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ICP-QQQ-MS for the accurate determination of S in organic matrices

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Agilent Spectroscopy Days
11th & 12th of June 2013

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A&MS Atomic and Mass Spectrometry

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Isotopic analysis

Trace element determination

Speciation

A & MS

Atomic and Mass Spectrometry

Ecotoxicology

Medicine

Pharmacy

Biology

Geology

Cosmochemistry

Archaeometry

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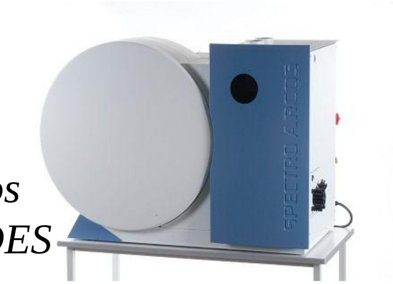
Elan DRC⁺
Q-ICP-MS

XSeries II
Q-ICP-MS

Agilent 8800
ICP-QQQ

A&MS
Atomic and Mass Spectrometry

Arcos
ICP-OES



Spectro MS
Mattauch-Herzog ICP-MS

Element XR
SF-ICP-MS

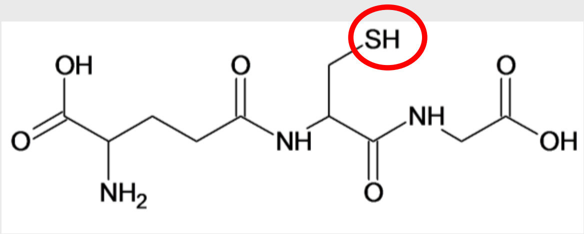
Neptune
MC-ICP-MS

ONE OF OUR RESEARCH PROJECTS…

- Pharmaceutical research
  - metabolism study:

➔ Chromatographic separation of metabolites

➔ Quantification of metabolites bound to glutathione (via S)



HPLC-ICP-MS

- Separation of metabolites: reversed-phase HPLC
  - **Gradient elution**: 95% NH_4Ac → 90% CH_3OH

- Quantification: ICP-MS
  - Calibration: online **isotope dilution**

➔ interference-free determination of ^{32}**S** and ^{34}**S**

➔ quadrupole ICP-MS: spectral interferences

SPECTRAL INTERFERENCES

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

→ quadrupole ICP-MS with reaction/collision cell:

$S^+ \rightarrow SO^+$

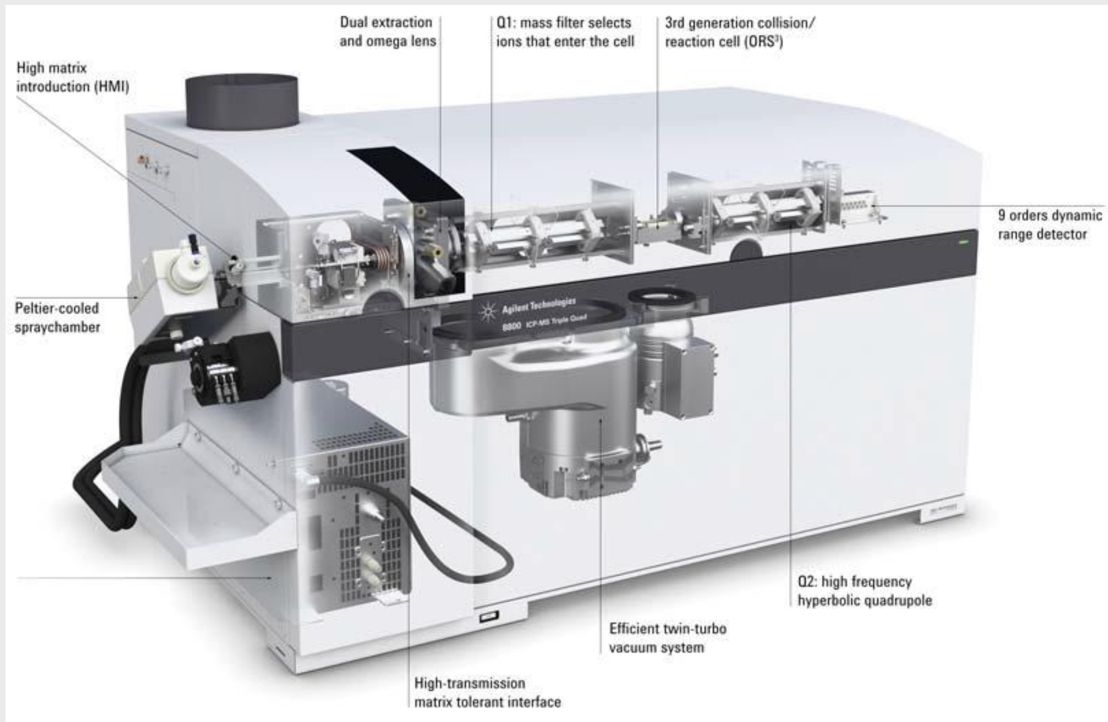
SPECTRAL INTERFERENCES

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	$^{50}Ti^+$, $^{50}Cr^+$, $^{50}V^+$, **$^{38}Ar^{12}C^+$**, $^{36}Ar^{14}N^+$, **$^{32}S^{18}O^+$, $^{33}S^{17}O^+$**

