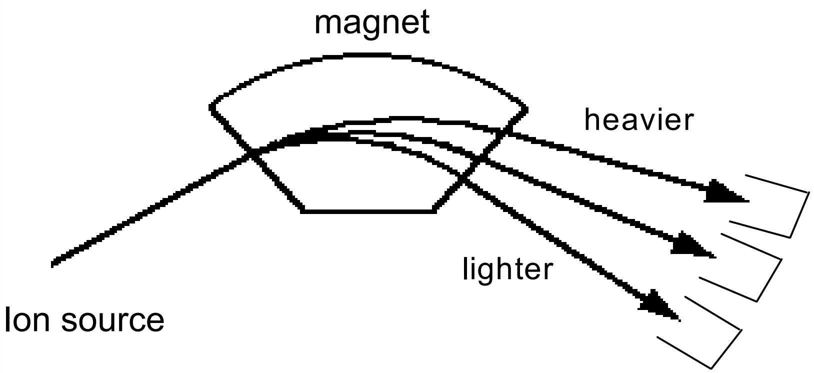
Stable isotope ratio measurements using the Finnigan NEPTUNE multicollector ICP-MS

Claudia Bouman
Thermo Electron (Bremen)

The *NEPTUNE*

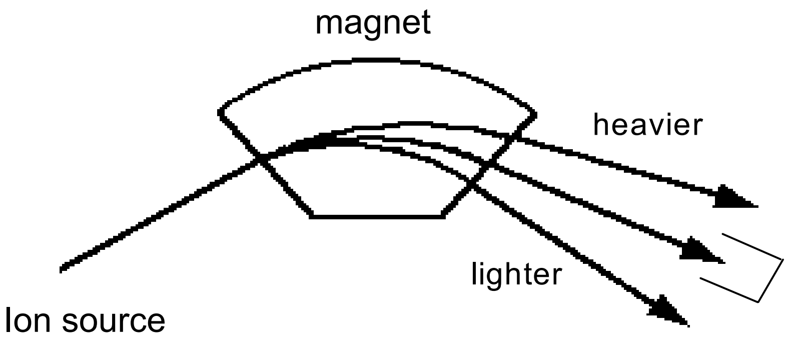
Introduced 2000

Multicollection vs. Single collection



3 (or more) detectors

Multicollection



1 detector

Single collection

- Detectors can be
  - – *Faraday collectors (least sensitive)*
  - – *Analog SEMs*
  - – *Counting SEMs (most sensitive)*
  - – *Or any mixture of above*

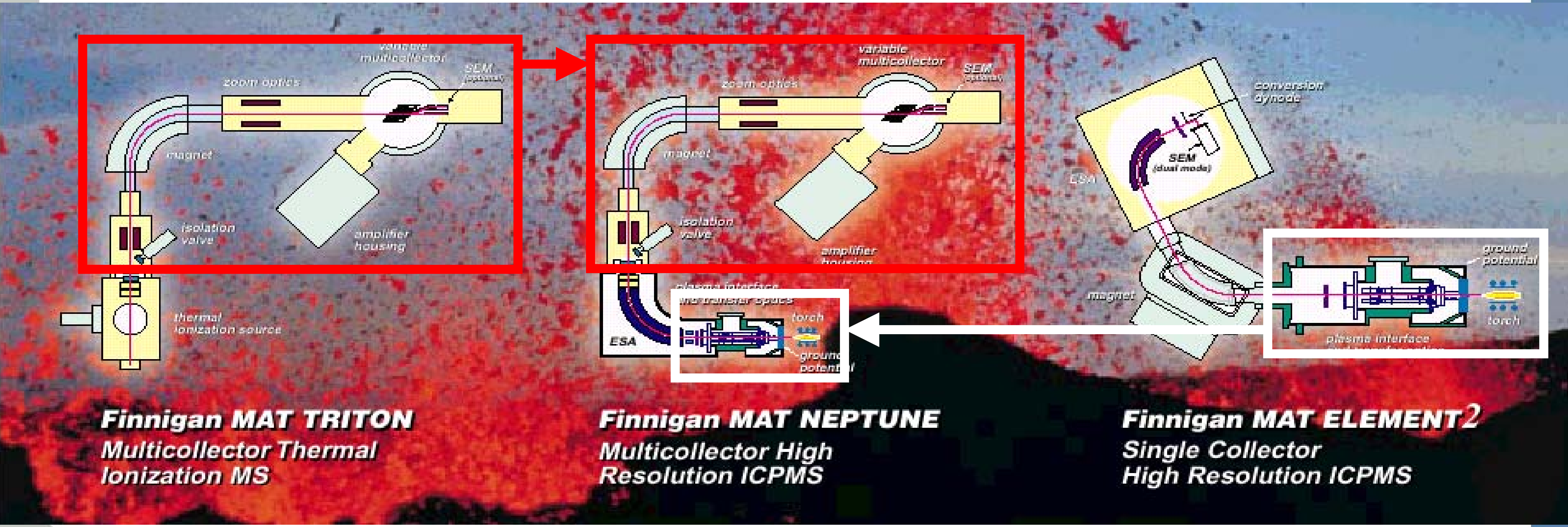
Multicollection vs. Single collection

- Multicollection: All isotopes of interest are measured simultaneously
  - *Highest sensitivity (100% duty cycle)*
  - *Fluctuations in signal intensity have no effect on isotope ratios*
  - *Need of detector cross calibration for accuracy*

- Single collection: One isotope is measured at any time
  - *No detector cross calibration error*
  - *Lower sensitivity (duty cycle < 100%)*
  - *Measured isotope ratio sensitive to signal fluctuation*

The Evolution of *NEPTUNE*

The ***NEPTUNE*** is an evolution of the ***TRITON*** multicollector combined with the proven ***ELEMENT2*** ICP source



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A FAMILY OF INSTRUMENTS FOR HIGH RESOLUTION ISOTOPIC AND ELEMENTAL ANALYSIS

