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ICP-TANDEM MASS SPECTROMETRY (ICP-MS/MS)

for the determination of (ULTRA)TRACES of CHALLENGING elements in COMPLEX matrices

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INTRODUCTION: ICP-MS/MS

APPLICATIONS:

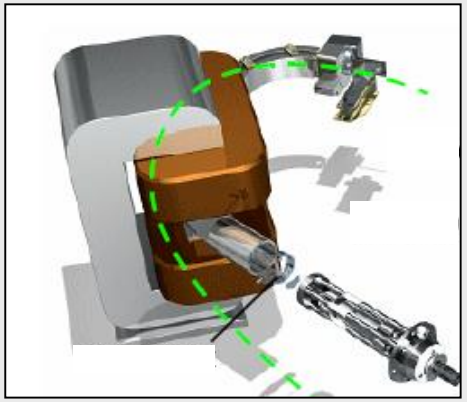
S in organic matrix

Al, Co, Cr, Mn, Ni, Ti, V (biofluids)

CONCLUSIONS

ICP-MS: dealing with SPECTRAL INTERFERENCES

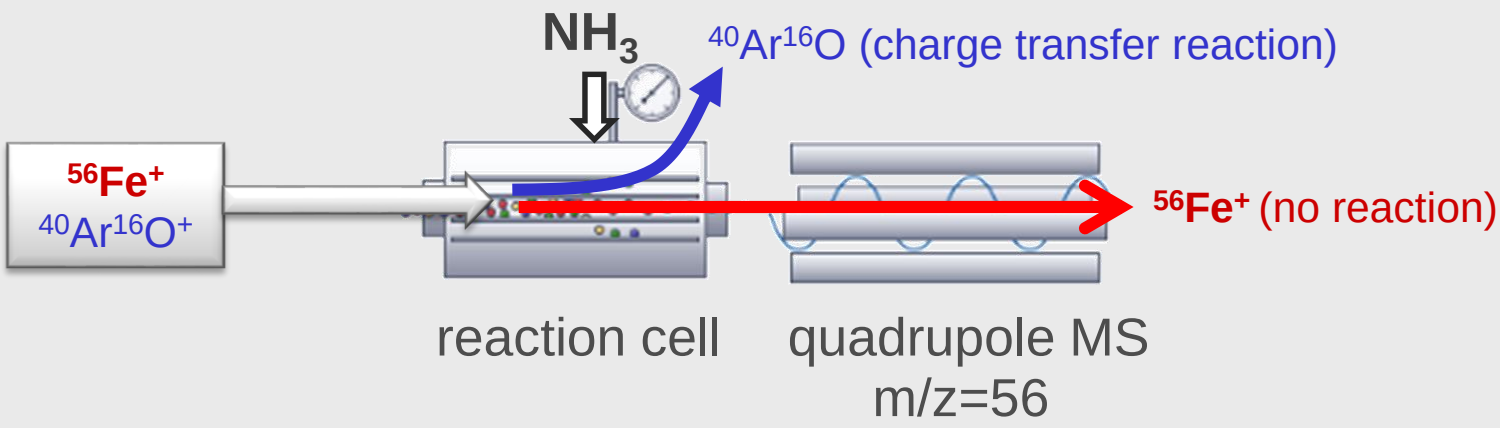
Sector field ICP-MS



Quadrupole ICP-MS with collision/reaction cell

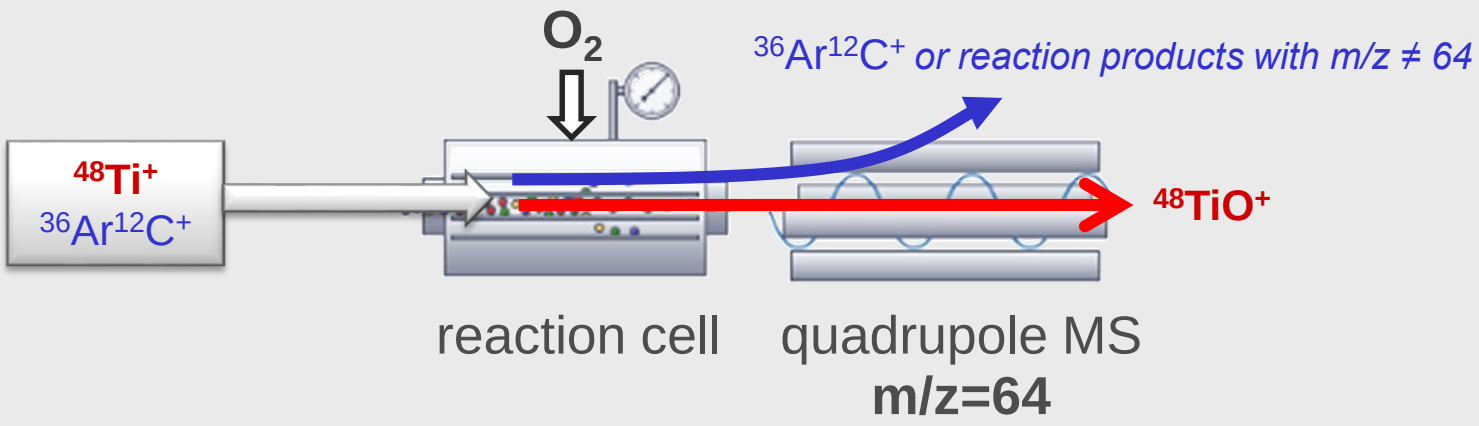
REDUCTION OF SPECTRAL OVERLAP: chemical resolution

1. Removal of interfering ions ➔ ON-MASS measurement



REDUCTION OF SPECTRAL OVERLAP: chemical resolution

2. Conversion of analyte ions ➔ MASS-SHIFT



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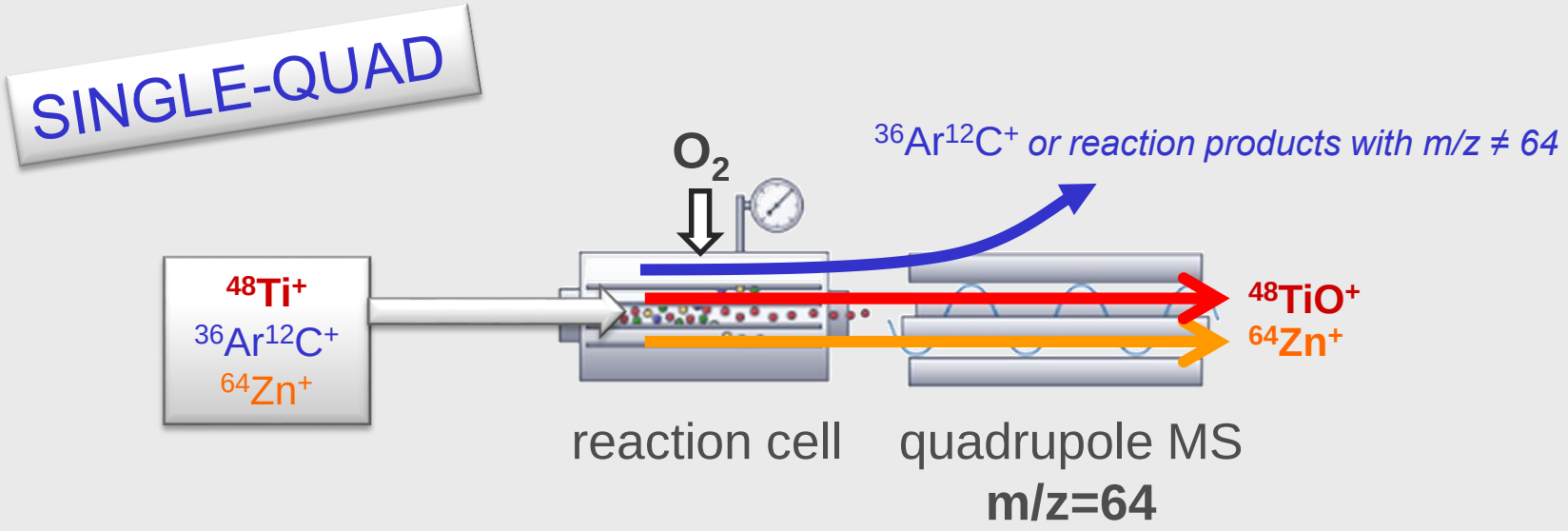
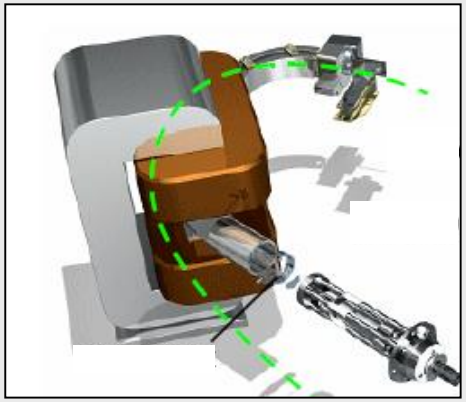
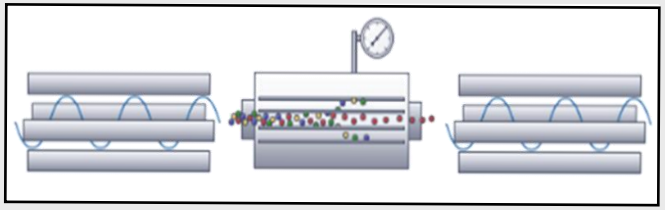


