# Agilent 8800 Triple Quadrupole ICP-MS: Understanding oxygen reaction mode in ICP-MS/MS

Agilent 8800 ICP-QQQ

Technical Overview
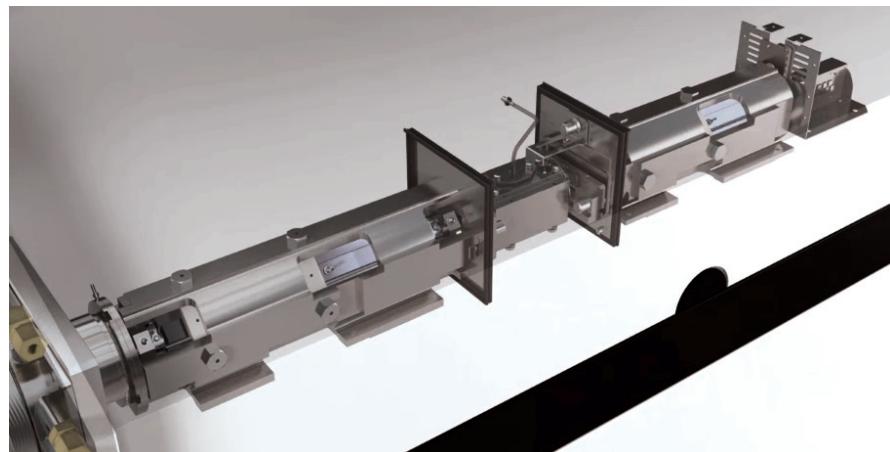
Introduction

The use of oxygen as a reaction gas for the removal of interferences in quadrupole ICP-MS is well established. However, prior to the development of the Agilent 8800 Triple Quadrupole ICP-MS (ICP-QQQ), the use of oxygen had been limited to determination of a small number of analytes in simple, well defined matrices. This is because oxygen can react with matrix components, analytes and polyatomic species in the cell resulting in the formation of new and unwanted interferences and loss of analyte. In order for oxygen reaction mode to be used reliably, the reaction environment within the cell must be strictly controlled. To this end, the Agilent 8800 ICP-QQQ employs an additional quadrupole mass filter before the reaction cell. This additional quadrupole (Q1) can be used to accurately control the species that enter the cell before any reactions can occur, resulting in precise control of the reaction chemistry even in the case of unknown or complex matrices. The use of an additional mass filter before the cell is refered to as MS/MS mode, and is currently only possible using ICP-QQQ. The use of MS/MS mode with ICP-QQQ permits reaction chemistry to be applied to the most complex

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and challenging interference problems. In addition to oxygen, the other common reaction gases used are hydrogen (H_2) and ammonia (NH_3). However, when properly controlled with the use of MS/MS technology, O_2 is the most powerful and useful gas for removing polyatomic interferences. For example, O_2 can remove the $^{129}Xe^+$ atomic isobaric interference on $^{129}I^+$ via charge transfer reaction. It can be used to convert an analyte ion such as As^+ to AsO^+, thereby overcoming both the $ArCl^+$ and REE^{2+} interferences on As^+. And finally, the WO^+ interference on Hg^+ can be removed by converting WO^+ to WOO^+.

The purpose of this technical note is to describe the various modes of action of oxygen reaction mode on the 8800 ICP-QQQ and provide insight into method development using O_2 reaction techniques.

Reactions in O_2 Mode

There are two main reaction mechanisms associated with the use of oxygen in the collision reaction cell (ORS^3), oxygen atom abstraction (oxygen atom transfer) and charge transfer (electron transfer) as shown below.

O-atom transfer:

$$X^+ + O_2 \rightarrow XO^+ + O, \ \ \Delta Hr = D(O_2) - D(X^+\text{-}O)$$

Charge transfer:

$$X^+ + O_2 \rightarrow X + O_2^+, \ \ \ \Delta Hr = IE(O_2) - IE(X)$$
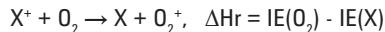
Where X = the analyte element, ΔHr = enthalpy of reaction, $D(O_2)$ = bond energy of oxygen molecule, $D(X^+\text{-}O)$ = bond energy of product ion XO^+, $IE(O_2)$ = ionization energy of oxygen molecule, $IE(X)$ = ionization energy of analyte atom

In the O-atom transfer reaction, one of the oxygen atoms is transferred from the O_2 molecule via reaction with X^+ ion, resulting in the formation of an oxide ion (XO^+) at a new mass of m_x+16, where m_x is the mass of the analyte ion. Thus, the analyte ion X^+ is mass shifted to a new mass away from the original interference(s) at $m/z = m_x$. In this case, the first quadrupole, Q1 is set to $m/z = m_x$, and the second quadrupole, Q2 is set to $m/z = m_x +16$. Figure 1 shows overlaid mass spectra of oxide ions produced through O-atom transfer reactions for a 1 ppb multielement standard solution. Because Q1 and Q2 are scanned synchronously 16 amu apart, only the oxide ions formed in the cell are present in the Q2 spectra.