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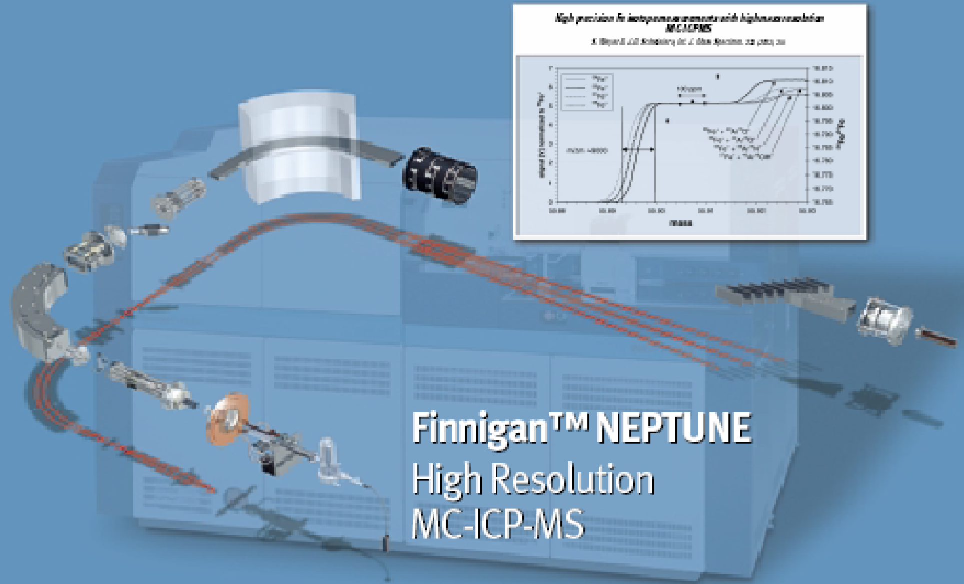
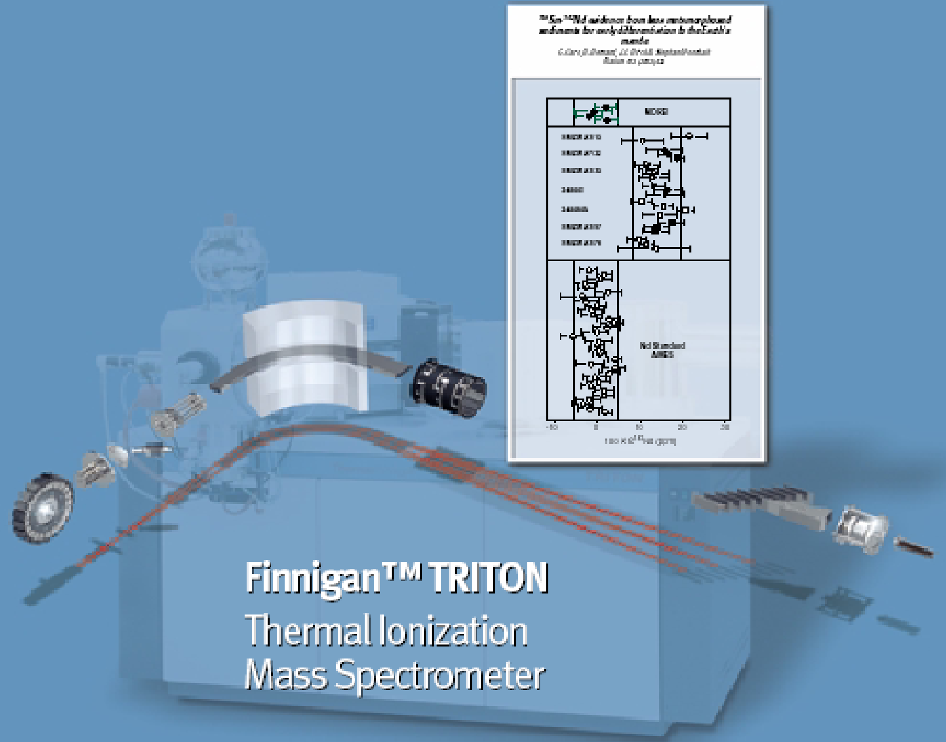
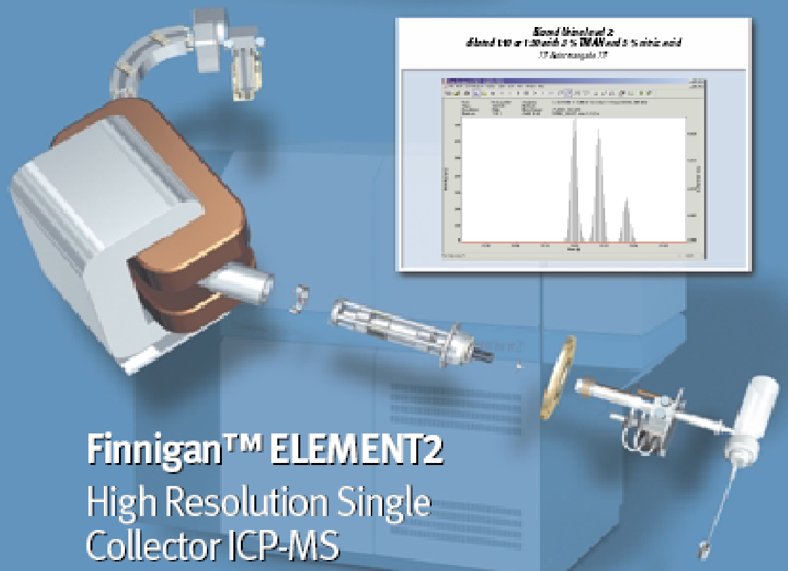


