Analysis of Environmental Samples, Routine or Specialized Using the Agilent QQQ-ICPMS

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Most Compact Instruments on the Market



Agilent 7800



Agilent 7900



Agilent 8800



Agilent 8900



Some of the Benefits of Single Quad ICP-MS

- Multi-elemental technique
- High sensitivity, ppq/ppt for most elements
- Short analysis time (~ 3 min to <60sec)
- Extremely linear with wide dynamic range
- Minimum number of interferences
- High Productivity



Most Important Performance Consideration for Environmental Analysis

- Sensitivity
- Interference Removal
- Matrix Tolerance
- Linear Dynamic Range

The QQQ-ICPMS allows for Interference Removal in more specialized applications





Interference removal; Transitioning from ICP-SQMS to ICP-MSMS

- Modes of Interference Removal:
 - Collision Mode
 He Gas
 Kinetic Energy Discrimination



tope	Principal Interfering Species (mixed matrix)
Sc	¹³ C ¹⁶ O ₂ , ¹² C ¹⁶ O ₂ H, ⁴⁴ CaH, ³² S ¹² CH, ³² S ¹³ C, ³³ S ¹² C
ï	³¹ P ¹⁶ O, ⁴⁶ CaH, ³⁵ Cl ¹² C, ³² S ¹⁴ NH, ³³ S ¹⁴ N
ï	³¹ P ¹⁸ O, ⁴⁸ CaH, ³⁵ Cl ¹⁴ N, ³⁷ Cl ¹² C, ³² S ¹⁶ OH, ³³ S ¹⁶ O
ï	34S16O, 32S18O, 35Cl14NH, 37Cl12CH
/	³⁵ Cl ¹⁶ O, ³⁷ Cl ¹⁴ N, ³⁴ S ¹⁶ OH
٦٢	³⁸ Ar ¹⁸ O, ⁴⁰ Ar ¹² C, ³⁵ Cl ¹⁸ OH, ³⁷ Cl ¹⁴ NH, ³⁴ S ¹⁸ O
)r	³⁶ Ar ¹⁶ OH, ⁴⁰ Ar ¹³ C, ³⁷ Cl ¹⁶ O, ³⁵ Cl ¹⁸ O, ⁴⁰ Ar ¹² CH
e	40Ar14N, 40Ca14N, 23Na31P
/In	³⁷ Cl ¹⁸ O, ²³ Na ³² S, ²³ Na ³¹ PH
e	⁴⁰ Ar ¹⁶ O, ⁴⁰ Ca ¹⁶ O
e	⁴⁰ Ar ¹⁶ OH, ⁴⁰ Ca ¹⁶ OH
li	40Ar18O, 40Ca18O, 23Na35Cl
ò	⁴⁰ Ar ¹⁸ OH, ⁴³ Ca ¹⁶ O, ²³ Na ³⁵ CIH
li	44Ca16O, 23Na37Cl
li	44Ca ¹⁶ OH, ³⁸ Ar ²³ Na, ²³ Na ³⁷ CIH
Cu	⁴⁰ Ar ²³ Na, ¹² C ¹⁶ O ³⁵ Cl, ¹² C ¹⁴ N ³⁷ Cl, ³¹ P ³² S, ³¹ P ¹⁶ O ₂
'n	³² S ¹⁶ O ₂ , ³² S ₂ , ³⁶ Ar ¹² C ¹⁶ O, ³⁸ Ar ¹² C ¹⁴ N, ⁴⁸ Ca ¹⁶ O
)u	³² S ¹⁶ O ₂ H, ³² S ₂ H, ¹⁴ N ¹⁶ O ³⁵ Cl, ⁴⁸ Ca ¹⁶ OH
ľn –	³⁴ S ¹⁶ O ₂ , ³² S ³⁴ S, ³³ S ₂ , ⁴⁸ Ca ¹⁸ O
'n	³² S ³⁴ SH, ³³ S ₂ H, ⁴⁸ Ca ¹⁸ OH, ¹⁴ N ¹⁸ O ³⁷ Cl, ¹⁸ O ₂ ³⁵ Cl
'n	³² S ¹⁸ O ₂ , ³⁴ S ₂
Sa	³² S ¹⁸ O ₂ H, ³⁴ S ₂ H, ¹⁸ O ₂ ³⁷ Cl
ľn	34S18O ₂ , 35Cl ₂
∋a	³⁴ S ¹⁸ O ₂ H, ³⁵ Cl ₂ H, ⁴⁰ Ar ³¹ P
3e	⁴⁰ Ar ³² S, ³⁵ Cl ³⁷ Cl, ⁴⁰ Ar ¹⁸ O ₂
Ge	40Ar ³² SH, ⁴⁰ Ar ³³ S, ³⁵ Cl ³⁷ ClH, ⁴⁰ Ar ¹⁸ O ₂ H
3e	40Ar34S, 37Cl ₂
s	40Ar34SH, 40Ar 35Cl, 40Ca 35Cl, 37Cl ₂ H
Se	40Ar 37Cl, 40Ca 37Cl
se	40Ar 38Ar
se	⁴⁰ Ar ₂ , ⁴⁰ Ca ₂ , ⁴⁰ Ar ⁴⁰ Ca, ³² S ₂ , ¹⁶ O, ³² S ¹⁶ O ₃