ICP-MS: dealing with SPECTRAL INTERFERENCES

Sector field ICP-MS



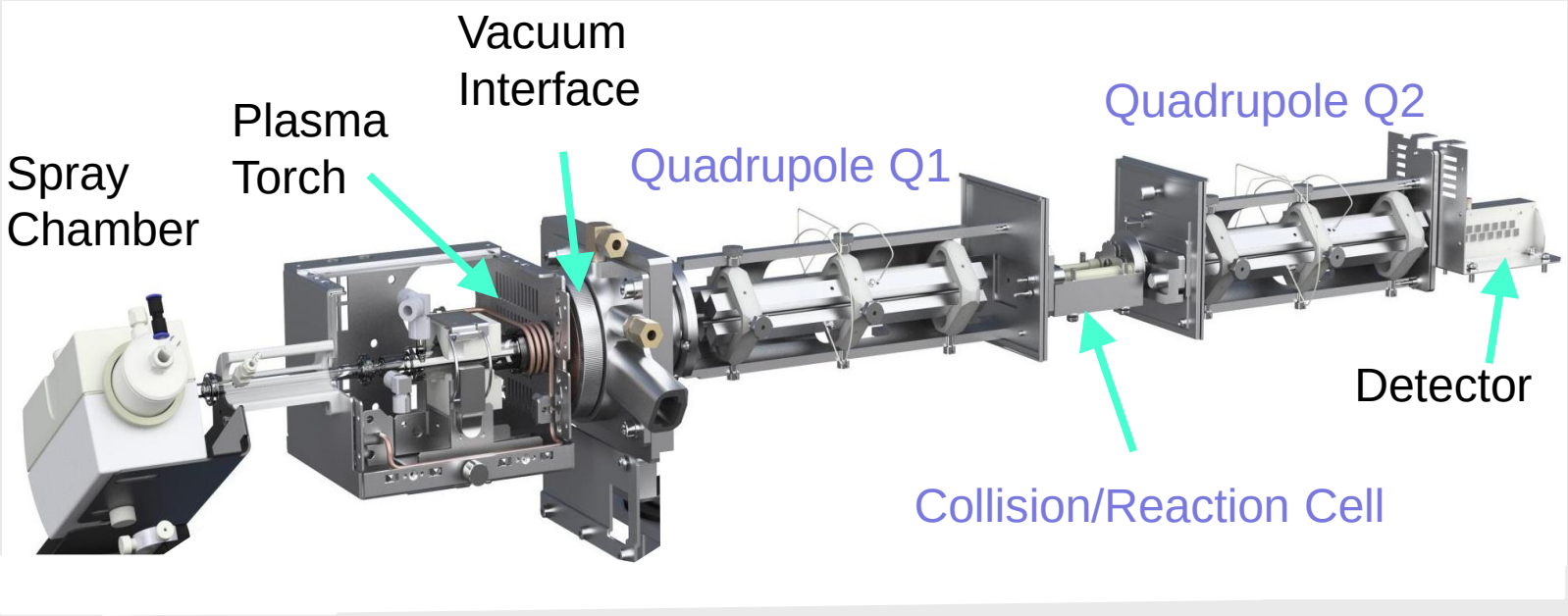
Quadrupole ICP-MS with collision/reaction cell and an extra quadrupole



ICP-MS/MS
(ICP-QQQ)

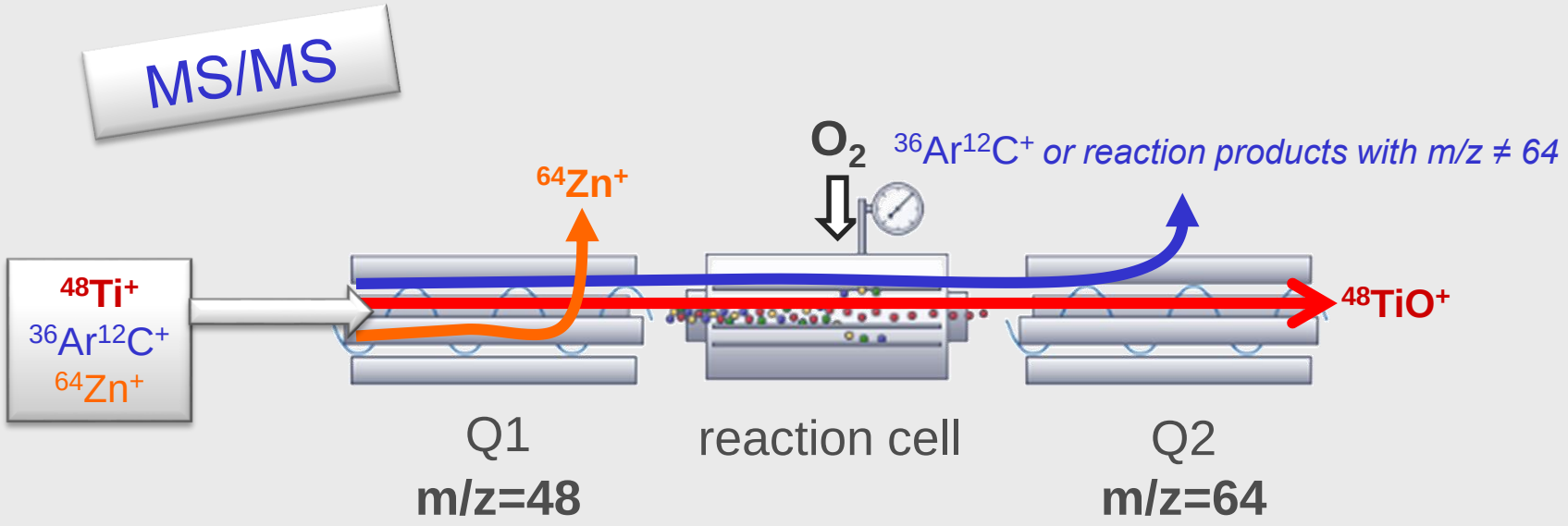
Quadrupole ICP-MS with collision/reaction cell

ICP- MS/MS (ICP-QQQ)