Finnigan™ NEPTUNE
High Resolution
MC-ICP-MS



Finnigan™ TRITON
Thermal Ionization
Mass Spectrometer



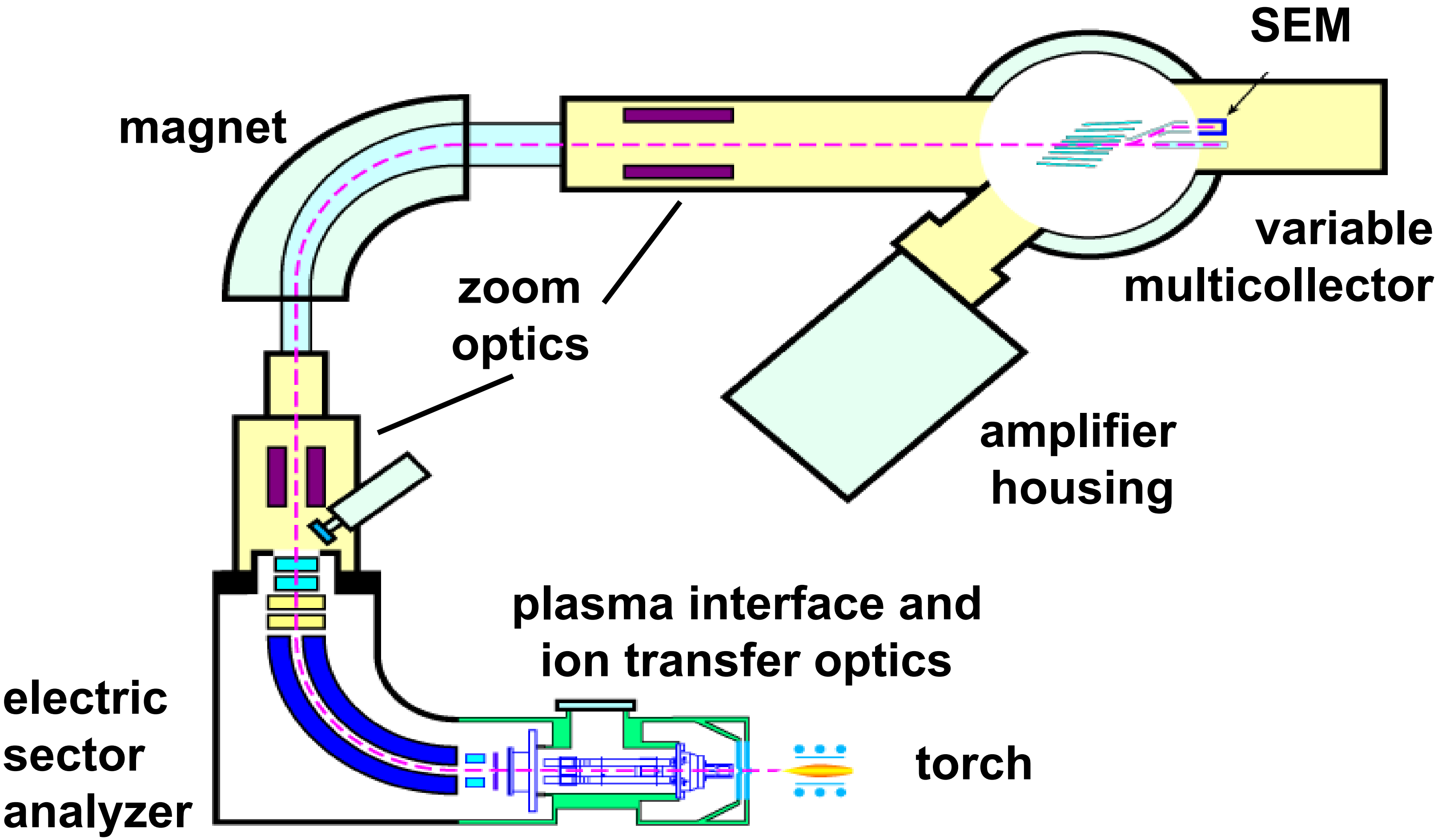
Finnigan™ ELEMENT2
High Resolution Single
Collector ICP-MS

The Neptune Fountain in Bremen

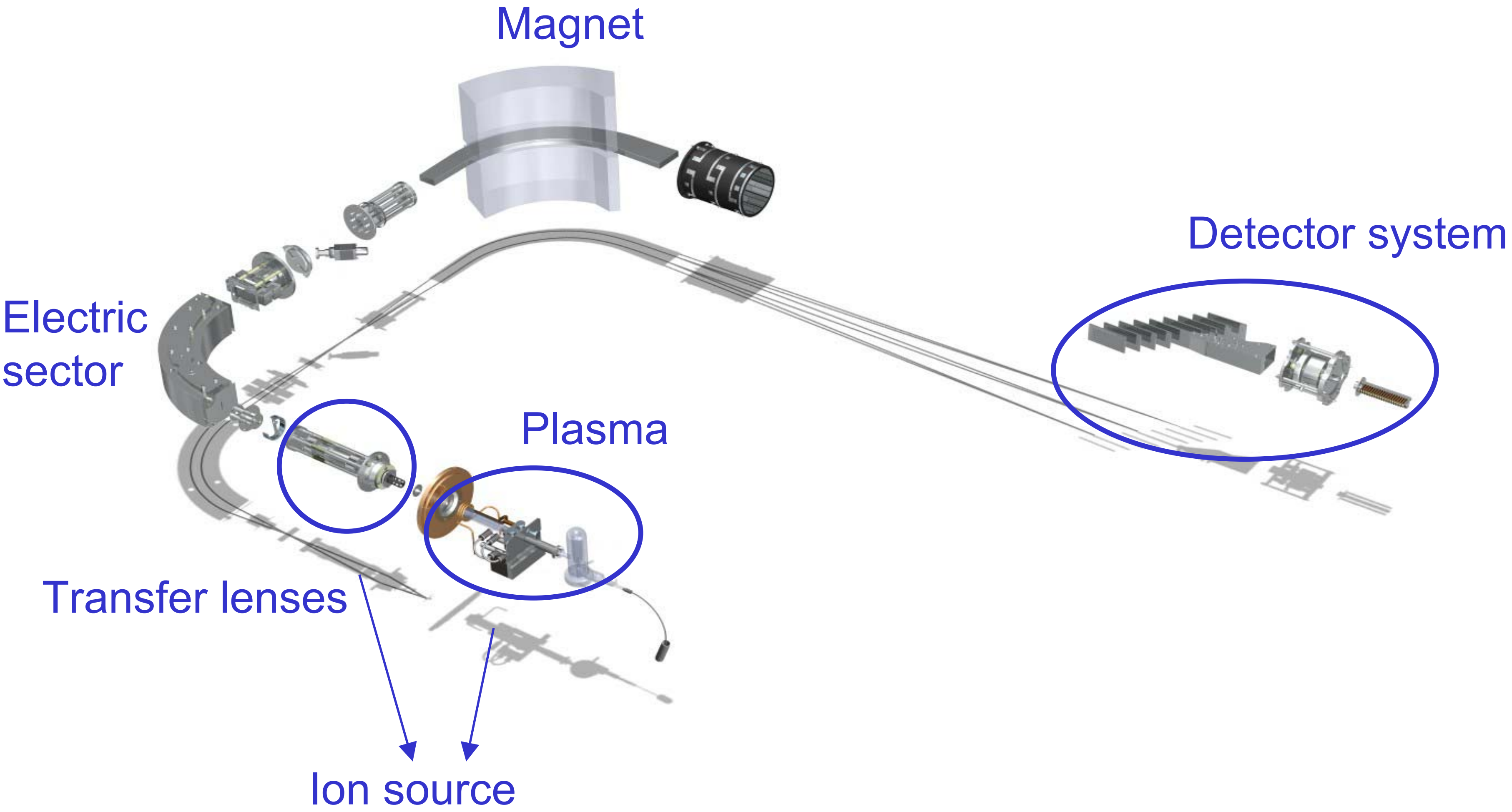
The powerful NEPTUNE

TRITON announces NEPTUNE

Schematic overview *NEPTUNE*



How does it look in reality?