In the case of charge transfer reactions, one of the electrons of the O_2 molecule is transferred to the reactant ion X^+, resulting in its reduction and formation of neutral X.

The intrinsic properties of both the products and reactants will dictate if and how these reactions will proceed. Since there is generally no activation barrier in these ion-molecule reactions, the enthalpy of reaction, ΔHr, indicates the reaction efficiency and whether the reaction will proceed forward.

Enthalpy of Reaction ΔHr

ΔHr is the amount of energy (heat) absorbed or released by a reaction. When ΔHr is positive ($\Delta Hr > 0$), the reaction is endothermic, meaning energy is required (absorbed) for the reaction to occur. When ΔHr is negative ($\Delta Hr < 0$), the reaction is exothermic, meaning energy is released by the reaction, which is spontaneous. Under the same conditions, an exothermic reaction will occur much more rapidly than an endothermic reaction, which may not occur at all. An exothermic ion-molecule reaction usually occurs spontaneously when the two reactants (e.g. X^+ and O_2) meet in the gas phase because no appreciable activation energy is required. Therefore the reaction is highly efficient. An estimate of ΔHr can easily be made from the bond energies and ionization energies of reactants and products (Table 1).

For the O-atom transfer reaction, ΔHr is the difference between the bond (binding) energy of the O_2 molecule and that of the product ion XO^+, which are expressed as $D(O_2)$ and $D(X^+\text{-}O)$ respectively. $D(O_2)$, ca. 5.1 eV, is also termed the dissociation energy of O_2, meaning the energy required to separate the two O-atoms of an O_2 molecule. Likewise $D(X^+\text{-}O)$ is the energy required to separate X^+ and O, which is also referred to as the O-atom affinity of X^+. Upon collision, if an O atom has a greater affinity for X^+ than for O, i.e. $D(X^+\text{-}O) > D(O_2)$, one of the O atoms leaves and binds to X^+. This process occurs spontaneously because $\Delta Hr = D(O_2) - D(X^+\text{-}O) < 0$, i.e, the reaction is exothermic. Table 1 shows actual values found in the literature or derived from the literature values of $D(X^+\text{-}O)$. Efficient oxide ion formation is expected in O_2 mode for the ions that go through exothermic O-atom transfer reactions. For the detection of such ions in O_2 mode using the 8800 ICP-QQQ, a mass-pair setting of (Q1 = m_x, Q2 = m_x +16) is recommended, where m_x is the mass of the reactant (analyte) ion. As shown in Figure 1, the intensities of TiO^+ and VO^+ are much higher than other oxide ions as these two oxide ions are formed through exothermic reactions while the others are endothermic reactions, which require energy to proceed.

For the charge transfer reaction, ΔHr is the difference between the ionization energies of O_2 (12.06 eV) and X, which are expressed as $IE(O_2)$ and $IE(X)$ respectively. If $IE(X) > IE (O_2)$ ($\Delta Hr < 0$), an efficient charge transfer is expected in the cell. Ions that go through such exothermic charge transfer reactions with O_2 include Cl^+, Ar^+, Kr^+, Xe^+, and CO^+.

Collision Energy for Endothermic Reaction

In mass shift mode, the reaction efficiency may not need to be very high. As long as sufficient signal is obtained at the $m_x + 16$ m/z, 100% of X^+ need not be converted. This is in contrast to the conventional reaction mode where interfering ions often have to be reduced by many orders of magnitude. Mass shift mode works by "shifting" the mass of analyte ions, not by reducing the intensity of interfering ions. Therefore less efficient endothermic reactions can also be made use of in many applications. The energy required for an endothermic reaction ($\Delta Hr > 0$) to proceed can be provided by the kinetic energy of the reactants (X^+ and O_2). In the ORS^3, the kinetic energy of the cell gas molecule (O_2) is only the energy of thermal motion at around room temperature, which is negligible compared to the kinetic energy of the reactant ion (X^+), which is controlled by the octopole bias potential. This is because the O_2, which is neutral, is not accelerated by the potential field in the cell. However, by setting the octopole bias to a negative voltage, reactant ions are accelerated, gaining kinetic energy before collision (reaction). In this case, the maximum energy available for the reaction is defined as center-of-mass collision energy, E_{cm}, as shown below.

$$E_{cm} = m_g / (m_g + m_i) E_i$$

Where m_g and m_i are the masses of the cell gas molecule (O_2) and the ion (X^+), respectively ($m_i = m_x$).