REDUCTION OF SPECTRAL OVERLAP: chemical resolution

2. Conversion of analyte ions ➔ MASS-SHIFT



METHOD DEVELOPMENT: Selection of REACTION GAS

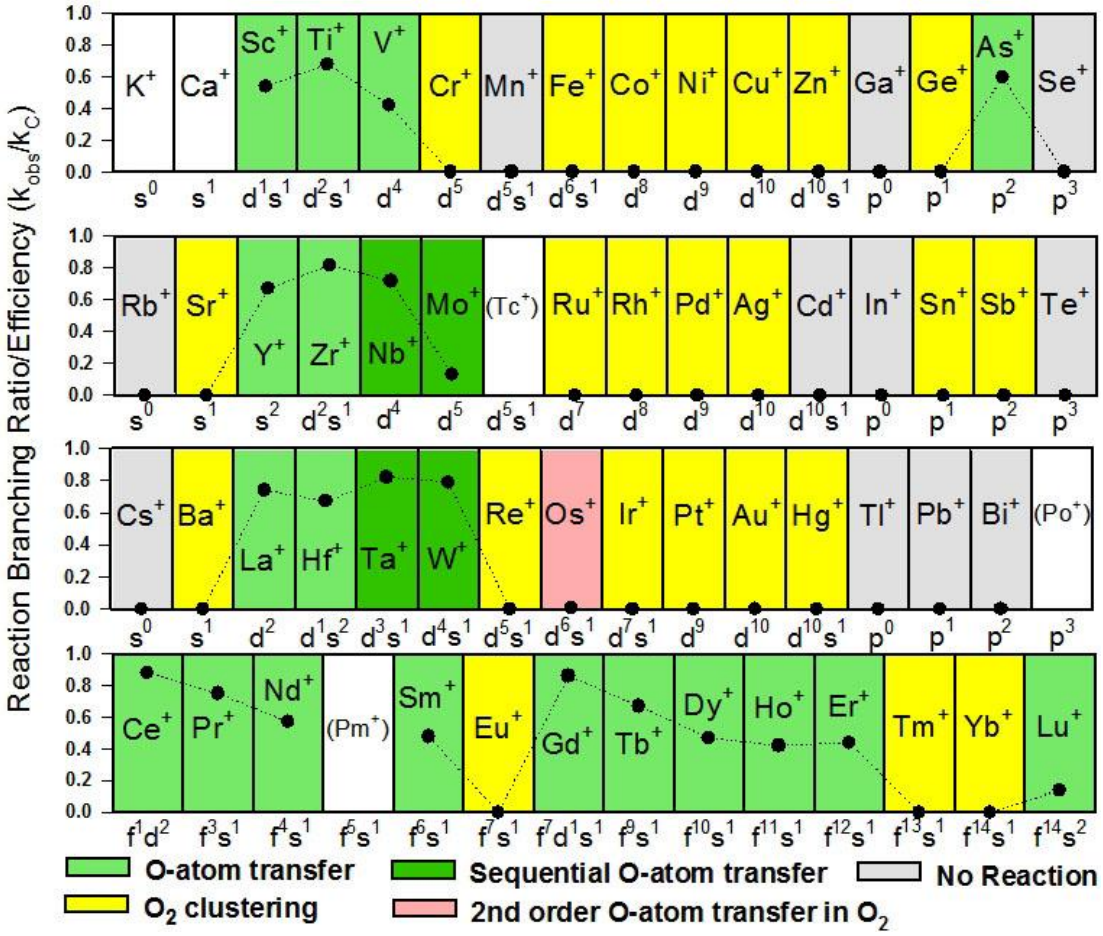
Most suited reaction gas:

Selective reaction with analyte ions ór interfering ions

→ Based on:

- Kinetics database:

  http://www.chem.yorku.ca/profs/bohme/research/selection_table.html


Reaction Branching Ratio/Efficiency (k_{obs}/k_C)
1.0
0.8
0.6
0.4
0.2
0.0
K+ Ca+ Sc+ Ti+ V+ Cr+ Mn+ Fe+ Co+ Ni+ Cu+ Zn+ Ga+ Ge+ As+ Se+
s0 s1 d1s1 d2s1 d4 d5 d5s1 d6s1 d8 d9 d10 d10s1 p0 p1 p2 p3
Rb+ Sr+ Y+ Zr+ Nb+ Mo+ (Tc+) Ru+ Rh+ Pd+ Ag+ Cd+ In+ Sn+ Sb+ Te+
s0 s1 s2 d2s1 d4 d5 d5s1 d7 d8 d9 d10 d10s1 p0 p1 p2 p3
Cs+ Ba+ La+ Hf+ Ta+ W+ Re+ Os+ Ir+ Pt+ Au+ Hg+ Tl+ Pb+ Bi+ (Po+)
s0 s1 d2 d1s2 d3s1 d4s1 d5s1 d6s1 d7s1 d9 d10 d10s1 p0 p1 p2 p3
Ce+ Pr+ Nd+ (Pm+) Sm+ Eu+ Gd+ Tb+ Dy+ Ho+ Er+ Tm+ Yb+ Lu+
f1d2 f3s1 f4s1 f5s1 f6s1 f7s1 f7d1s1 f9s1 f10s1 f11s1 f12s1 f13s1 f14s1 f14s2
O-atom transfer
Sequential O-atom transfer
No Reaction
O2 clustering
2nd order O-atom transfer in O2

SELECTION of REACTION GAS

Most suited reaction gas:

Selective reaction with analyte ions ór interfering ions

→ Based on:

- Kinetics database:

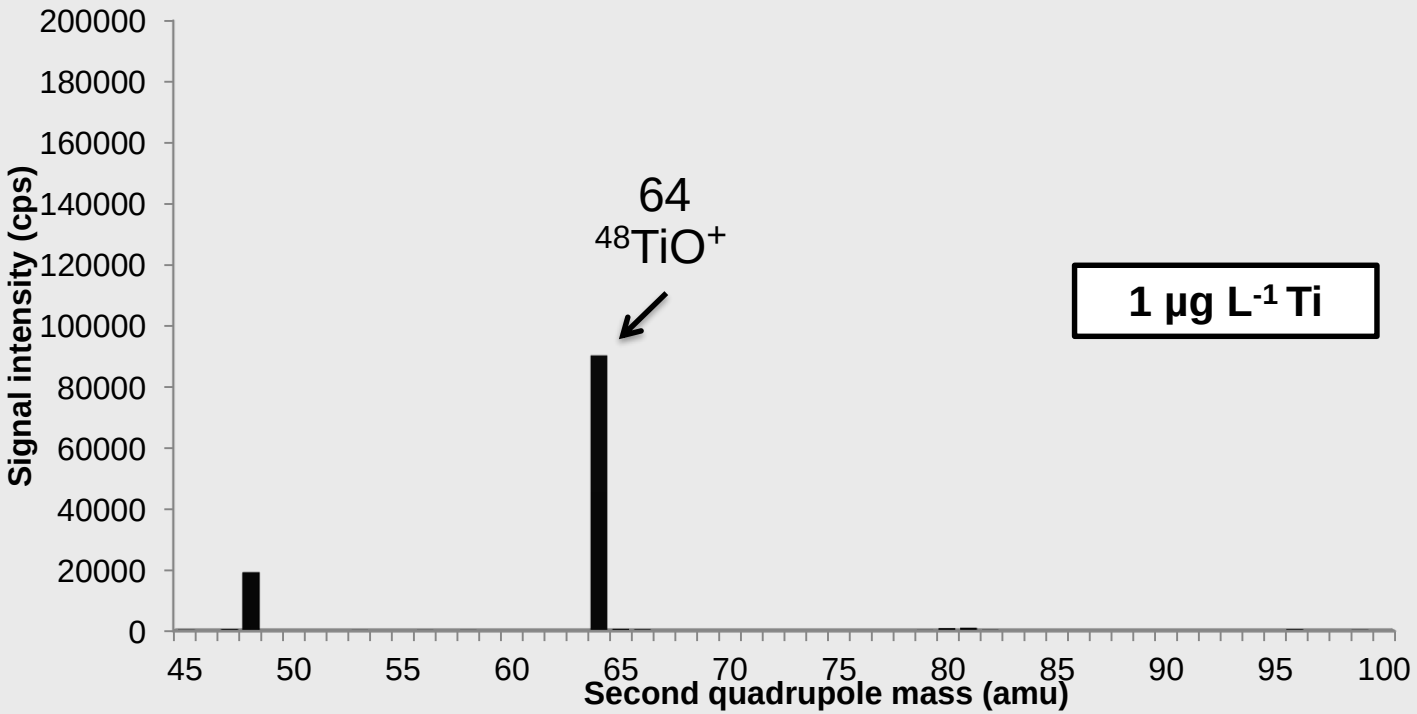
  http://www.chem.yorku.ca/profs/bohme/research/selection_table.html