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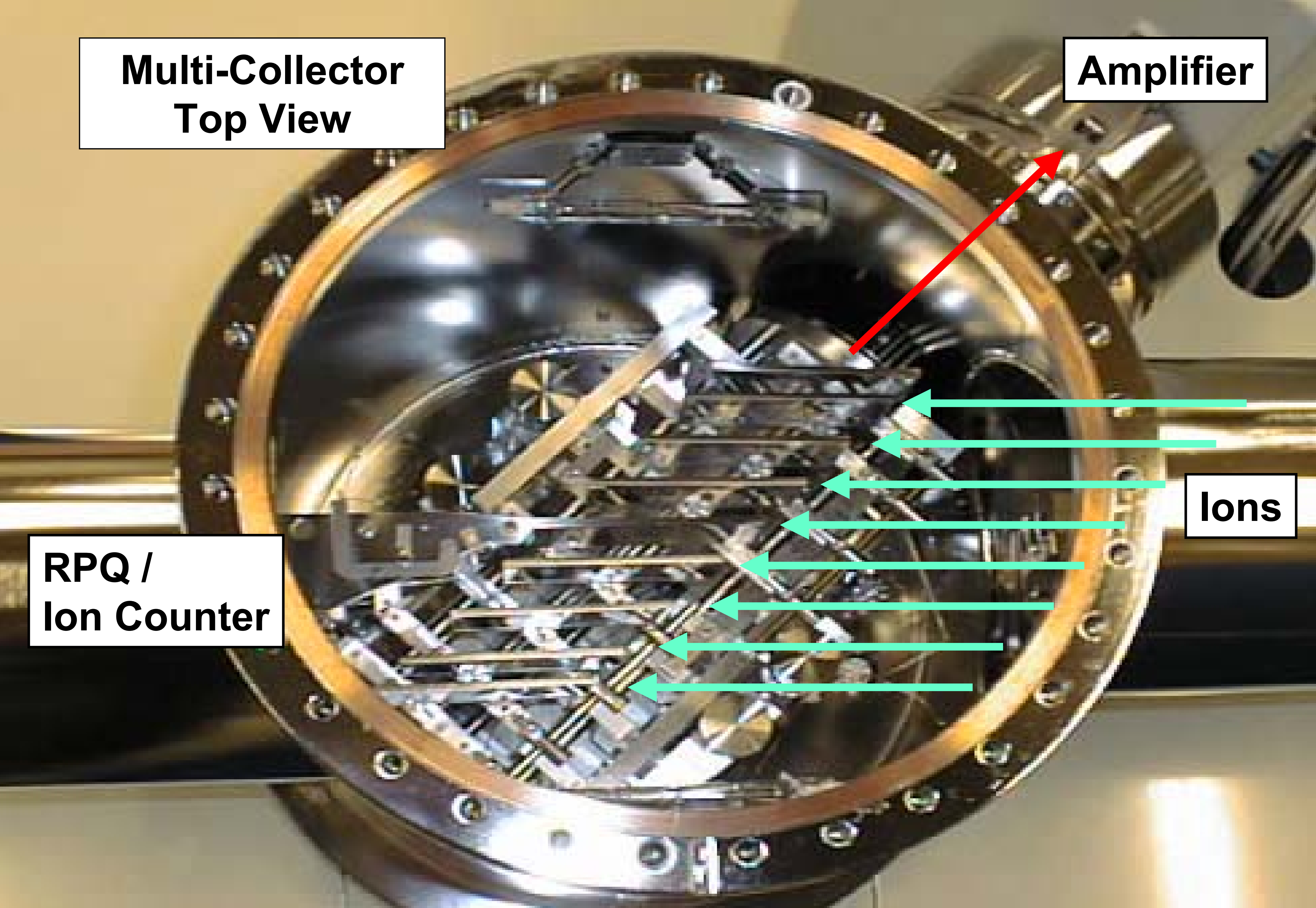