E_i is the ion kinetic energy in the laboratory frame of reference, described as:

$$E_i = V_p + (m_i/m_{Ar}) (5/2) kT_0 - V_{oct}$$

Where V_p is the plasma potential (ca. 2 eV). The second term ((m_i/m_{Ar}) (5/2) kT_0) is the energy that the ion acquired through free jet expansion in the interface, where m_{Ar} is the mass of argon atom; k is Boltzmann constant; and T_o is plasma gas temperature (ca. 5000 K).

The term V_{oct} is bias potential of the octopole, that is, the potential energy of a singly charged positive ion in the ORS^3. For example, when the octopole bias voltage is set to -10 V, V_{oct} is about -10 eV around the central axis of the octopole where ions travel. The sum of the first and second terms corresponds to the ion energy of X^+, which is conserved until X^+ collides with a gas molecule in the ORS^3.

If $E_{cm} > \Delta Hr$, the collision energy exceeds the energy required for the reaction. However, this does not necessarily mean that the reaction occurs whenever $E_{cm} > \Delta Hr$. For example, alkali metal ions do not react at an appreciable rate to form oxide ions in the ORS^3 even when $E_{cm} > \Delta Hr$. For the ions that produce oxides through endothermic reactions, reasonable ion intensity of XO^+ is obtained only when E_{cm} is at least a few times higher than ΔHr. When the octopole bias voltage is made more negative, the resulting increased collision energy, E_{cm}, promotes the endothermic reactions as shown in Figure 1. The intensities of CrO^+, FeO^+, MnO^+, NiO^+, CuO^+ and ZnO^+ all increase as the octopole bias is changed from -5 V to -20 V
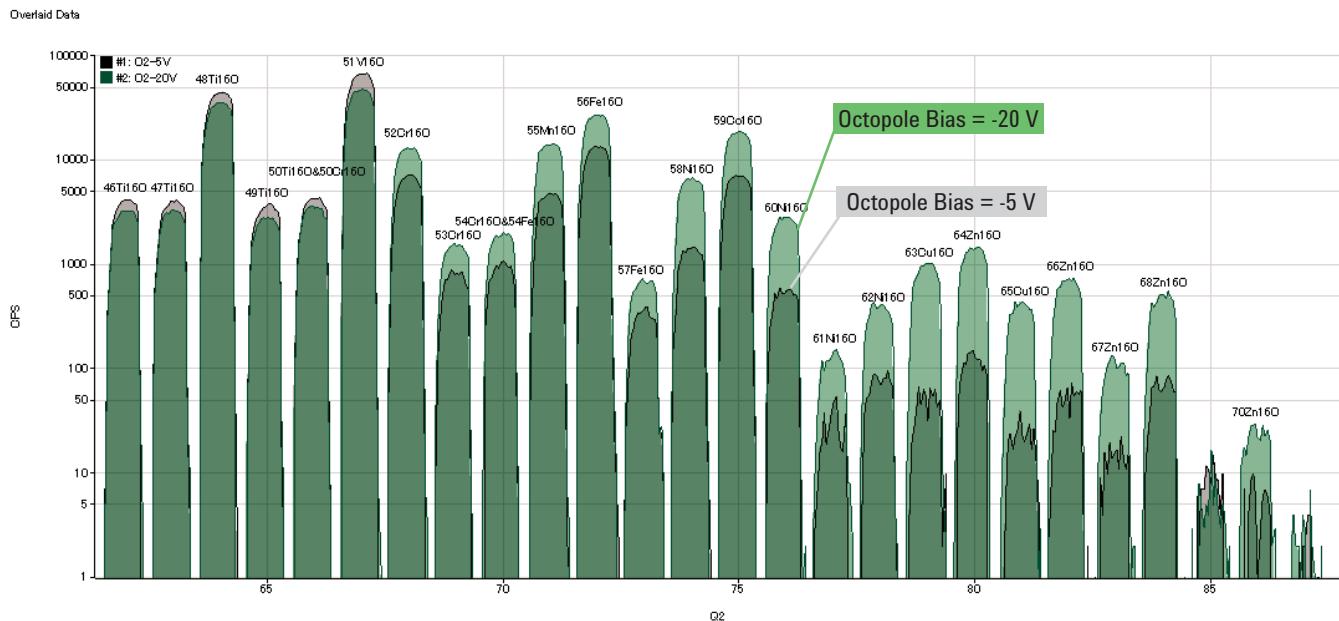