→ ICP-DRC-Q-MS only partial solution

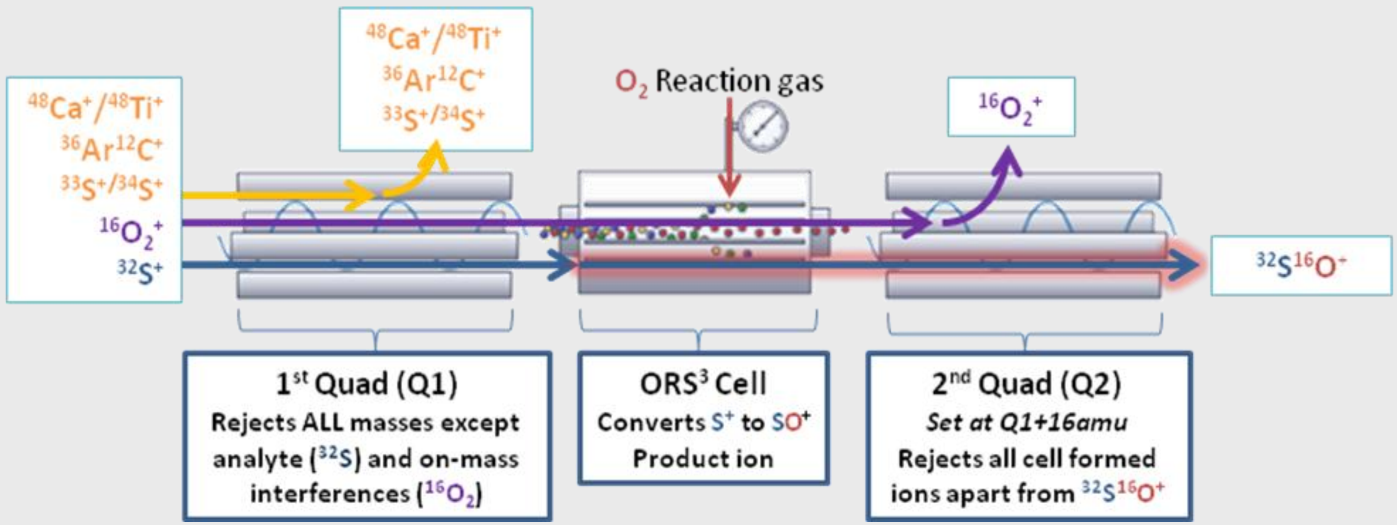
(use of sector field – ICP – MS (more expensive – less robust))

2012: AGILENT 8800 ICP-QQQ



AGILENT 8800

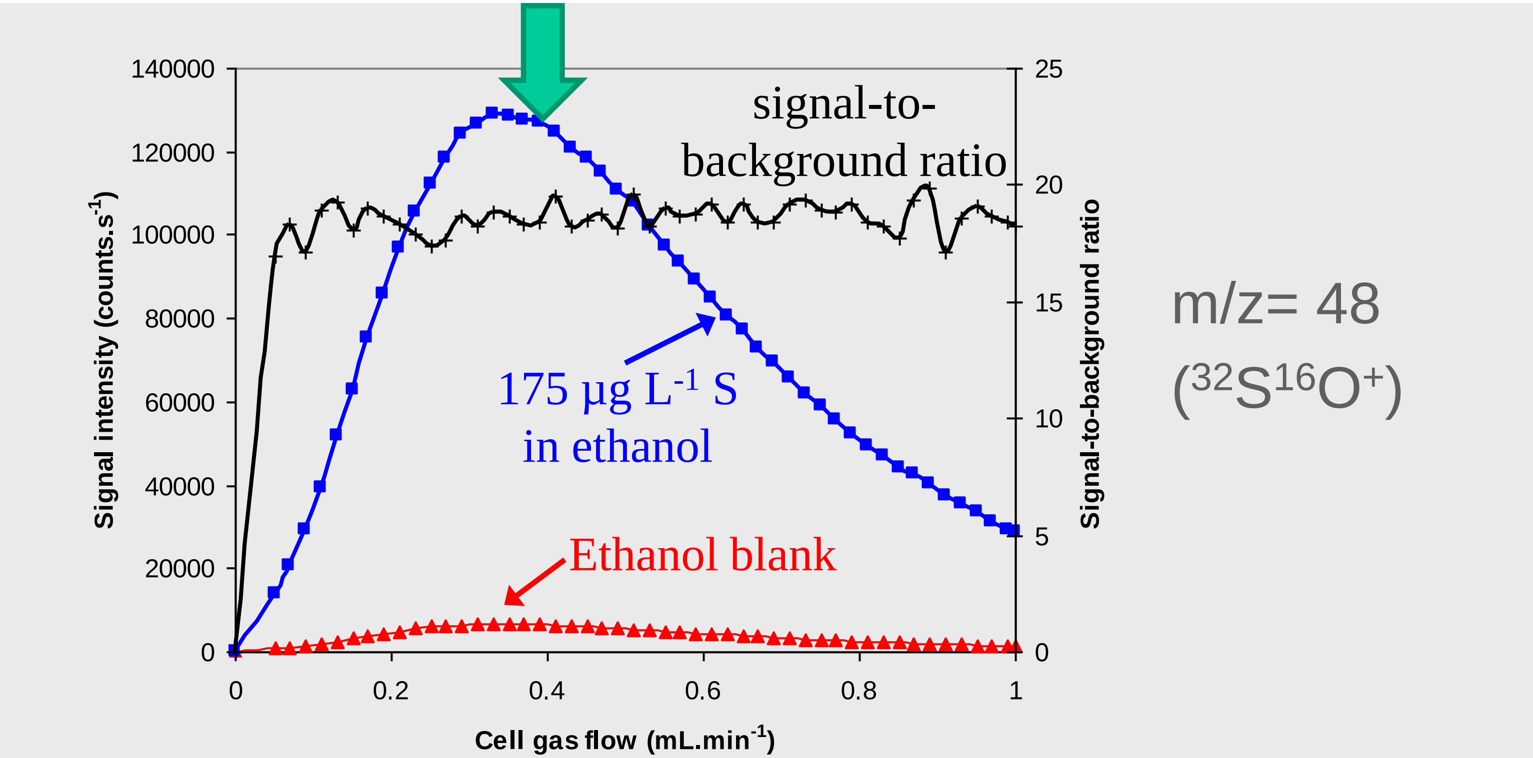
- $S^+ \rightarrow SO^+$ - S detection at m/z=48 and 50
- MS/MS mode: avoid interferences on m/z= 48 and 50 ?