- Modes of Interference Removal Continued: Typically yielding the lowest DL
 - Reaction Mode

 $^{40}Ca^+ + {}^{40}Ar^+ + H_2 (g) \rightarrow {}^{40}Ca^+ + Ar + H_2^+$







The Problem with Single Q ICP-MS (BPMS)

In quadrupole ICP-MS (ICP-QMS), the analyzer comes after the collision/ reaction cell (with or without bandpass). There is **no 1amu mass filter** before the cell, which means there is practically no control on which ions enter the cell.



No control of what comes out

Reaction chemistry can be used to separate analytes from <u>known</u>, onmass interferences.

But <u>all other ions enter</u> the cell and can react to form new product ions

<u>Many different ions and</u> <u>product ions can</u> <u>contribute to the</u> <u>measured signal, giving</u> <u>errors</u>



The Answer: ICP-QQQ using MS/MS Mode

With Triple Quadrupole ICP-MS (ICP-QQQ) there is an additional mass filter before the reaction cell, controlling which ions enter and react in the cell



ICP-MSMS; Unsurpassed Interference Removal Capabilities

Plasma-source mass spectrometer

- High ionization efficiency
- Full-size quad before reaction cell
 - Unit mass resolution (MS/MS)
- Octopole Reaction System (ORS)
 - High transmission efficiency cell
- 5-stage vacuum system
- Full-size quad after reaction cell
- High speed 11-order detector
 - Wide dynamic range
 - Fast acquisition for nano





Operational Modes

Single Quad	 Q1 opens allowing all ions into ORS³
Single Quad with Band Pass Filter	 Q1 allows a range of ^m/_z into ORS³
MS/MS – On Mass	 Both Q1 and Q2 set to same mass
MS/MS – Mass Shift	 Q1 and Q2 set to different masses



Example: Mass-Shift Mode by **ICP-MSMS** Selenium Analysis by Mass-Shift with O₂ Reaction Gas

Same reaction with O₂ cell gas for Se on 8900 ICP-QQQ with MS/MS:

⁸⁰Se⁺ + O_{2 (g)} \rightarrow ⁸⁰Se¹⁶O⁺ (*m*/*z* 96) ⁴⁰Ar₂⁺, Gd⁺⁺, Dy⁺⁺ + O₂ \rightarrow no reaction

In MS/MS, Q1 rejects any ions (Zr⁺, Mo⁺, Ru⁺) that could overlap SeO⁺ product ion at mass 96



Allows measurement of SeO⁺ at product ion mass, after removal of original Ar_2^+/REE^{++} interference, and existing ions at SeO⁺ product ion mass



The Determination of 31P+ as P+O, Q1 @ 1u res



Contamination?



Accuracy of P+O Analysis with Q1 @ 1u and 2u Resolution ¹⁵N¹⁶O⁺

 $\mathbf{0}_2$

14N¹⁷O⁺

Q2(m/z=47)

P+O

13C18O16 O+

R =	.u∓ 2u		1	ર = 1 u		
1s IT		1s IT	31 ->	47 X [02]	
Sample Name		Sample Name	Conc. [ppb]	CPS	3SD [ppb]	
UPW		UP 211	0.00	1,089		
2PPB P		2PP 28 P	2.14	7,395		
10PPB P		10PF 2B P	10.07	30,762		
25PPB P		25PF3861P	24.96	74,679		
UPW LOD		UPW280D	0.01	1,109	0.03	
100PPM SI LOD		100P P,095,626 D	1.5	5,449	0.09	
10% CH3COOH LO	D	% CH32201016 LOD	3.1	10,217	0.06	