Figure 1. Mass spectra of a 1 ppb multielement standard solution measured in O_2 mode with the mass setting of Q1 and Q2 set to m_x and m_x +16 respectively. As a result, only the elemental oxides are present. Two spectra measured with Octopole Bias = -5 V and -20 V are overlaid with Q2 mass on the abscissa. About -5 V was found to be optimum for the oxide ions formed through exothermic O-atom transfer (TiO^+ and VO^+). At the more negative Octopole Bias of -20 V, the intensity of the other oxide ions (CrO^+, MnO^+, FeO^+, NiO^+, CuO^+ and ZnO^+), which are formed through endothermic reactions, was increased because of increased collision energy. Deflect lens voltage was optimized for each Octopole Bias voltage. The O_2 flow rate was set to 0.35 mL/min.

since these oxides are all produced though endothermic reactions as indicated in Table 1. The table shows the collision energy E_{cm} calculated with the typical octopole bias voltages of -5 V and -20 V, in comparison with ΔHr.

If $E_{cm} < \Delta Hr$, endothermic reactions will not proceed because the energy necessary for the reaction is not available. It should be noted however that oxide ions can also be formed though reaction channels other than O-atom transfer, for example via reaction between X^+ and a residual water molecule present in the cell.

Secondary O-atom Transfer

For the ions X^+ = Nb^+, Mo^+, Ta^+, W^+ and U^+, dioxide ions XO_2^+ are produced as well in O_2 mode. This is because secondary O-atom transfer occurs efficiently between their initial reaction products, XO^+, and a second molecular oxygen in the cell since the reaction enthalpy $\Delta Hr = D(O_2) - D(XO^+-O)$ is negative for XO^+ = NbO^+, MoO^+, TaO^+, WO^+ and UO^+ as shown in Table 1.

Initial reaction: $X^+ + O_2 \rightarrow XO^+ + O$, $\Delta Hr = D(O_2) - D(X^+-O)$

Secondary reaction: $XO^+ + O_2 \rightarrow XO_2^+ + O$, $\Delta Hr = D(O_2) - D(XO^+-O)$
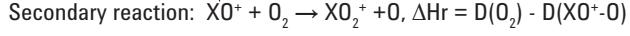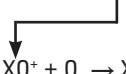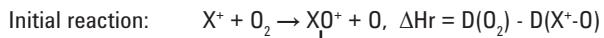
In this case, whether the dominant product is XO^+ or XO_2^+ depends mainly on the O_2 density in the ORS[3]. In general, the higher the O_2 flow rate, more XO_2^+ and less XO^+ are produced by these reactions.

It should be noted that there are also monoxide ions XO^+ produced in the ICP (plasma) and they may be polyatomic interferences. In that case, O_2 mode can be useful as they are converted to dioxide ions through the efficient exothermic O-atom transfer reactions.

Table 1. Enthalpy of reaction and collision energy for atomic and oxide ions in O_2 mode.