- **ICP-MS/MS – Product ion scans:**

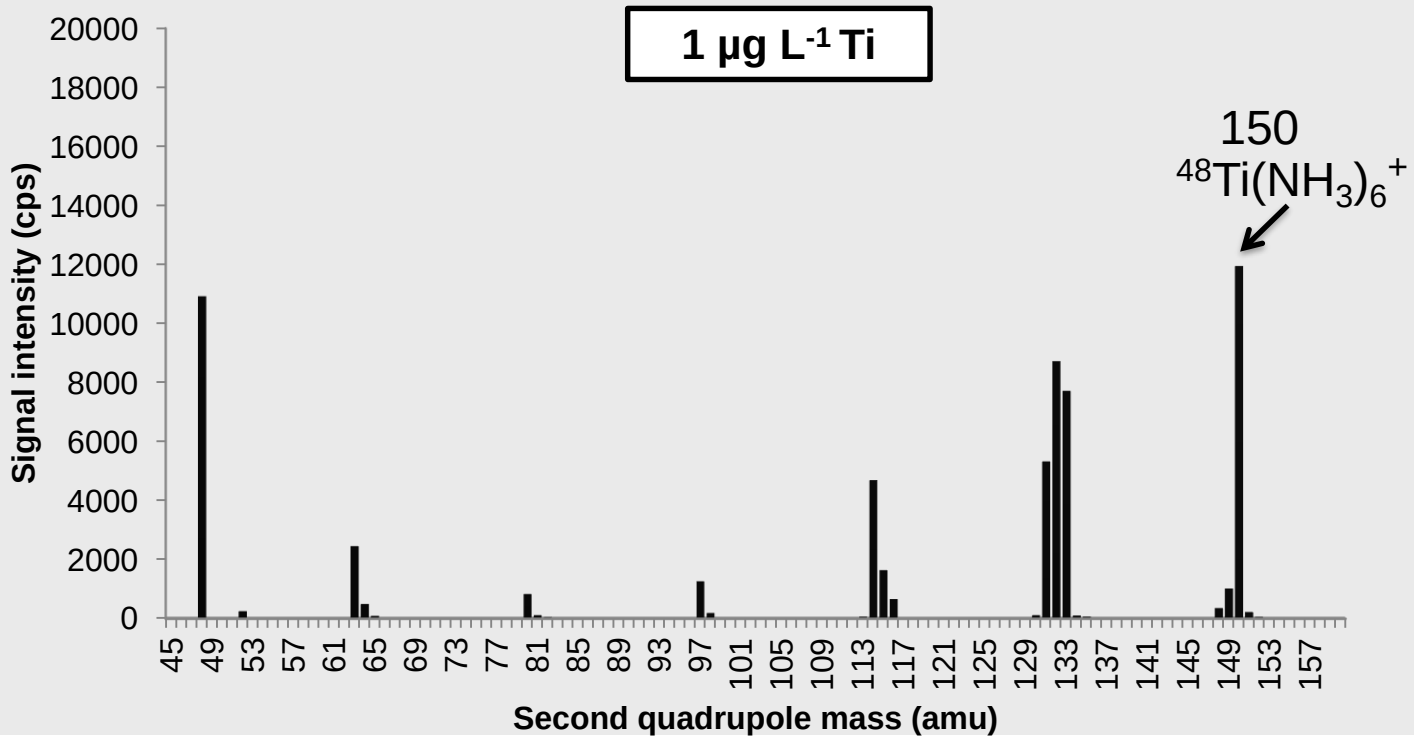
  Q1: m/z fixed (analyte ion)

  Q2: scan over mass range

PRODUCT ION SCAN - O_2 - Q1: m/z=48



PRODUCT ION SCAN – NH_3 - Q1: m/z=48



GENERAL CONCLUSION

ICP-MS/MS: double mass selection

➔ Enhanced control over reactions in the reaction cell

→ Increasing use of “reactive” gases

→ Systematic study of reactions in the cell

→ Very efficient approach to deal with spectral interferences

Determination of S in an organic matrix

Balcaen et al., JAAS, 28, 33-39, 2013

S: spectral interferences

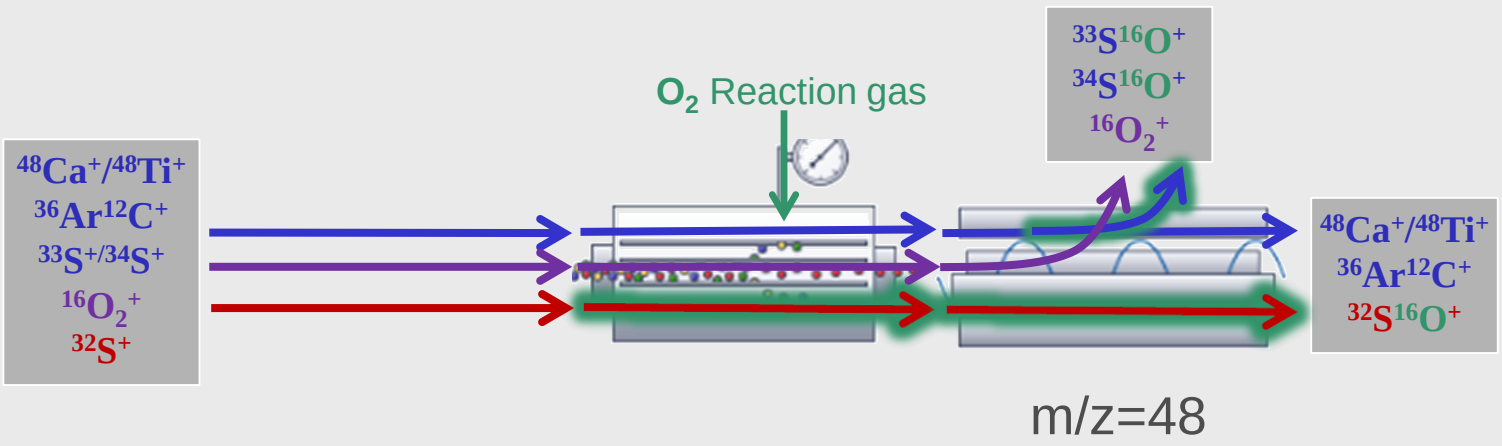
Analyte	Abundance (%)	Ions causing spectral interference
$^{32}S^+$	95.04	$^{16}O^{16}O^+$, $^{14}N^{18}O^+$, $^{15}N^{16}O^1H^+$
$^{33}S^+$	0.75	$^{32}S^1H^+$, $^{16}O^{16}O^1H^+$, $^{16}O^{17}O^+$, $^{15}N^{18}O^+$, $^{14}N^{18}O^1H^+$
$^{34}S^+$	4.20	$^{33}S^1H^+$, $^{16}O^{18}O^+$