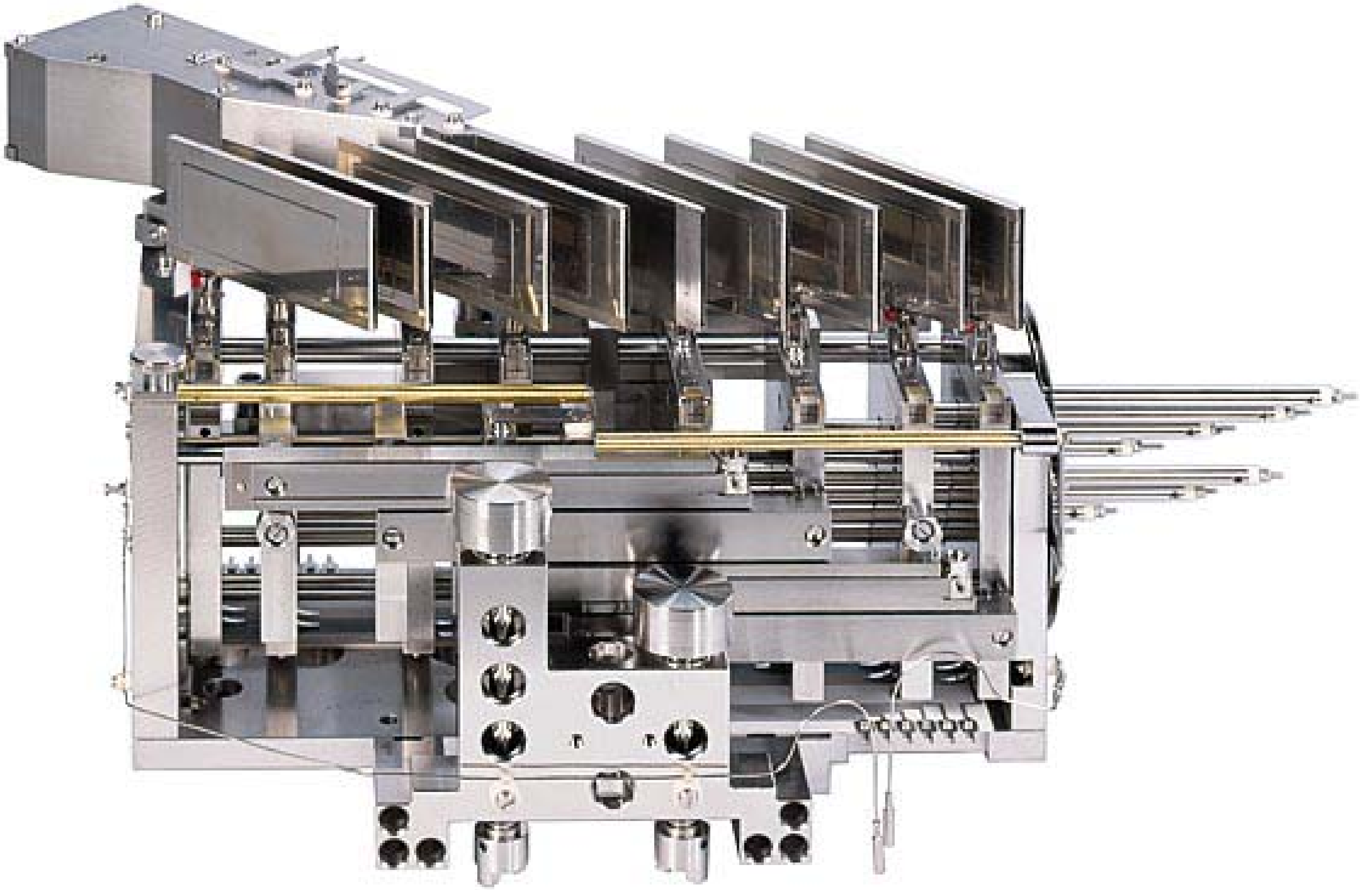
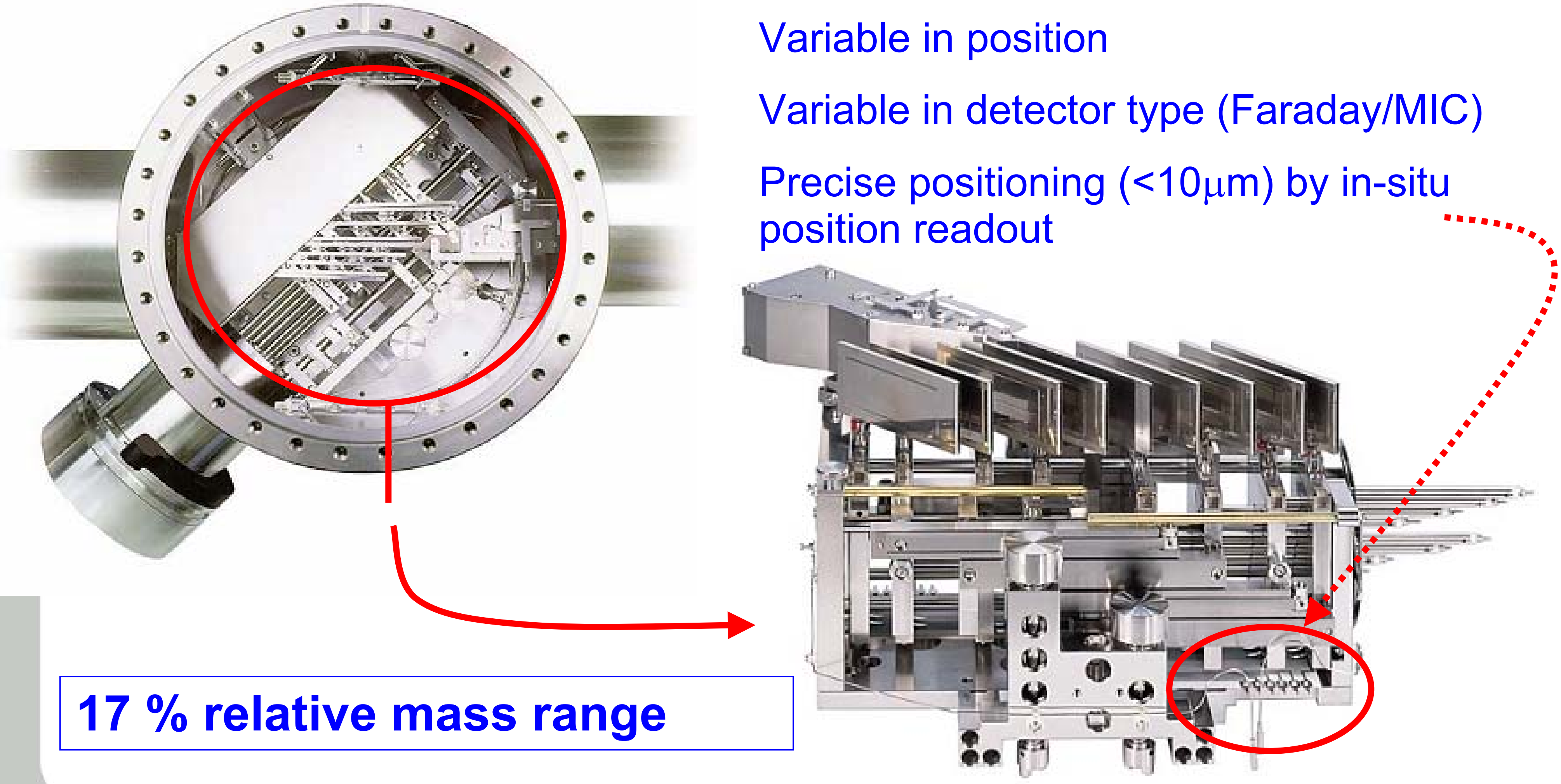
Multi-Collector Top View