Reactant ion	Mass number (typical)	Product ion	Dissciation energy D(X⁺-O)	ΔHr enthalpy of reaction	Reactant ion energy (calc.)	Ecm [eV] center-of-mass collision energy	
X⁺	[u]	XO⁺	[eV]	[eV]	[eV]	V_{oct} = -5 eV	V_{oct} = -20 eV
Li⁺	7	NA	0.35	4.75	2.19	5.90	18.21
Be⁺	9	BeO⁺	3.76	1.34	2.24	5.65	17.36
B⁺	11	BO⁺	3.71	1.39	2.30	5.43	16.59
C⁺	12	CO⁺	8.35	-3.25	2.32	5.33	16.24
N⁺	14	NO⁺	11.00	-5.90	2.38	5.13	15.57
Na⁺	23	NA	0.56	4.54	2.62	4.43	13.16
Mg⁺	24	MgO⁺	1.53	3.57	2.65	4.37	12.94
Al⁺	27	AlO⁺	1.81	3.29	2.73	4.19	12.33
Si⁺	28	SiO⁺	4.99	0.11	2.75	4.14	12.14
Si⁺	28	SiO⁺	4.74	0.36	2.75	4.14	12.14
CO⁺	28	O_2^+	5.60	-1.95	2.75	4.14	12.14
P⁺	31	PO⁺	8.27	-3.17	2.84	3.98	11.60
S⁺	32	SO⁺	5.44	-0.34	2.86	3.93	11.43
Cl⁺	35	O_2^+	5.25	-0.91	2.94	3.79	10.96
Ar⁺	40	O_2^+	NA	-3.70	3.08	3.59	10.26
K⁺	39	NA	0.13	4.97	3.05	3.63	10.39
Ca⁺	40	CaO⁺	3.57	1.53	3.08	3.59	10.26
Sc⁺	45	ScO⁺	6.77	-1.67	3.21	3.41	9.65
Ti⁺	48	TiO⁺	6.73	-1.63	3.29	3.32	9.32
V⁺	51	VO⁺	5.95	-0.85	3.37	3.23	9.01
Cr⁺	52	CrO⁺	3.72	1.38	3.40	3.20	8.91
Mn⁺	55	MnO⁺	2.95	2.15	3.48	3.12	8.64
Fe⁺	56	FeO⁺	3.53	1.57	3.51	3.09	8.55
Co⁺	59	CoO⁺	3.32	1.78	3.59	3.02	8.30
Ni⁺	60	NiO⁺	2.74	2.36	3.62	3.00	8.21
Cu⁺	63	CuO⁺	1.62	3.48	3.70	2.93	7.98
Zn⁺	66	ZnO⁺	1.65	3.45	3.78	2.87	7.76
Ga⁺	71	NA	NA	NA	3.91	2.77	7.43
Ge⁺	72	NA	NA	NA	3.94	2.75	7.37
As⁺	75	AsO⁺	5.73	-0.63	4.02	2.70	7.18
Se⁺	78	SeO⁺	4.39	0.71	4.10	2.65	7.01
Br⁺	79	BrO⁺	4.03	1.14	4.13	2.63	6.96
Kr⁺	84	O_2^+	NA	-1.94	4.26	2.56	6.69
Rb⁺	85	NA	0.30	4.80	4.29	2.54	6.64
Sr⁺	88	SrO⁺	4.88	0.22	4.37	2.50	6.50
Y⁺	89	YO⁺	7.79	-2.69	4.40	2.49	6.45
Zr⁺	90	ZrO⁺	7.85	-2.75	4.43	2.47	6.41
Nb⁺	93	NbO⁺	9.03	-3.93	4.51	2.43	6.27
NbO⁺	109	NbO_2^+	5.73	-0.63			