$S^+ \rightarrow SO^+$ with O_2 as a reaction gas

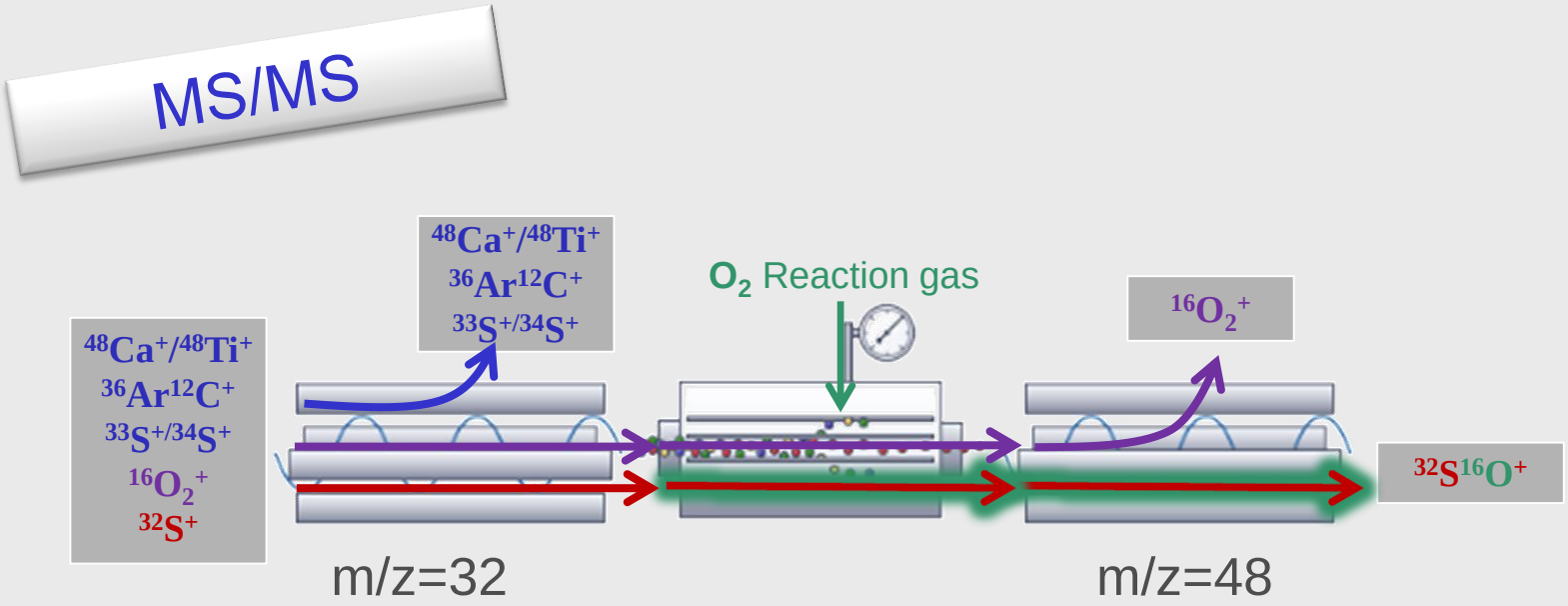
Analyte	Abundance (%)	Ions causing spectral interference
$^{32}S^{16}O^+$	95.04	$^{48}Ti^+$, $^{48}Ca^+$, $^{36}Ar^{12}C^+$
$^{33}S^{16}O^+$	0.75	$^{49}Ti^+$, $^{32}S^{17}O^+$
$^{34}S^{16}O^+$	4.20	$^{50}Ti^+$, $^{50}Cr^+$, $^{50}V^+$, $^{38}Ar^{12}C^+$, $^{36}Ar^{14}N^+$, $^{32}S^{18}O^+$, $^{33}S^{17}O^+$