Detector system



Variable Multicollector



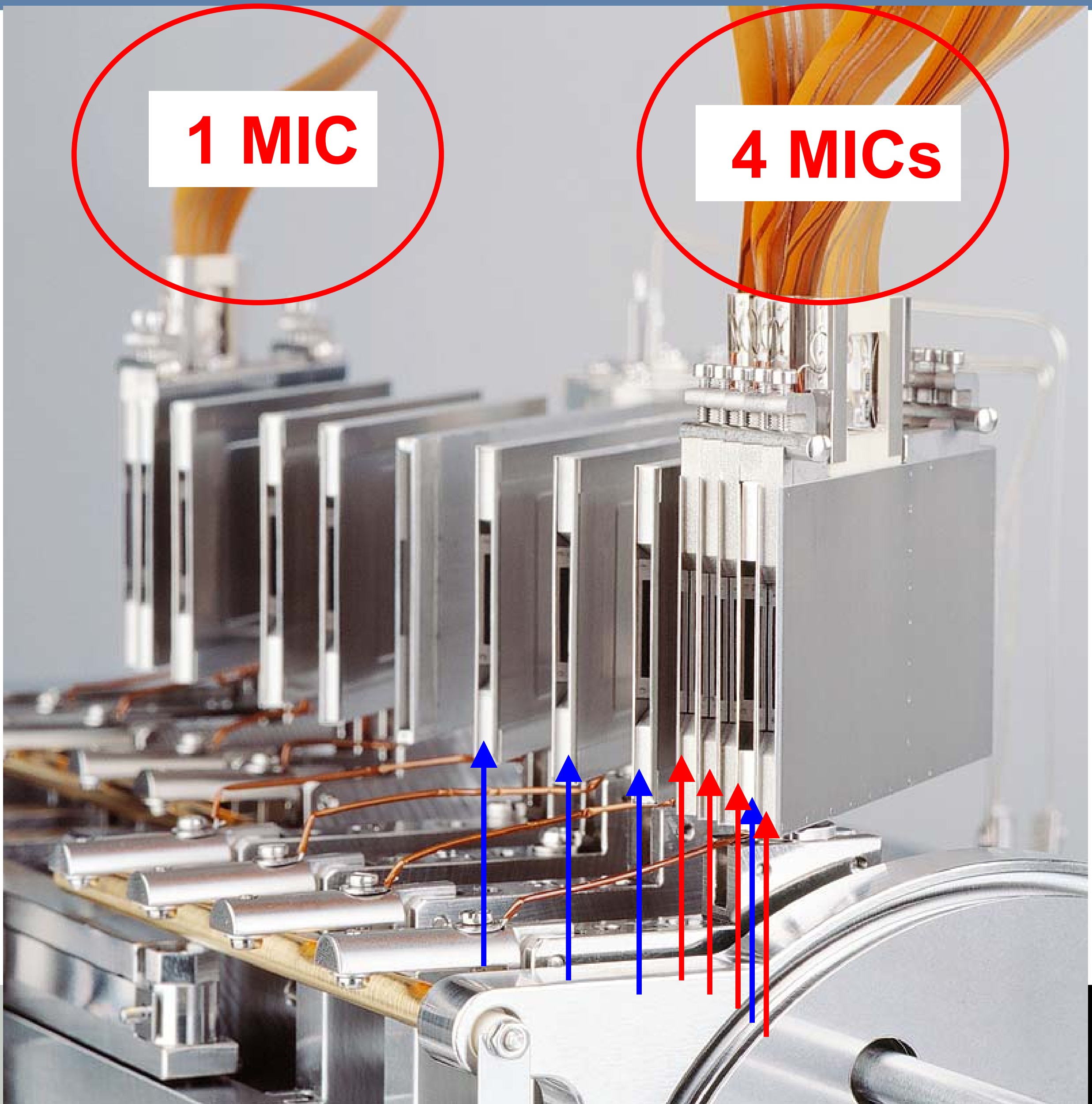
Variable in position

Variable in detector type (Faraday/MIC)

Precise positioning (<10µm) by in-situ position readout

17 % relative mass range

Multicollector with Multi Ion Counting



- “plug-in” MIC detectors identical in size and inter-changeable with Faraday cups
- up to 8 MIC channels plus 9 Faraday cups can be installed simultaneously

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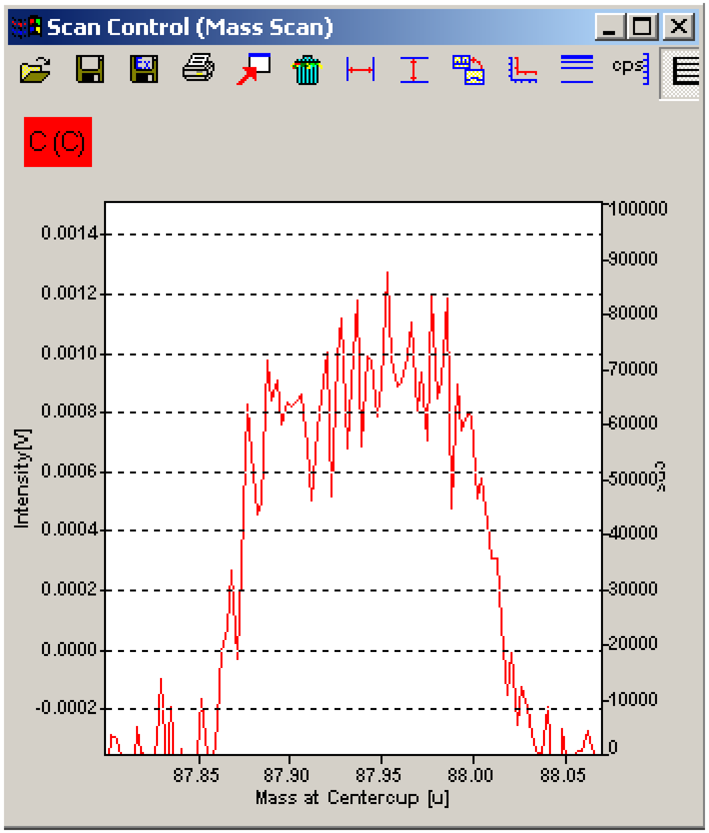
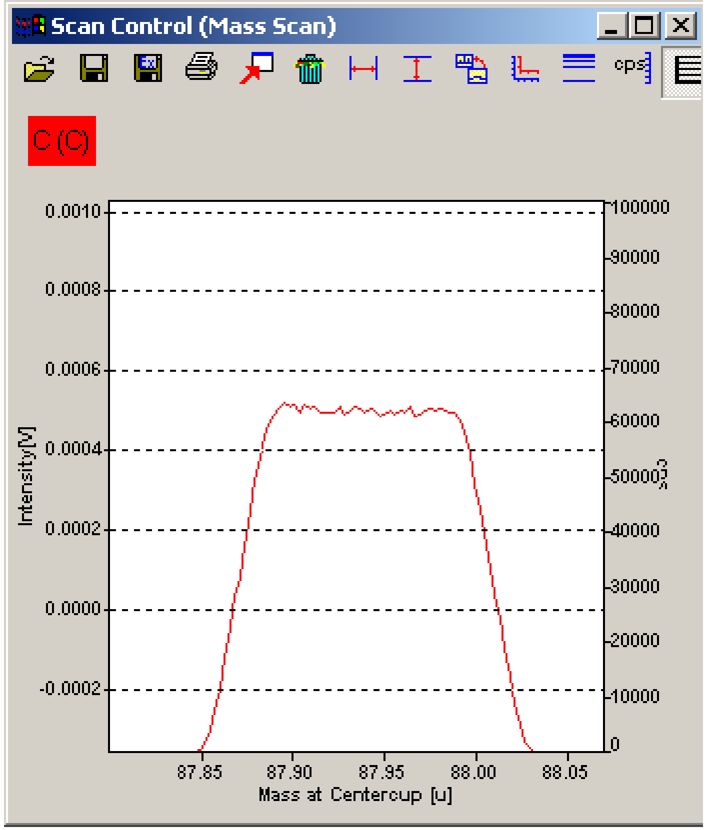
Why Multi Ion Counting ?