DETERMINATION of S in pure ETHANOL

- S – standards in pure ethanol (0 to 850 µg L^{-1} S)
  - Spray chamber : - 5 °C
  - 1 mm i.d. injector (standard: 2.5 mm)
  - O_2 (20% in Ar) to avoid carbon build-up
  - O_2 reaction gas: optimization of gas flow

OPTIMIZATION REACTION GAS FLOW (O_2)



m/z= 48

($^{32}S^{16}O^{+}$)

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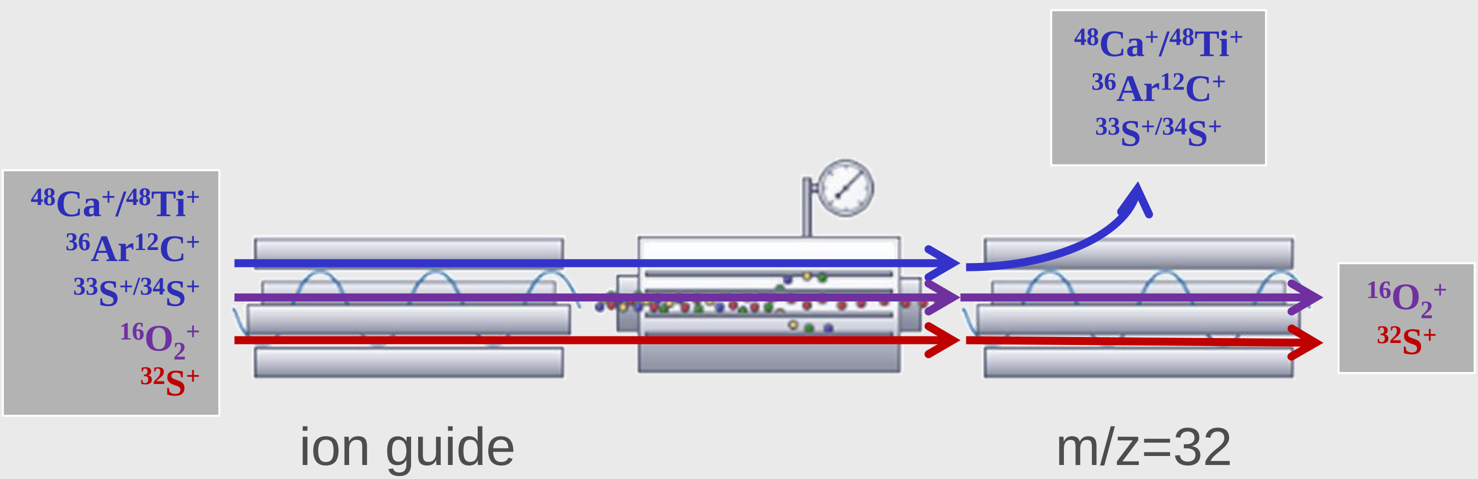
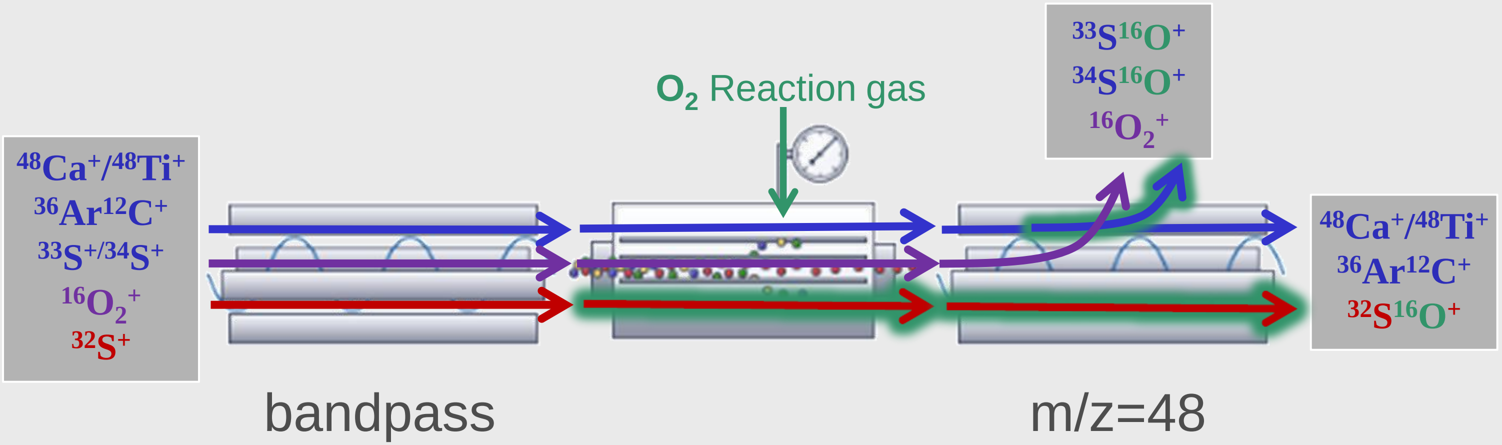
CALIBRATION CURVES – standard mode