Q1(01h(12+3+30-32)



Ti Analysis; MSMS with Unit Mass Resolution

Product lon Scan: Setting Q1 on a single mass and scanning Q2 Precursor lon Scan: Scanning Q1 and setting Q2 on a single mass





Ti Analysis; ICP-MS Vs. ICP-MSMS





8900 – Ti analysis under MS/MS



MS/MS capability using fixed mass Q1/Q2 scanning (Neutral Gain Scan) shows true isotopic pattern under mass shift ammonia



Figure 2. Neutral gain scan for two Ti \rightarrow Ti cluster ion transitions: For TiNH₃(NH₃)₄ cluster ions, Q2 = Q1+ 84 amu, and for Ti(NH₃)₆ cluster ions, Q2 = Q1+102 amu. The preservation of the natural Ti isotope abundance pattern (⁴⁶Ti⁺, ⁴⁷Ti⁺, ⁴⁸Ti⁺, ⁴⁹Ti⁺ and ⁵⁰Ti⁺) can be seen, confirming that MS/MS mode provides complete control over the complex Ti-NH, reaction chemistry.



8900 – Ti analysis under Bandpass mode



When using restricted bandpass mode for Q1 (2.1amu window) the reaction is not as controlled and other reaction by-products are formed – isotopic information is not preserved as unwanted side-reactions can still occur

MS/MS is essential for precise reaction control





BP Ti Neutral Gain Scan



Limited isotope Neutral Gain Scan for Ti on TQ

The isotopic pattern does not fit the true, expected isotopic template

Similar to 8900 under bandpass mode



the isotopic fingerprint of the molecular ions APPROXIMATES with the isotopic abundances of the five major titanium isotopes, atem/zcofon/47.coff8, 49pagrosc50//article/articleDetail.js p?id=828042&sk=&date=&%0A%09 %09%09&pageID=2



(Bunseki Kagaku Conference September 2016)

Agilent



Natural Abundance

Ti46-8.25% (Ca-0.004%) Ti47-7.44% Ti48-73.72% (Ca-0.187%) Ti49-5.41% Ti50-5.18% (V-0.25%, Cr-4.345%)

"It can be clearly seen that the isotopic fingerprint of the molecular ions APPROXIMATES with the isotopic abundances of the five major titanium isotopes at m/z 46, 47, 48, 49 and 50"

http://www.spectroscopyonline.com /spectroscopy/article/articleDetail.js p?id=828042&sk=&date=&%0A%09 %09%09&pageID=2



Isotope Analysis and Qualifying Ions

When using reaction chemistry, it is an absolute MUST to control the reaction cell chemistry.



Two Full Size Quads; Dealing with Peak Analysis of Trace Color High Ni Matrix

	Co Natural Abundance %		Ni Natural Abundance %	Interferences	
⁵⁹ Co	100	⁵⁸ Ni ⁶⁰ Ni	67.8 26.2	⁵⁸ NiH ⁺	-







Two Full-Size Quadrupole Mass Filters



	Abundance Sensitivity based on ¹³³ Cs ⁺	Mass 132	Mass 134
	Q1	5 x 10 ⁻⁷	1 x 10 ⁻⁷
	Q2	5 x 10 ⁻⁷	1 x 10 ⁻⁷
Theoretical	Q1 * Q2	2.5 x 10 ⁻¹³	1 x 10 ⁻¹⁴
	Guarantee	10 -10	10 ⁻¹⁰





Boron in Organic Solvent – Xylene SQ/BP mode 5.77 µg Kg⁻¹ B spike into pure xylene



Boron's main isotope is at 11amu if there are large amounts of carbon present the ¹²C peak can interfere with the neighbouring ¹¹B peak.