S: spectral interferences

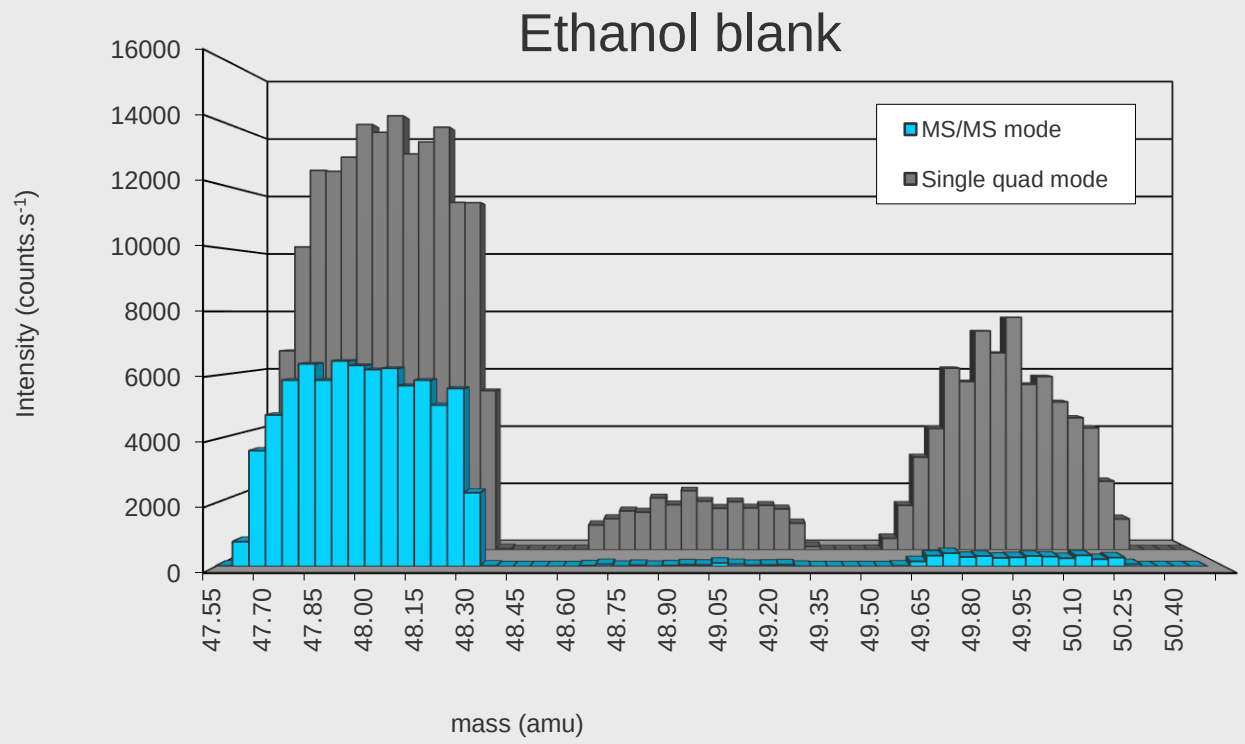
SINGLE-QUAD



S: spectral interferences



SO^+: comparison SQ and MS/MS mode



SO^+: comparison SQ and MS/MS mode

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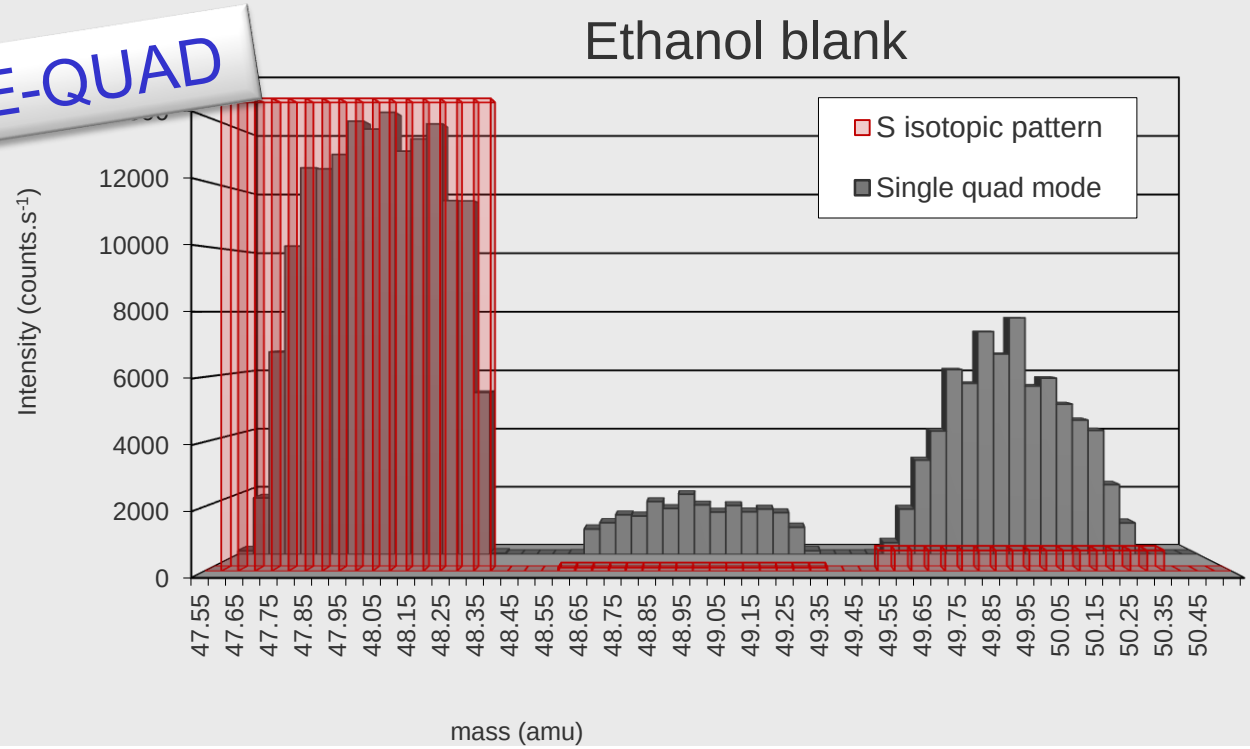

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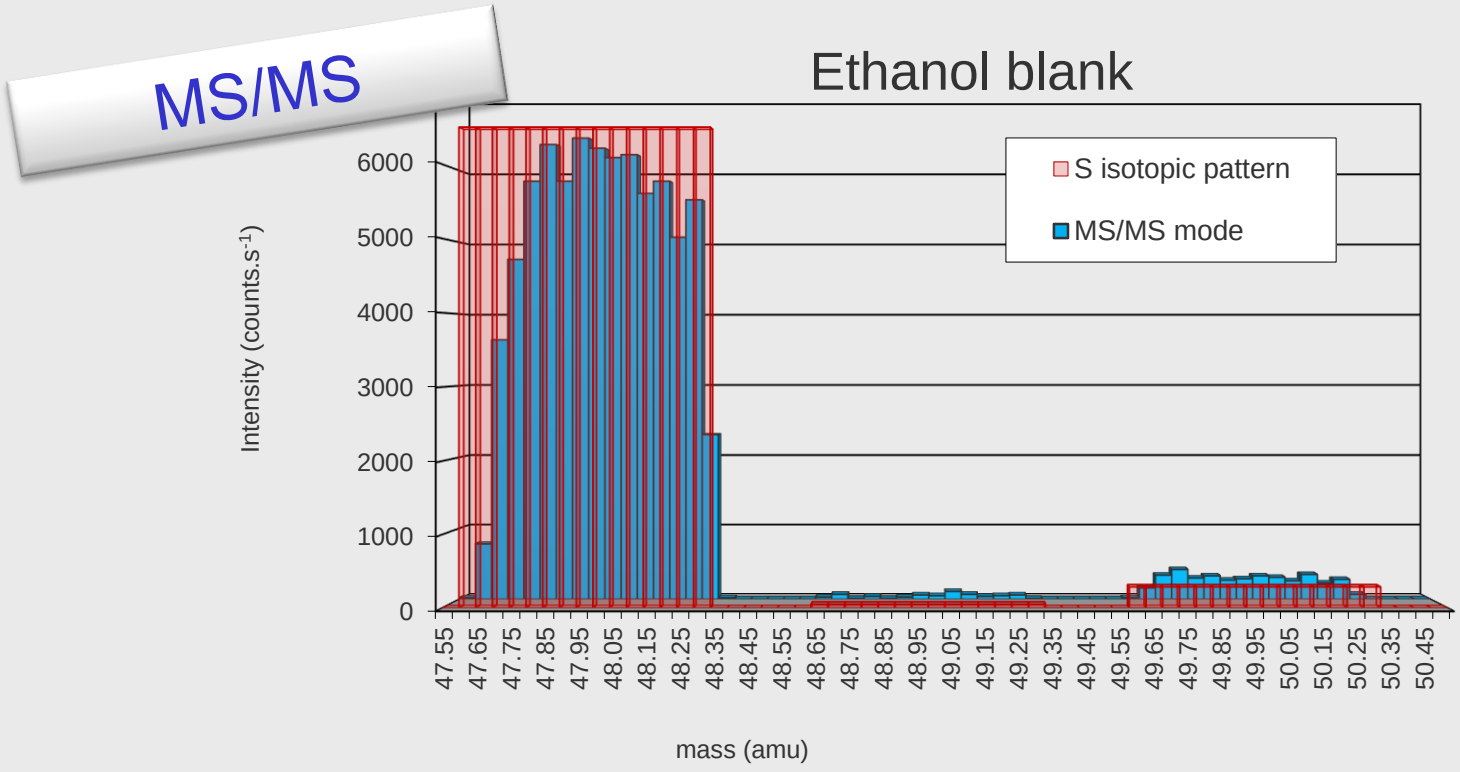
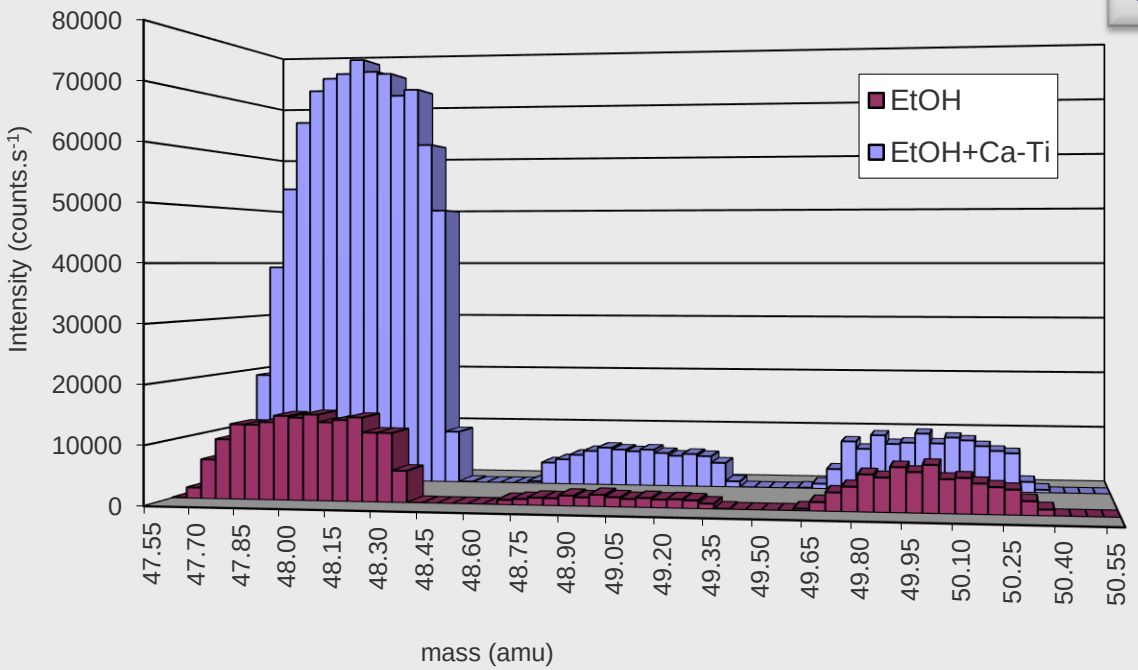