- 3 MODES:
  - 'ion guide' mode (single-Q ~ Q1: ion guide ~ no reaction)



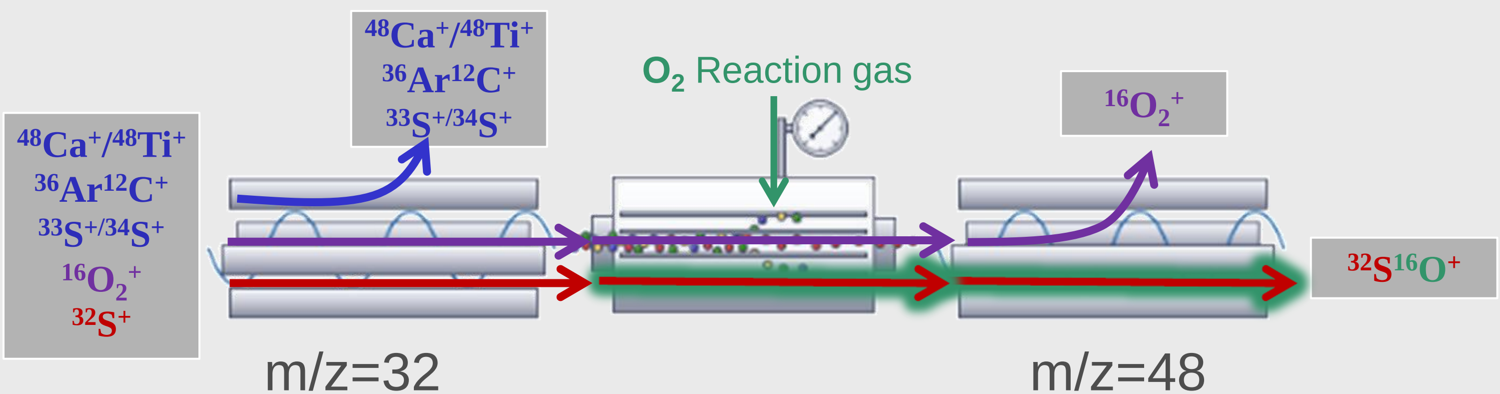
CALIBRATION CURVES – bandpass mode

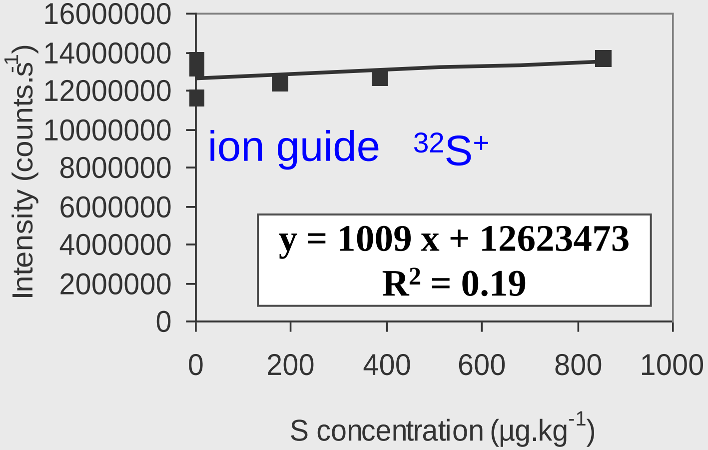
- 3 MODES:
  - ‘ion guide' mode (single-Q ~ Q1: ion guide ~ no reaction)
  - 'bandpass' mode (single-Q ~ Q1: bandpass filter ~ reaction)