In extreme cases (as here) it can even spread to the ¹⁰B peak even under B.P. mode



Boron in Organic Solvent – Xylene MS/MS mode 5.77 µg Kg⁻¹ B spike into pure xylene





- ISO20899 is a new proposal for the measurement of Pu and Np in the environment
- Residual Pu & Np from leaks, disposal and bomb testing
- Natural Np formation from neutron capture in U deposits
- Np from Am decay used in smoke detectors
- Both difficult & suffer from U-based interferences





²³⁷Np – abundance sensitivity overlap from ²³⁸U in ICP-MS





$^{237}Np - ^{238}U$ overlap removed under MS/MS





²³⁷Np – ²³⁸U overlap removed under MS/MS



Use O2 reaction mode! $^{237}Np + O_2 \rightarrow ^{237}Np^{16}O_2$









	NMBU results			Certified results / *Literature results			*n		
	²³⁹ Pu, ng/kg	SD	²⁴⁰ Pu, ng/kg	SD	²³⁹ Pu, ng/kg	SD	²⁴⁰ Pu, ng/kg	SD	
IAEA 384	41	0.8	2.18	0.003	42	2	2	0.2	
NIST 4353a	5.0	0.50	0.30	0.020	*5.26	*0.060	*0.30	*0.010	19
NIST 4357a	2.1	0.10	0.56	0.050	*2.27	*0.070	*0.53	0.11	19
IAEA13 5	49	1.0	10.2	0.40	*54	*3	*11.2	*0.90	28
IAEA 315	15,0	0.30	3.11	0.070	*16	*2.0	*3.3	*0.60	2

Norwegian University of Life Sciences



Confirming Accuracy by Natural Abundance

What if there is a way of confirming monoisotopic elements by ICP-MS?

How about looking at the isotopic pattern that the metal oxide forms?

	10ppb	
89 -> 105 Y	367616	99.75%
89 -> 106 Y	152	0.04%
89 -> 107 Y	767	0.2%
141 -> 157 Pr	710690	99.76%
141 -> 158 Pr	266	0.04%
141 -> 159 Pr	1431	0.2%
159 -> 175 Tb	722870	99.76%
159 -> 176 Tb	310	0.04%
159 -> 177 Tb	1461	0.2%
165 -> 181 Ho	668866	99.75%
165 -> 182 Ho	323	0.05%
165 -> 183 Ho	1362	0.2%
169 -> 185 Tm	717574	99.74%
169 -> 186 Tm	424	0.06%
169 -> 187 Tm	1471	0.2%

¹⁶O-99.762%, ¹⁷O-0.038%, ¹⁸O-0.205%

MSMS O₂ – Confirming Accuracy by Natural Abundance





Unit mass resolution MSMS vs Bandpass - 8900



¹³⁶Ce-0.19%
¹³⁸Ce-0.25%
¹⁴⁰Ce-88.45%
¹⁴²Ce-11.11%



True MSMS vs Bandpass - Bandpass





True MSMS vs Bandpass - Bandpass





True MSMS vs Bandpass - 8900





True MSMS vs Bandpass - 8900





Single Quad ICP-MS with bandpass ICP-MS/MS with Unit Mass filter in or before the cell.

What do you want to analyze?



What elements enter the cell?



This excluding the polyatomics !

Resolution Before the Cell

What do you want to analyze?



What elements enter the cell?



True MS/MS with unit mass resolution before the cell... when you must have **Trusted Answers!**



Single Quad ICP-MS with bandpass filter in or before the cell.