SO^+: comparison SQ and MS/MS mode

Ethanol blank + 50 µg/L Ti & Ca

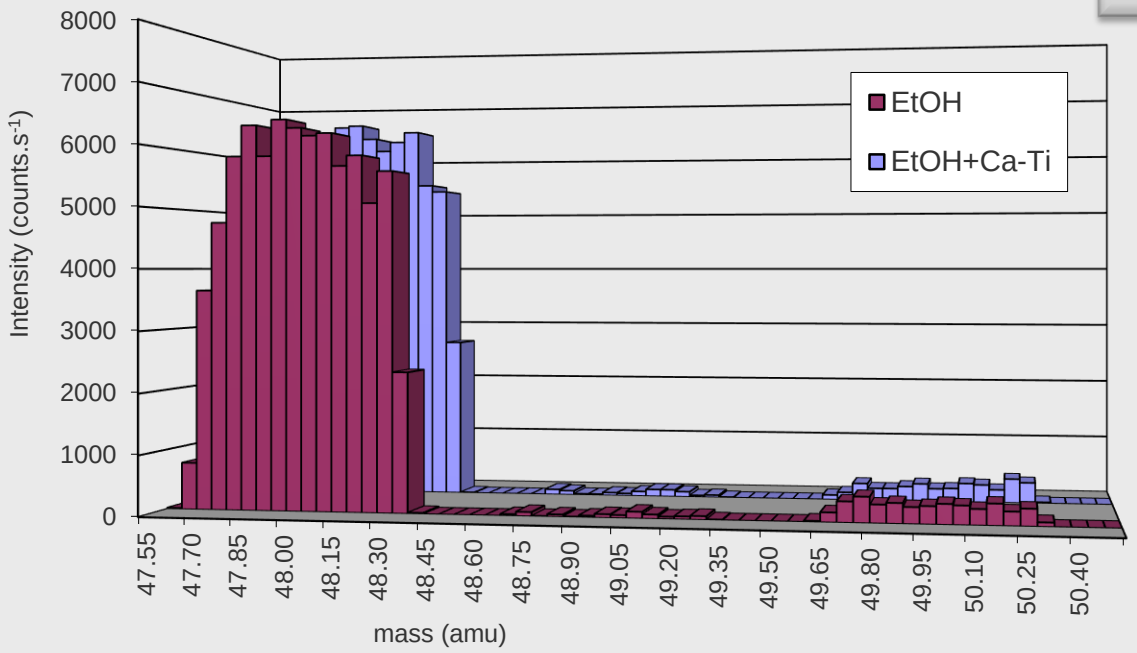
SINGLE-QUAD



SO^+: comparison SQ and MS/MS mode

Ethanol blank + 50 µg/L Ti & Ca

MS/MS



S in an ORGANIC MATRIX: Conclusion

- Accurate determination of ^{32}S, ^{33}S and ^{34}S possible, independent of the matrix
- LoD in the order of 1-5 µg/L (similar to sector field ICP-MS)

Multi-element

Determination of Al, Co, Cr, Mn, Ni, Ti, V in biofluids

Bolea-Fernandez et al., Anal. Chem., 2014, 86, 7969-7977

Al, Co, Cr, Mn, Ni, Ti, V IN BIOFLUIDS

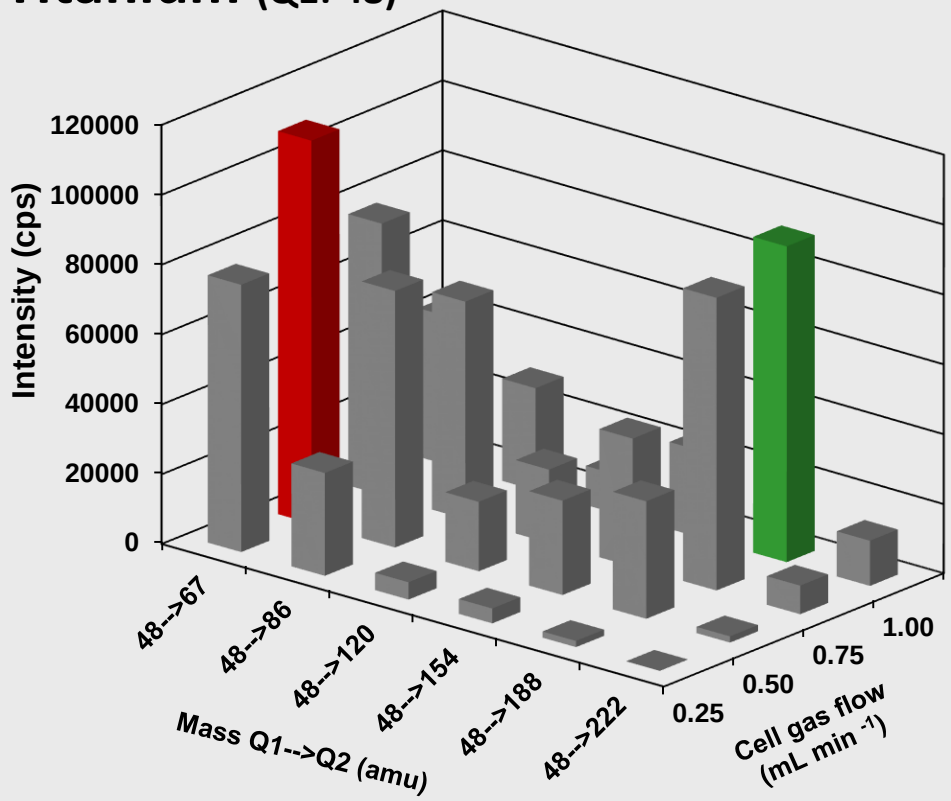
- Medically relevant metals (e.g., disease, implants,…)
- Often low concentration

➔ Sensitive, multi-element analysis of biofluids (serum, urine,…)
➔ Complex matrix → Spectral overlap !

Multi-element method with ICP-MS/MS ?

➔ Reaction gas? Main reaction product ions ?
➔ Product ion scans

Titanium (Q1: 48)

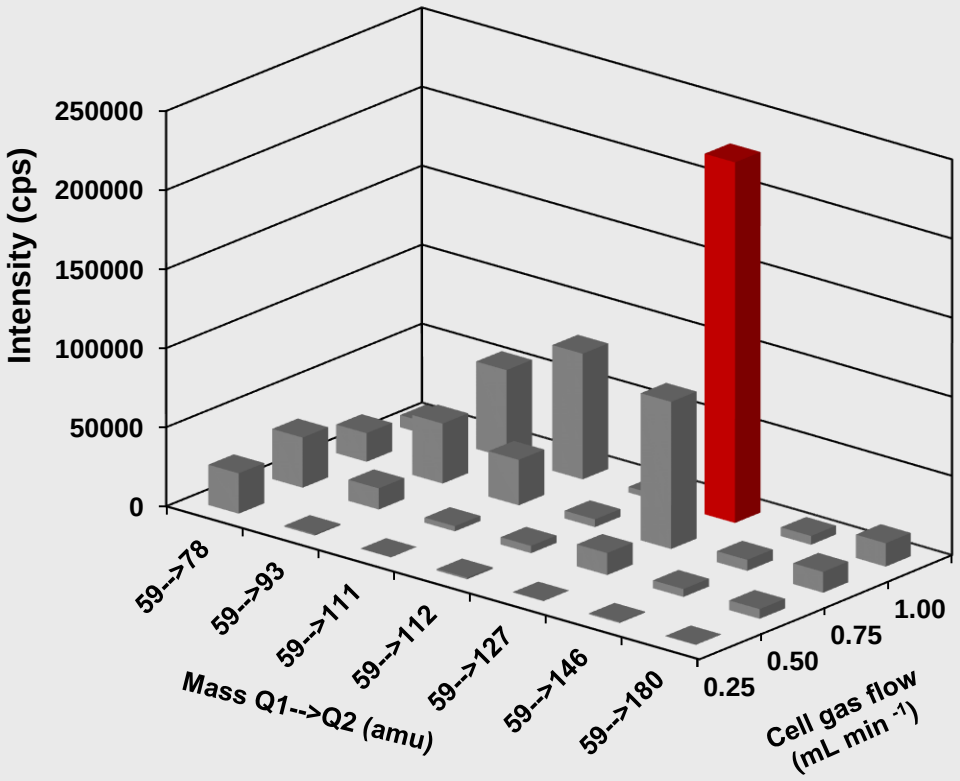


Low flow rate: **TiF^+**
(F addition)