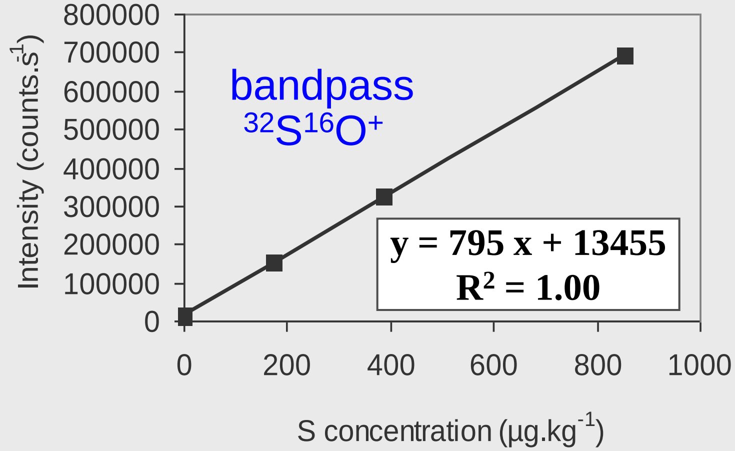


CALIBRATION CURVES – MS/MS mode

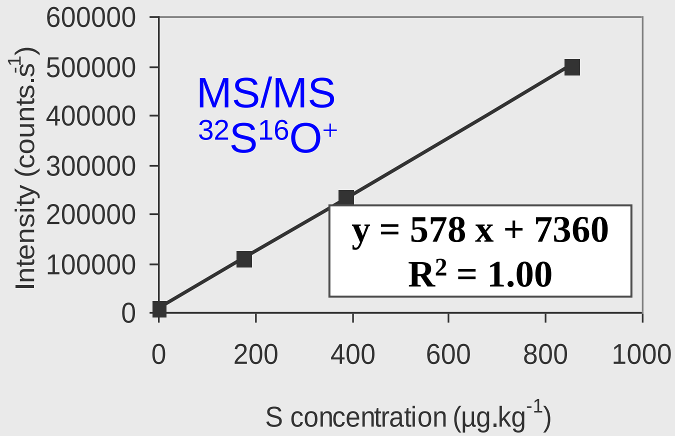
- 3 MODES:
  - ‘ion guide' mode (single-Q ~ Q1: ion guide ~ no reaction)
  - 'bandpass' mode (single-Q ~ Q1: bandpass filter ~ reaction)
  - 'MS/MS' mode (triple-Q ~ Q1: precursor ion mass ~ reaction)




16000000
14000000
12000000
10000000
8000000
6000000
4000000
2000000
0
Intensity (counts.s-1)
ion guide $^{32}S^+$
y = 1009 x + 12623473
R^2 = 0.19
0
200
400
600
800
1000
S concentration (µg.kg-1)


800000
700000
600000
500000
400000
300000
200000
100000
0
Intensity (counts.s-1)
bandpass
$^{32}S^{16}O^+$
y = 795 x + 13455
R^2 = 1.00
0
200
400
600
800
1000
S concentration (µg.kg-1)

^{32}S


600000
500000
400000
300000
200000
100000
0
Intensity (counts.s-1)
MS/MS
$^{32}S^{16}O^+$
y = 578 x + 7360
R^2 = 1.00
0
200
400
600
800
1000
S concentration (µg.kg-1)

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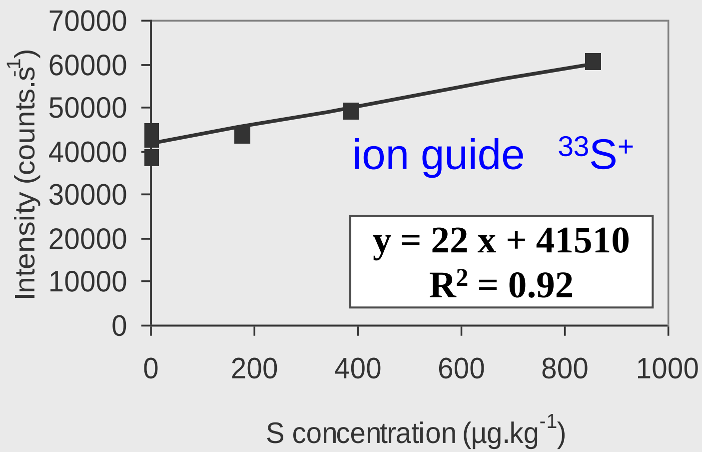
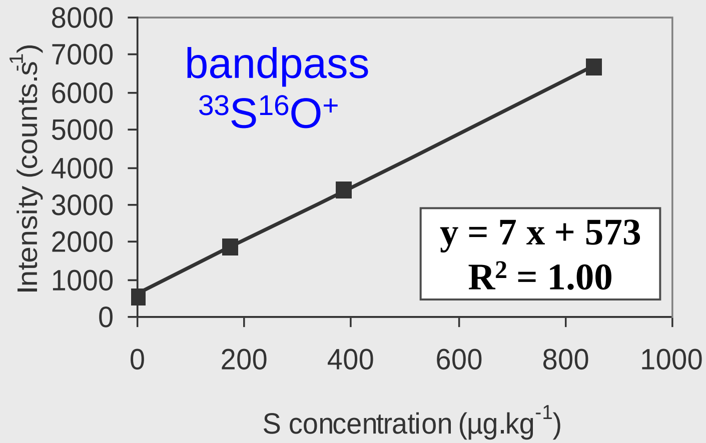
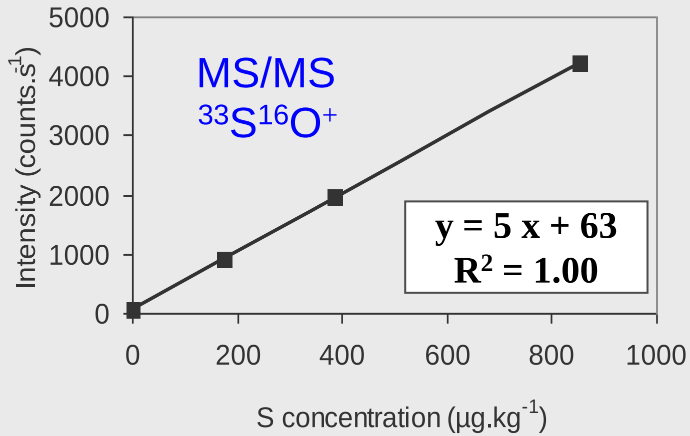
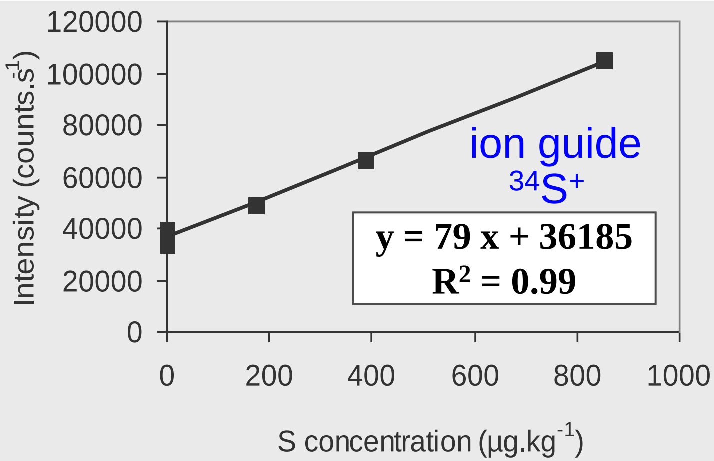
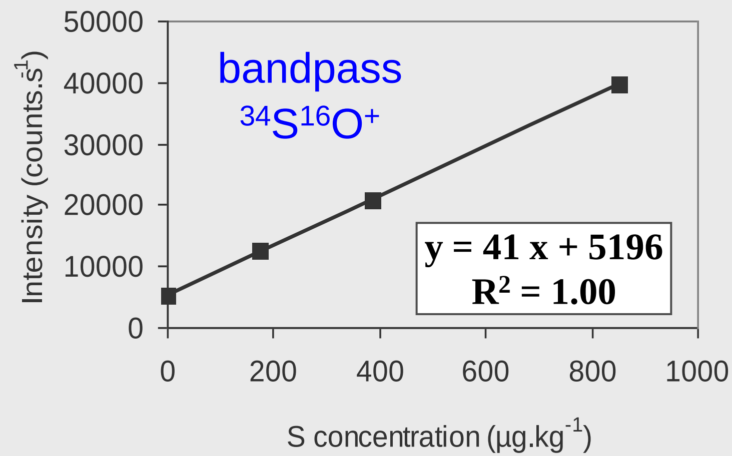