Element of Interest	Isotopes entering the Cell
Ti-50, V-50, Cr-50	Sc-45, Ca-46, Ti-46, Ti-47, Ca-48, Ti-48, Ti-50, V-50, Cr-50, V-51, V-51, Cr-52, Cr-53, Cr-54, Fe-54 and
	Mn-55
V-51	Ca-46, Ti-46, Ti-47, Ca-48, Ti-48, Ti-49, V-51, Cr-52, Cr-52, Cr-53, Cr-54, Fe-54, Mn-55 and Fe-56
Cr-52	Ti-47, Ca-48, Ti-48, Ti-49, Ti-50, V-50, Cr-50, Cr-52, Cr-53, Cr-53, Cr-54, Fe-54, Mn-55, Fe-56 and Fe-57
Cr-53	Ca-48, Ti-48, Ti-49, Ti-50, V-50, Cr-50, V-51, Cr-53, Cr-54, Fe-54, Cr-54, Fe-54, Mn-55, Fe-56, Fe-57, Fe-58 and Ni-58
Cr-54, Fe-54	Ti-49, Ti-50, V-50, Cr-50, V-51, Cr-52, Cr-54, Fe-54, Mn-55, Mn-55, Fe-56, Fe-57, Fe-58, Ni-58 and Co-59
Mn-55	Ti-50, V-50, Cr-50, V-51, Cr-52, Cr-53, Mn-55, Fe-56, Fe-56, Fe-57, Fe-58, Ni-58, Co-59 and Ni-60
Fe-56	V-51, Cr-52, Cr-53, Cr-54, Fe-54, Fe-56, Fe-57, Fe-57, Fe-58, Ni-58, Co-59, Ni-60 and Ni-61
Fe-57	Cr-52, Cr-53, Cr-54, Fe-54, Mn-55, Fe-57, Fe-58, Ni-58, Fe-58, Ni-58, Co-59, Ni-60, Ni-61 and Ni-62
Fe-58, Ni-58	Cr-53, Cr-54, Fe-54, Mn-55, Fe-56, Fe-58, Ni-58, Co-59, Co-59, Ni-60, Ni-61, Ni-62 and Cu-63
Co-59	Cr-54, Fe-54, Mn-55, Fe-56, Fe-57, Co-59, Ni-60, Ni-60, Ni-61, Ni-62, Cu-63, Ni-64 and Zn-64
Ni-60	Mn-55, Fe-56, Fe-57, Fe-58, Ni-58, Ni-60, Ni-61, Ni-61, Ni-62, Cu-63, Ni-64, Zn-64 and Cu-65
Ni-61	Fe-56, Fe-57, Fe-58, Ni-58, Co-59, Ni-61, Ni-62, Ni-62, Cu-63, Ni-64, Zn-64, Cu-65 and Zn-66
Ni-62	Fe-57, Fe-58, Ni-58, Co-59, Ni-60, Ni-62, Cu-63, Cu-63, Ni-64, Zn-64, Cu-65, Zn-66 and Zn-67
Cu-63	Fe-58, Ni-58, Co-59, Ni-60, Ni-61, Cu-63, Ni-64, Zn-64, Ni-64, Zn-64, Cu-65, Zn-66, Zn-67 and Zn-68
Ni-64, Zn-64	Co-59, Ni-60, Ni-61, Ni-62, Ni-64, Zn-64, Cu-65, Cu-65, Zn-66, Zn-67, Zn-68 and Ga-69
Cu-65	Ni-60, Ni-61, Ni-62, Cu-63, Cu-65, Zn-66, Zn-66, Zn-67, Zn-68, Ga-69, Zn-70 and Ge-70
Zn-66	Ni-61, Ni-62, Cu-63, Ni-64, Zn-64, Zn-66, Zn-67, Zn-67, Zn-68, Ga-69, Zn-70, Ge-70 and Ga-71
Zn-67	Ni-62, Cu-63, Ni-64, Zn-64, Cu-65, Zn-67, Zn-68, Zn-68, Ga-69, Zn-70, Ge-70, Ga-71 and Ge-72
Zn-68	Cu-63, Ni-64, Zn-64, Cu-65, Zn-66, Zn-68, Ga-69, Ga-69, Zn-70, Ge-70, Ga-71, Ge-72 and Ge-73
Ga-69	Ni-64, Zn-64, Cu-65, Zn-66, Zn-67, Ga-69, Zn-70, Ge-70, Zn-70, Ge-70, Ga-71, Ge-72, Ge-73, Ge-74 and
	Se-74
Zn-70, Ge-70	Cu-65, Zn-66, Zn-67, Zn-68, Zn-70, Ge-70, Ga-71, Ga-71, Ge-72, Ge-73, Ge-74, Se-74 and As-75



ICP-MS/MS with Unit Mass Resolution Before the Cell

1

Element of Interest	Isotopes entering the Cell
Ti-50, V-50, Cr-50	Ti-50, V-50, Cr-50
V-51	V-51
Cr-52	Cr-52
Cr-53	Cr-53
Cr-54, Fe-54	Cr-54, Fe-54
Mn-55	Mn-55
Fe-56	Fe-56
Fe-57	Fe-57
Fe-58, Ni-58	Fe-58, Ni-58
Co-59	Co-59
Ni-60	Ni-60
Ni-61	Ni-61
Ni-62	Ni-62
Cu-63	Cu-63
Ni-64, Zn-64	Ni-64, Zn-64
Cu-65	Cu-65
Zn-66	Zn-66
Zn-67	Zn-67
Zn-68	Zn-68
Ga-69	Ga-69
Zn-70, Ge-70	Zn-70, Ge-70



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