r (enthalpy) kJ/mol(eV)
$^{75}As^+ + O_2 \rightarrow {}^{75}As^{16}O^+ + O$	4*10^{-10}(→Rapid)	-928(-9.6)
$^{59}Co^+ + O_2 \rightarrow {}^{59}Co^{32}O_2^+ + O$	1.5*10^{-13}(→Slow)	No data
$Zr^+ + O_2 \rightarrow ZrO^+ + O$	5*10^{-10}(→Rapid)	-705(-7.3)

Figure 3 shows the mass spectrum for a 100 ppm Co solution. A lot of spectra signals were observed for (1) Single-Quad mode. On the other hand, almost no signal except the target mass (m/z75) was observed for (2) MS/MS mode. When O_2 is introduced into the reaction cell, a new ion is produced at m/z 91 ($^{75}As^{16}O^+$) from a solution containing As (Figure 4 (blank), Figure 5 (10ppb As)). The reaction is exothermic (-928kjmol^{-1}) as shown in Table1. Bohme et al. report that the reaction of As^+ with O_2 to form AsO^+ is efficient, with a kinetic rate constant around 4*10^{-10}cm^3 mol^{-1} s^{-1}. On the other hand the reaction of Co^+ with O_2 to form CoO_2^+ is very slow, with a kinetic rate constant around 1.5*10^{-13}cm^3 mol^{-1} s^{-1}. $^{1)}$

Table 2 shows the comparison of As quantitative results in a 100 ppm cobalt solution based on an external calibration in 1% HNO_3. In no gas mode (#1), serious interference from $^{59}Co^{16}O$ resulted in a measured value for As of 32 ppb. The result using Helium mode (#2) was 3.7 ppb. While helium collision was able to reduce the interference about 1 order of magnitude better than no gas mode, it was still incapable of sufficiently removing the interference. On the other hand, using oxygen reaction mode (#3) (1) Single-Quad mode to convert $^{75}As^+$ to $^{75}As^{16}O^+$ was effective at separating the $^{59}Co^{16}O$ interference from the As measurement of 63 ppt. Moreover, the result of (#4) (2) MS/MS mode using Q1 as 1 amu-window band pass filter showed the best overall reduction of interference at 29 ppt.

The result difference was 34 ppt (63-29). In the case of (1) Single-Quad mode, it is probable that slight CoO_2^+ was generated in the cell because the signals of Co^+ and CoO^+ are higher than that of (2) MS/MS mode, as shown in Figure 6. **Figure 7** shows a mass spectrum of the m/z 85–110 region for 10 ppm Zr solution because ^{91}Zr (11.22% abundance) could cause a spectral overlap with $^{75}As^{16}O$. The reaction of Zr^+ with O_2 to form ZrO^+ is effective, as the signal due to ZrO^+ is approximately 3 orders of magnitude higher than that of Zr^+. However, the As quantitative result was 30 ppb for (1) Single-Quad mode because of the residual $^{91}Zr^+$ interference. On the other hand the result of (2) MS/MS mode was 0 ppt because Zr^+ was completely eliminated by Q1.

Table 2. Comparison of As quantitative results in 100 ppm Co and 10 ppm Zr (ppt)

#	Collision/ Reaction	Mass	Co(100ppm)	Zr (10ppm)	Interference
1	No gas	75	32000	0(**)	CoO
2	Helium	75	3700	0(**)	CoO
3	Oxygen(1) Single-Quad mode	91(*)	63	30000	CoO_2 (Slight), Zr
4	Oxygen(2) MS/MS mode	91(*)	29	0	Lowest BEC

(*) $As^{75}As^{16}O$,(**) as theoretical value (no experimental data)

Conclusions

Trace level arsenic measurement in high concentrations of cobalt is not possible using conventional techniques with quadrupole ICP-MS. This poster has demonstrated the following:

- ICP Triple Quad can provide a solution

- MS/MS mode using O_2 reaction was effective at solving the interference by CoO_2, Zr etc., because the 1st Quadpole (set to 1 amu-window band pass filter) rejected all ions except the target mass (*m/z* 75) ions such as As^+ and CoO^+.

- The result of MS/MS mode showed the best overall reduction of interference at 29 ppt.

Reference

1) John W. Olesik and Deanna R. Jones, J. Anal. At. Spectrom., 2006 ,21, 141-159