Higher flow rate:
$TiF_2(CH_3F)_3^+$
(higher order reaction products)

➔ Similar behavior for Cr, V ($XF_a(CH_3F)_b^+$)

Cobalt



Main reaction product:
$Co(CH_3F)_2^+$

➔ Similar behavior for Al, Mn, Ni ($X(CH_3F)_b^+$)

LoD in MS/MS mode @ ~ 1 mL.min^{-1} CH_3F (multi-element method)

Isotope	Reaction Product ion	Q1 (amu)	Q2 (amu)	LoD (µg L^{-1})
^{27}Al	$^{27}AlCH_3F^+$	27	61	**0.01**
^{47}Ti	$^{47}TiF_2(CH_3F)_3^+$	47	187	**0.001**
^{49}Ti	$^{49}TiF_2(CH_3F)_3^+$	49	189	**0.002**
^{51}V	$^{51}VF_2(CH_3F)_3^+$	51	191	**0.0002**
^{52}Cr	$^{52}Cr(CH_3F)_2^+$	52	120	**0.004**
^{53}Cr	$^{53}Cr(CH_3F)_2^+$	53	121	**0.01**
^{55}Mn	$^{55}Mn(CH_3F)^+$	55	89	**0.001**
^{59}Co	$^{59}Co(CH_3F)_2^+$	59	127	**0.0006**
^{58}Ni	$^{58}Ni(CH_3F)_2^+$	58	126	**0.002**
^{60}Ni	$^{60}Ni(CH_3F)_2^+$	60	128	**0.003**

VALIDATION – Seronorm Serum & Urine

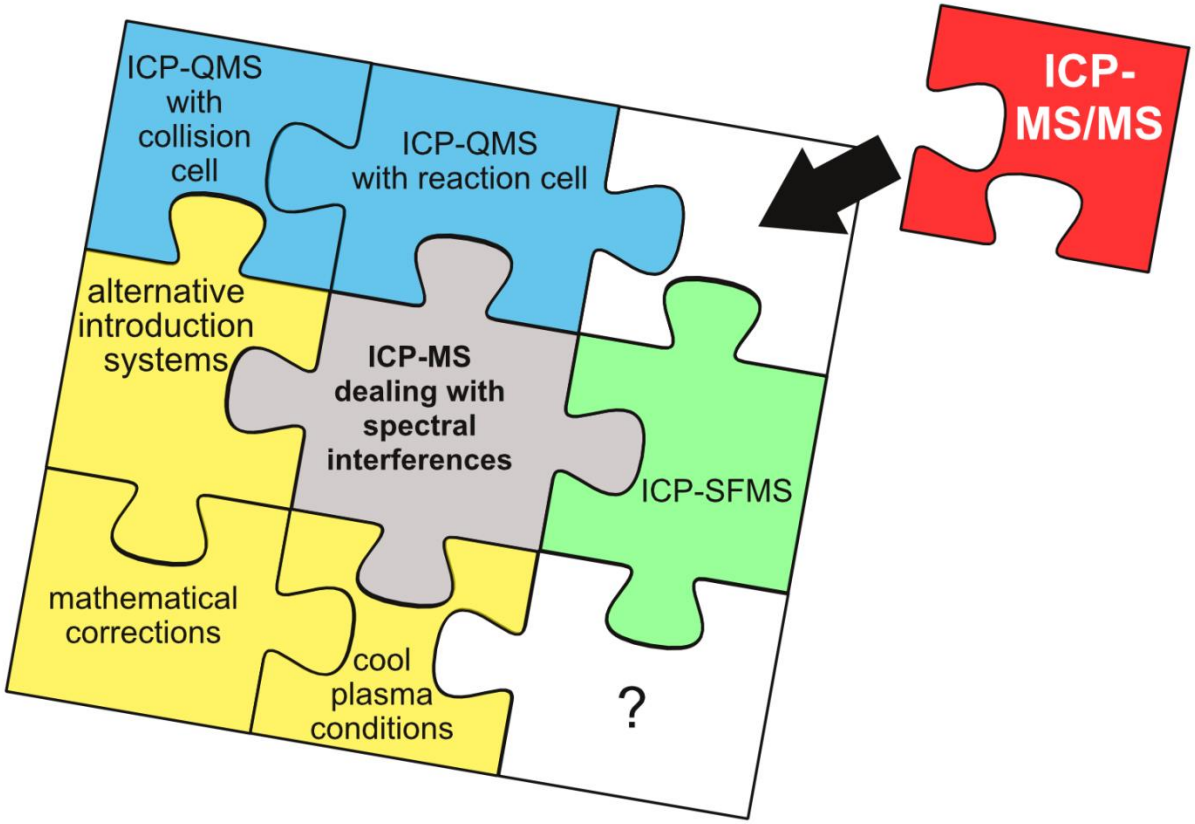
		Seronorm Trace Elements SERUM L-1		Seronorm Trace Elements URINE L-1	
Isotope	Reaction product ion	ICP-MS/MS (µg L^{-1})	Reference value (µg L^{-1})	ICP-MS/MS (µg L^{-1})	Reference value (µg L^{-1})
^{27}Al	$^{27}AlCH_3F^+$	**40.00 ± 0.55**	40.73 ± 0.83	**13.88 ± 0.55**	14.62 ± 0.22
^{47}Ti	$^{47}TiF_2(CH_3F)_3^+$	**11.83 ± 0.49**	11.58 ± 0.53	**12.38 ± 0.49**	12.76 ± 0.20
^{49}Ti	$^{49}TiF_2(CH_3F)_3^+$	**11.90 ± 0.48**	11.81 ± 0.33	**12.62 ± 0.57**	12.72 ± 0.21
^{51}V	$^{51}VF_2(CH_3F)_3^+$	**1.23 ± 0.01**	1.19 ± 0.03	**0.77 ± 0.04**	0.74 ± 0.01
^{52}Cr	$^{52}Cr(CH_3F)_2^+$	**1.46 ± 0.08**	1.46 ± 0.06	**1.61 ± 0.27**	1.65 ± 0.27
^{53}Cr	$^{53}Cr(CH_3F)_2^+$	**1.43 ± 0.10**	1.41 ± 0.10	**1.63 ± 0.29**	1.63 ± 0.05
^{55}Mn	$^{55}Mn(CH_3F)^+$	**15.25 ± 0.13**	15.0 ± 0.9	**0.69 ± 0.05**	0.73 ± 0.15
^{59}Co	$^{59}Co(CH_3F)_2^+$	**1.22 ± 0.05**	1.2 ± 0.2	**0.72 ± 0.01**	0.72 ± 0.15
^{58}Ni	$^{58}Ni(CH_3F)_2^+$	**5.58 ± 0.08**	5.8 ± 0.7	**1.56 ± 0.06**	1.51 ± 0.30
^{60}Ni	$^{60}Ni(CH_3F)_2^+$	**5.58 ± 0.20**	5.8 ± 0.7	**1.58 ± 0.11**	1.51 ± 0.30

CONCLUSIONS

ICP-MS/MS

Systematic study of reactions in the reaction cell

~~**Spectral overlap**~~


ICP-QMS with collision cell
ICP-QMS with reaction cell
ICP-MS/MS
alternative introduction systems
ICP-MS dealing with spectral interferences
ICP-SFMS
mathematical corrections
cool plasma conditions
?

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