1 mV Faraday signal



ca. 60.000 cps on IC



Finnigan NEPTUNE: Applications

Radiogenic isotopes:

Sr, Nd, Hf, Pb and U

Used in geology to:
- date rocks and meteorites
- study evolution processes of Earth and Solar System

Stable isotopes:

e.g., **Ca**, **Fe** and **Si**

Used in biology and chemistry to:
- study biochemical processes in humans, animals and plants

e.g., **Li** and **B**

Used in geochemistry to:
- study recycling processes on Earth

Stable isotopes

Major difficulties in measuring stable isotope ratios by ICP techniques:

-Low sensitivity

-Interferences

Interferences ..... part 1

Isobaric *elemental* interferences:

→ caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z) as the isotopes of interest.

example: $^{48}Ti^{+}$ interferes on $^{48}Ca^{+}$

Isobaric *doubly-* (or *multiply-*) *charged* ion interferences:

→ caused by ions consisting of more than one charge

example: $^{86}Sr^{++}$ interferes in $^{43}Ca^{+}$

Interferences ..... part 2

Isobaric *molecular* (or poly-atomic) interferences:

→ caused by ions consisting of more than one atom

example: $^{40}Ar^{16}O$ interferes in $^{56}Fe^{+}$

Intense adjacent signals:

→ signals of neighbouring ions with a very high intensity may contribute to the signal of an adjacent isotope by tailing

example: $^{238}U^{+}$ tails on $^{236}U^{+}$

How to deal with interferences ?

Example 1:

Interference of $^{48}Ti^+$ on $^{48}Ca^+$

Measure an interference-free Ti isotope, i.e. $^{47}Ti^+$.

Determine the amount of $^{48}Ti^+$ using the natural relative abundances.

$$^{48}Ca^+_{\text{corrected for Ti interference}} = {}^{48}Ca^+_{\text{measured}} - \underbrace{^{48}Ti^+}_{^{47}Ti^+_{\text{measured}} \times (^{48}Ti/^{47}Ti)_{\text{natural}}}$$

Example 2:

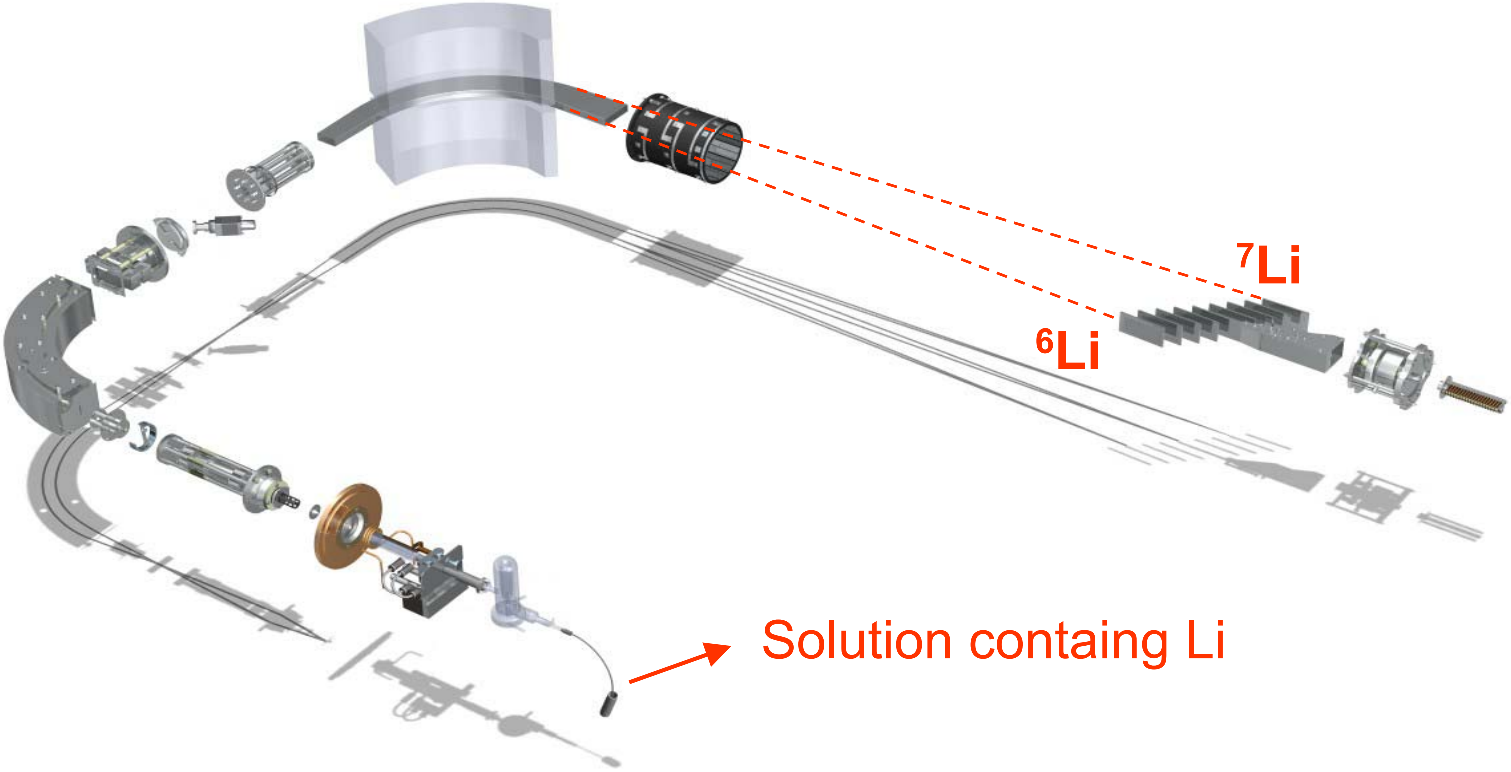
Interference of $^{86}Sr^{++}$ interferes in $^{43}Ca^+$