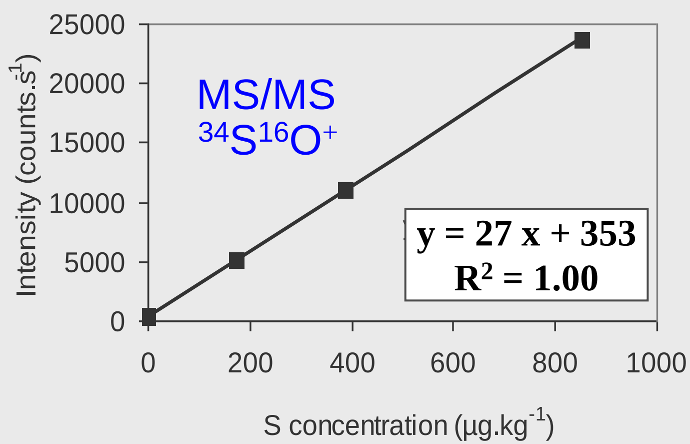
^{33}S



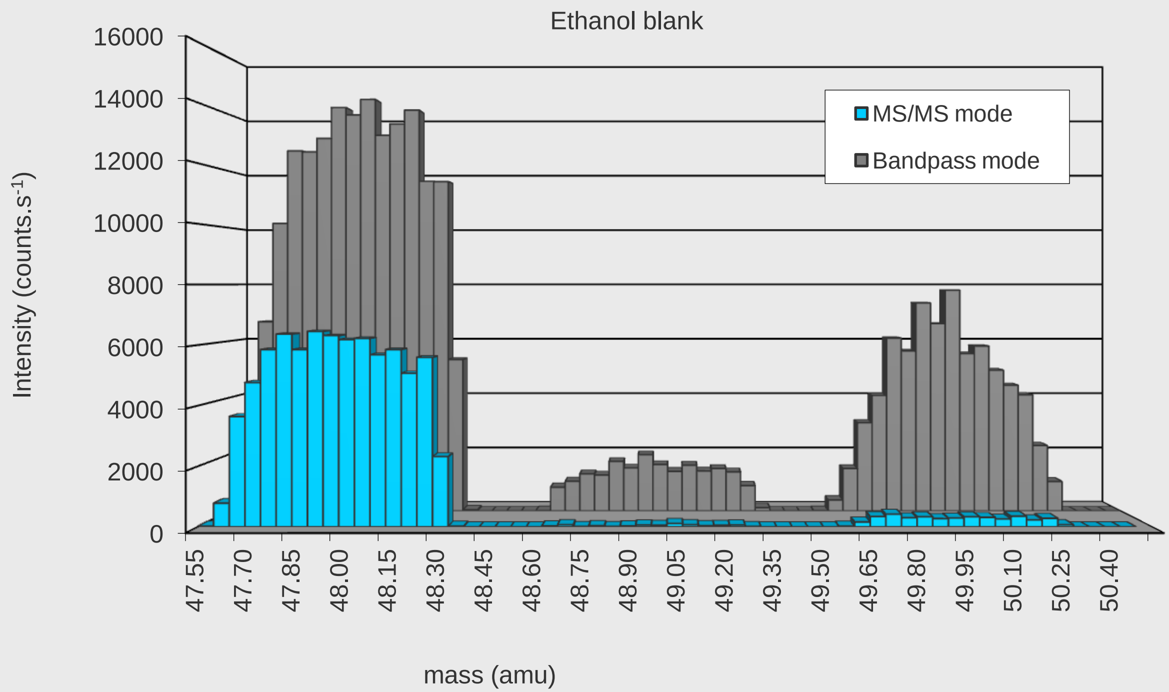

ion guide
$^{34}S^+$
y = 79 x + 36185
R^2 = 0.99
Intensity (counts.s^{-1})
S concentration (µg.kg^{-1})
0
20000
40000
60000
80000
100000
120000
200
400
600
800
1000


bandpass
$^{34}S^{16}O^+$
y = 41 x + 5196
R^2 = 1.00
Intensity (counts.s^{-1})
S concentration (µg.kg^{-1})
0
10000
20000
30000
40000
50000
