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 analyte ion and interfering polyatomic ion and so are effective on all interferences caused by polyatomic ions. Since collision cells don't 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 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

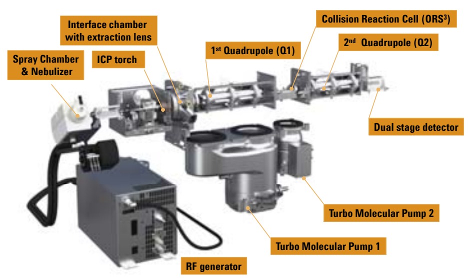


Fig.1 Configuration of Agilent ICP-QQQ

Agilent ICP-QQQ

Agilent Technologies developed a new high-end ICP-MS, Triple Quadrupole ICP-MS (ICP-QQQ). As shown in Fig.1, it has two Quadrupoles before and after Collision/Reaction Cell. The 1st quadrupole selects ions enter the cell, providing consistent reaction conditions to changing sample composition(→Fig.2 (2)MS/MS mode). It solves problem of current cell technologies using reaction gas, allowing analysts to use reaction mode for more elements/applications, more effectively. Fig.2 illustrates the principle of two different mode 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(Plasma Condition: CeO^+/Ce^+=0.9%).

(1) Single-Quad mode(Q1 as an ion guide) **(2) MS/MS mode**(Q1 as 1amu-window(m/z75) band pass)

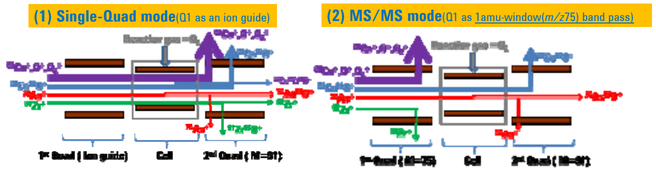


Fig.2 Illustration of O_2 mass shift method of ICP-QQQ using 2 different mode(^{75}As as $^{75}As^{16}O^+$ at m/z 91)

(1) Single-Quad mode : allows all ions through into the collision/reaction cell(as an ion guide), so system works like a single-quad ICP-MS (Functions 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 reaction cell.

Results and Discussion

(1) Single-Quad mode(Q1 as an ion guide) **(2) MS/MS mode**(Q1 as 1amu-window(m/z75) band pass)

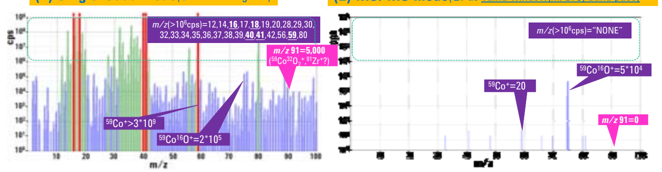


Fig.3 ICP-QQQ mass spectra for 100ppm(mg L-1) **Co in 1%HNO_3 by no gas mode** (Octopole bias:-8V,Q2 bias:-5V)

(1)Single-Quad mode: Red color spectra(m/z16,18,40,41,59) was measured as "EM protection(>3*10^9cps)"

(2)MS/MS mode: : Q1 rejected all masses except target mass(m/z75). Only target-mass ions(m/z75) entered the cell

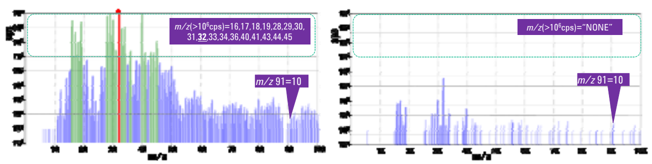


Fig.4 ICP-QQQ mass spectra for 1%HNO_3 by O_2 mode (Octopole bias:-16V,Q2 bias:-26V)

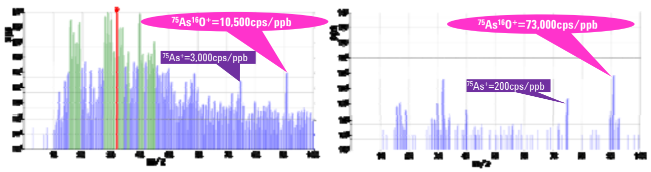


Fig.5 ICP-QQQ mass spectra for 10ppb(μg L-1) **As in 1%HNO_3 by O_2 mode** (Octopole bias:-16V,Q2 bias:-26V)

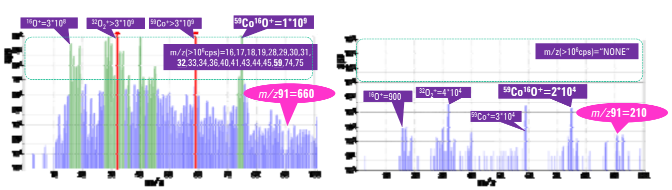


Fig.6 ICP-QQQ mass spectra for 100ppm(mg L-1) **Co in 1%HNO_3 by O_2 mode** (Octopole bias:-16V,Q2 bias:-26V)

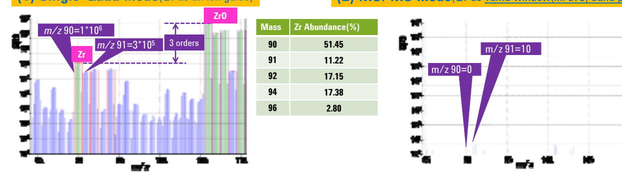
(1)Single-Quad mode: m/z91=660cps(As63ppt as AsO)

(2)MS/MS mode: : m/z91=210cps(As29ppt as AsO)

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

Results and Discussion

(1) Single-Quad mode(Q1 as an ion guide) **(2) MS/MS mode**(Q1 as 1amu-window(m/z75) band pass)



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

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

(1)Single-Quad mode: Correct match with isotopic template confirms presence of Zr and ZrO

(2)MS/MS mode: : No Zr interference on m/z91(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)

Fig.3 shows the mass spectra for a 100ppm 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 introduced into the reaction cell a new ion is produced at m/z91($^{75}As^{16}O^+$) from a solution containing As(→Fig.4(blank),Fig.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 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 100ppm 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 32ppb. The result using Helium mode (#2) was 3.7ppb. 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 63ppt. Moreover, The result of (#4) (2)MS/MS mode using Q1 as 1amu-window band pass filter showed the best overall reduction of interference at 29ppt. The result difference was 34ppt(=63-29). In 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 surprisingly higher than that of (2)MS/MS mode as shown in Fig.6.

Next, Fig.7 shows a mass spectra of the m/z85-110 region for 10ppm 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 form ZrO^+ is effective as the signals of ZrO^+ is about 3 orders of magnitude higher than that of Zr^+. But the As quantitative result was 30ppb for (1)Single-Quad mode because of the residual $^{91}Zr^+$ interference. On the other hand the result of (2)MS/MS mode was 0ppt because Zr^+ was completely eliminated by Q1, as shown in Fig.7.

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

#	Collision/Reaction	Mass	Co100ppm	Zr10ppm	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

Regarding to As analysis in Cobalt 100ppm solution,

- ✓ Mass spectra comparison between (1) Single-Quad mode and (2)MS/MS mode are discussed.
- ✓ MS/MS mode using O_2 reaction was surprisingly effective to solve the interference by CoO_2,Zr etc., because 1st Quadpole (set to 1 amu-window band pass filter) rejected all ions except the target mass (m/z75) ions such as As^+ and CoO^+ .
- ✓ The result of MS/MS mode showed the best overall reduction of interference at 29ppt.

Reference

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