Table 1. Continued

Reactant ion	Mass number (typical)	Product ion	Dissciation energy D(X⁺-O)	ΔHr enthalpy of reaction	Reactant ion energy (calc.)	Ecm [eV] center-of-mass collision energy	
X^+	[u]	XO^+	[eV]	[eV]	[eV]	$V_{oct} = -5\ eV$	$V_{oct} = -20\ eV$
Mo^+	95	MoO^+	4.27	0.83	4.56	2.41	6.19
Mo^+	95	MoO^+	4.93	0.17	4.56	2.41	6.19
MoO^+	111	MoO_2^+	5.56	-0.46			
Tc^+	99	NA	NA	NA	4.67	2.36	6.03
Ru^+	101	RuO^+	4.08	1.02	4.72	2.34	5.95
Rh^+	103	RhO^+	2.43	2.67	4.78	2.32	5.87
Pd^+	105	PdO^+	2.31	2.79	4.83	2.30	5.80
Sn^+	118	SnO^+	3.20	1.90	5.18	2.17	5.37
Sb^+	121	SbO^+	3.23	1.87	5.26	2.15	5.28
Te^+	125	TeO^+	4.13	0.97	5.37	2.11	5.17
I^+	127	IO^+	3.02	2.08	5.42	2.10	5.12
Xe^+	132	O_2^+	NA	-0.07	5.56	2.06	4.99
Cs^+	133	NA	0.61	4.49	5.58	2.05	4.96
Ba^+	137	BaO^+	5.60	-0.50	5.69	2.02	4.86
La^+	139	LaO^+	8.23	-3.13	5.75	2.01	4.82
La^+	139	LaO^+	8.73	-3.63	5.75	2.01	4.82
Ce^+	140	CeO^+	8.30	-3.20	5.77	2.00	4.80
Ce^+	140	CeO^+	8.80	-3.70	5.77	2.00	4.80
Pr^+	141	PrO^+	8.23	-3.13	5.80	2.00	4.77
Nd^+	146	NdO^+	7.76	-2.66	5.94	1.97	4.66
Sm^+	147	SmO^+	5.80	-0.70	5.96	1.96	4.64
Eu^+	153	EuO^+	4.00	1.10	6.12	1.92	4.52
Gd^+	157	GdO^+	7.47	-2.37	6.23	1.90	4.44
Tb^+	159	TbO^+	7.33	-2.23	6.29	1.89	4.40
Dy^+	163	DyO^+	6.11	-1.01	6.39	1.87	4.33
Ho^+	165	HoO^+	6.24	-1.14	6.45	1.86	4.30
Er^+	166	ErO^+	5.96	-0.86	6.47	1.85	4.28
Tm^+	169	TmO^+	4.92	0.18	6.56	1.84	4.23
Yb^+	172	YbO^+	3.87	1.23	6.64	1.83	4.18
Yb^+	172	YbO^+	4.33	0.77	6.64	1.83	4.18
Lu^+	175	LuO^+	5.34	-0.24	6.72	1.81	4.13
Hf^+	178	HfO^+	7.30	-2.20	6.80	1.80	4.08
Hf^+	178	HfO^+	7.53	-2.43	6.80	1.80	4.08
Ta^+	181	TaO^+	8.20	-3.10	6.88	1.78	4.04
TaO^+	197	TaO_2^+	6.08	-0.98			
W^+	182	WO^+	5.52	-0.42	6.91	1.78	4.02
WO^+	198	WO_2^+	5.73	-0.63			
Re^+	185	ReO_2^+	4.43	NA	6.99	1.77	3.98
Os^+	189	OsO^+	4.34	0.76	7.09	1.75	3.92
Ir^+	193	IrO^+	2.60	2.50	7.20	1.74	3.87

Table 1. Continued

Reactant ion	Mass number (typical)	Product ion	Dissciation energy D(X⁺-O)	ΔHr enthalpy of reaction	Reactant ion energy (calc.)	Ecm [eV] center-of-mass collision energy	
X^+	[u]	XO^+	[eV]	[eV]	[eV]	V_{oct}= -5 eV	V_{oct}= -20 eV
Pt^+	195	PtO^+	2.60	2.50	7.26	1.73	3.84
Au^+	197	NA	NA	NA	7.31	1.72	3.82
Hg^+	202	NA	NA	NA	7.44	1.70	3.75
Tl^+	205	NA	NA	NA	7.53	1.69	3.72
Pb^+	208	PbO^+	2.20	2.90	7.61	1.68	3.68
Bi^+	209	BiO^+	1.81	3.29	7.63	1.68	3.67
Th^+	232	ThO^+	8.97	-3.87	8.25	1.61	3.42
U^+	238	UO^+	7.99	-2.89	8.41	1.59	3.37
UO^+	254	UO_2^+	7.73	-2.63			
Np^+	239	NpO^+	8.01	-2.91	8.44	1.59	3.36
Pu^+	242	PuO^+	7.08	-1.98	8.52	1.58	3.33

1.   Ions undergoing exothermic reactions are shown in red. Shown in blue are the ions undergoing slightly endothermic reactions and producing oxide ions at reasonable intensity. Ions undergoing exothermic charge transfer reactions are shown shaded.
2.   Two different enthalpies of reaction for the same ion indicate that they are derived from two different literature sources.
3. $D(O_2)$ = 5.1 eV is assumed.
4.   The plasma potential of 2 eV and the plasma gas temperature of 5000 K are assumed approximations for the calculation of reactant ion energies.

Conclusions

The Agilent 8800 Triple Quadrupole ICP-MS, when operated in MS/MS mode has significantly expanded the applicability and improved the performance of oxygen reaction mode when compared to traditional single quadrupole ICP-MS. Two different strategies can now fully take advantage of reactions with oxygen in the cell. Mass shift mode can shift either the analyte mass or interferent mass by 16 amu, effectively separating them via the second quadrupole. Alternatively, the interfering ion can be neutralized via the transfer of an electron from oxygen. By using the first quadrupole to strictly control the ions entering the ORS[3] cell, previous limitations to the use of O_2, such as formation of new interferences and unwanted loss of analyte can be avoided.

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