200
400
600
800
1000

^{34}S


MS/MS
$^{34}S^{16}O^+$
y = 27 x + 353
R^2 = 1.00
Intensity (counts.s^{-1})
S concentration (µg.kg^{-1})
0
5000
10000
15000
20000
25000
200
400
600
800
1000

COMPARISON BANDPASS & MS/MS MODE



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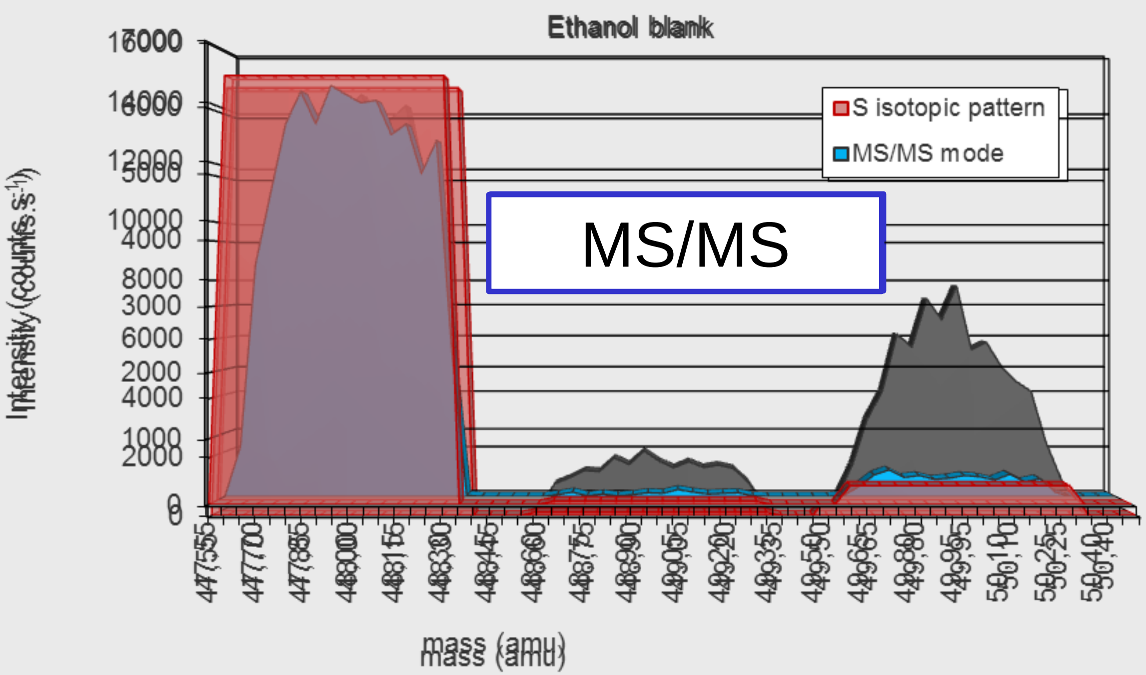
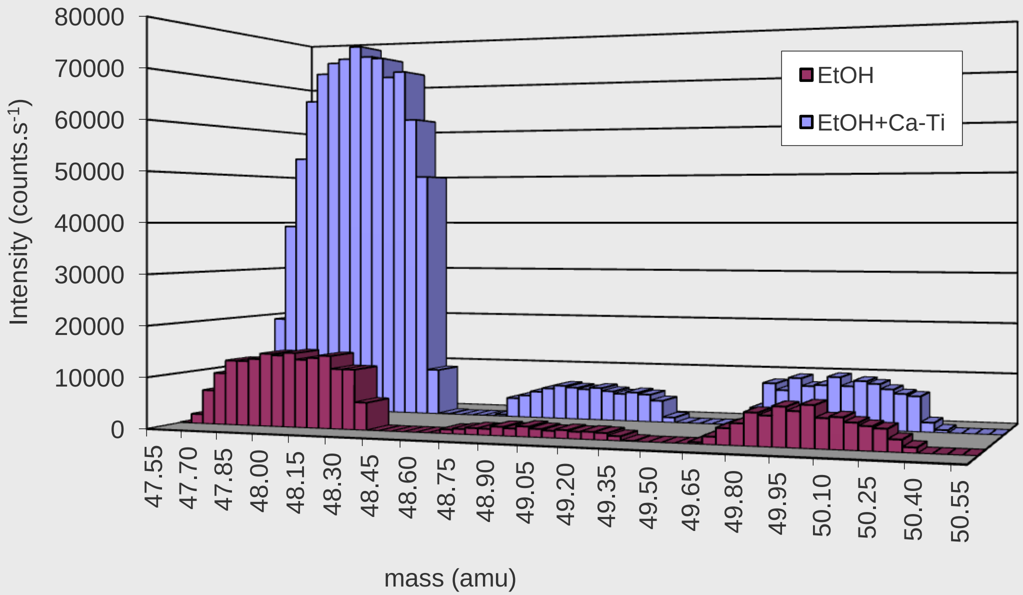
COMPARISON BANDPASS & MS/MS MODE



LET'S MAKE LIFE EVEN MORE COMPLEX…

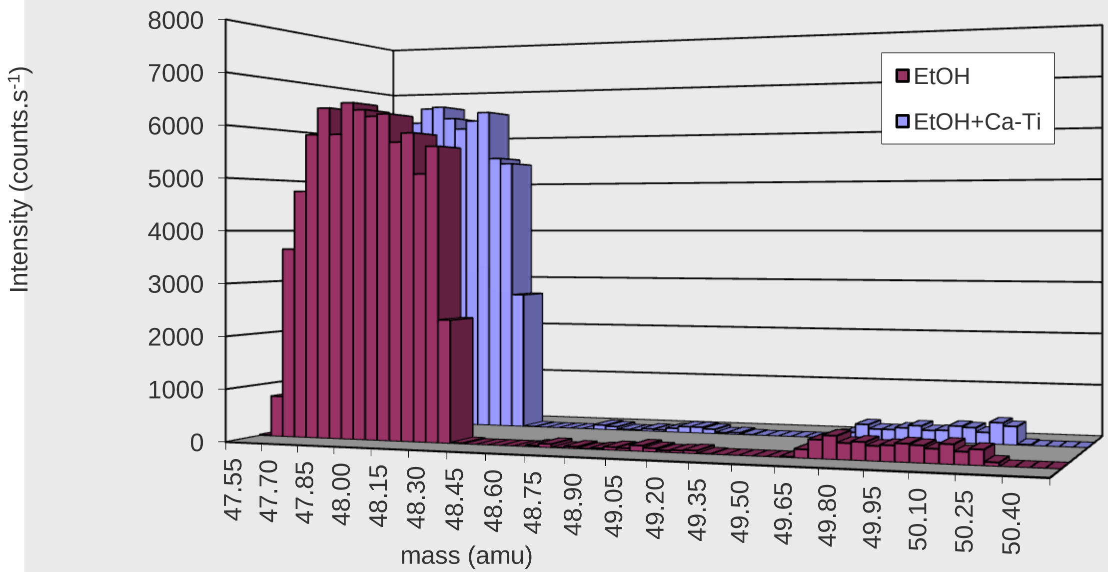
- Matrix: Ethanol + 50 µg.L^{-1} Ca + Ti



Bandpass mode

LET'S MAKE LIFE EVEN MORE COMPLEX…

- Matrix: Ethanol + 50 µg.L^{-1} Ca + Ti



MS/MS mode

LIMIT OF DETECTION (LOD)

LOD (µg.L^{-1})	^{32}S	^{33}S	^{34}S
MS/MS (s (external))	4	3	6
MS/MS (s (internal))	0.4	5	1.6
Literature values			
reaction cell ICP-MS	*10 - 100*		*300*
sector field ICP-MS	*1*		*2*

VALIDATION: Analysis of SRM 2773 biodiesel

- NIST SRM 2773: animal-based biodiesel
  - Isotope dilution for calibration
  - Simple dilution with ethanol

- Sample preparation:

~ 1 g biodiesel

~ 0.2 g ^{34}S spike
(0,711 µg mol^{-1} ^{34}S)

24 mL ethanol

VALIDATION: Analysis of SRM 2773 biodiesel

Parameter	Value
RF power	1450 W
Carrier gas flow rate	0.98 L min^{-1}
O_2 option gas flow rate	75 mL min^{-1}
Spray chamber temp.	- 5 °C
O_2 reaction gas flow rate	0.4 mL min^{-1}
Q1 bias	- 2 V
Octopole bias	- 9V
Q2 bias	- 18V

VALIDATION: Analysis of SRM 2773 biodiesel

Q1: m/z = 32 / 34 ~ Q2: m/z = 48 / 50

	Concentration	Certified value
SRM 2773 – 1	7.234 mg g^{-1}	
SRM 2773 – 2	7.227 mg g^{-1}	
SRM 2773 – 3	7.231 mg g^{-1}	
Average	***7.231 mg g^{-1}***	***7.39 ± 0.39 mg g^{-1}***
S	*0.003 mg g^{-1}*	
95% CI	*7.231 ± 0.015 mg g^{-1}*	

CONCLUSIONS

- Analysis of organic matrices is possible
- Almost interference-free determination of ^{32}S, ^{33}S and ^{34}S, independent of the matrix
- Accurate results obtained for a biodiesel SRM

- Flexible, all-round instrument
  - “normal” quadrupole-based ICP-MS
  - large range of possibilities to deal with interferences


Agilent Technologies
8800 ICP-MS Triple Quad