Measure $^{87}Sr^{++}$ on mass 43.5 (87/2).

Determine the amount of $^{86}Sr+^+$ using the natural relative abundances.

$$^{43}Ca^+_{\text{corrected for Sr interference}} = {}^{43}Ca^+_{\text{measured}} - \underbrace{^{86}Sr+^+}_{^{87}Sr^{++}_{\text{measured}} \times (^{86}Sr/^{87}Sr)_{\text{natural}}}$$

Example: Lithium isotopes



Lithium isotopes: challenges

- *High mass bias for light elements*
- *Sensitivity*
- *Background*
- *Potential interferences*

Instrumental mass bias

- Li-standard NIST L-SVEC:

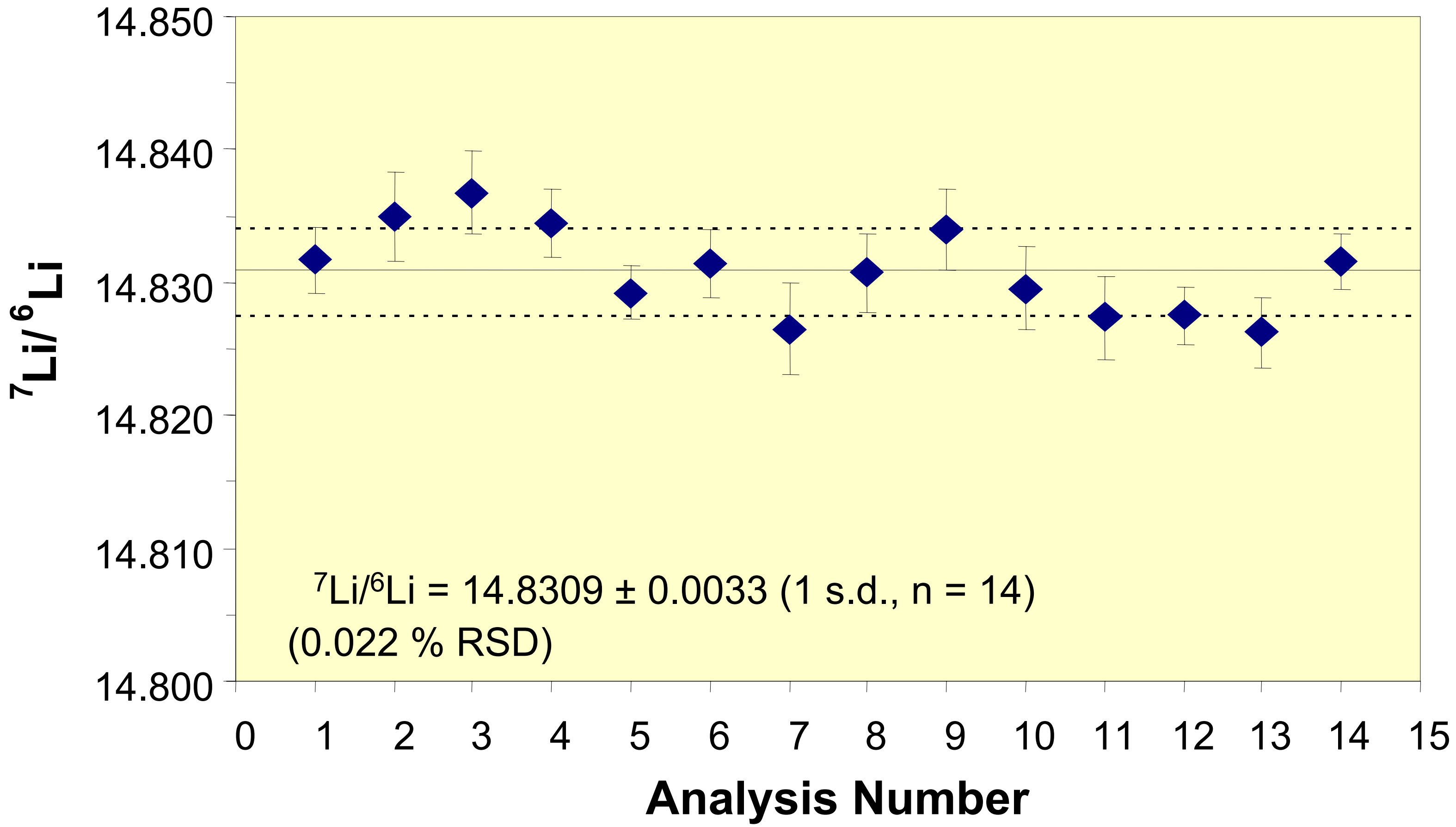
  measured ^{7}Li/^{6}Li ratio ~15
  true ^{7}Li/^{6}Li ratio ~12.15 (Qi et al. 1997)
  → mass bias ~ 25% !!

- No internal correction possible

- External correction by "sample-standard bracketing"

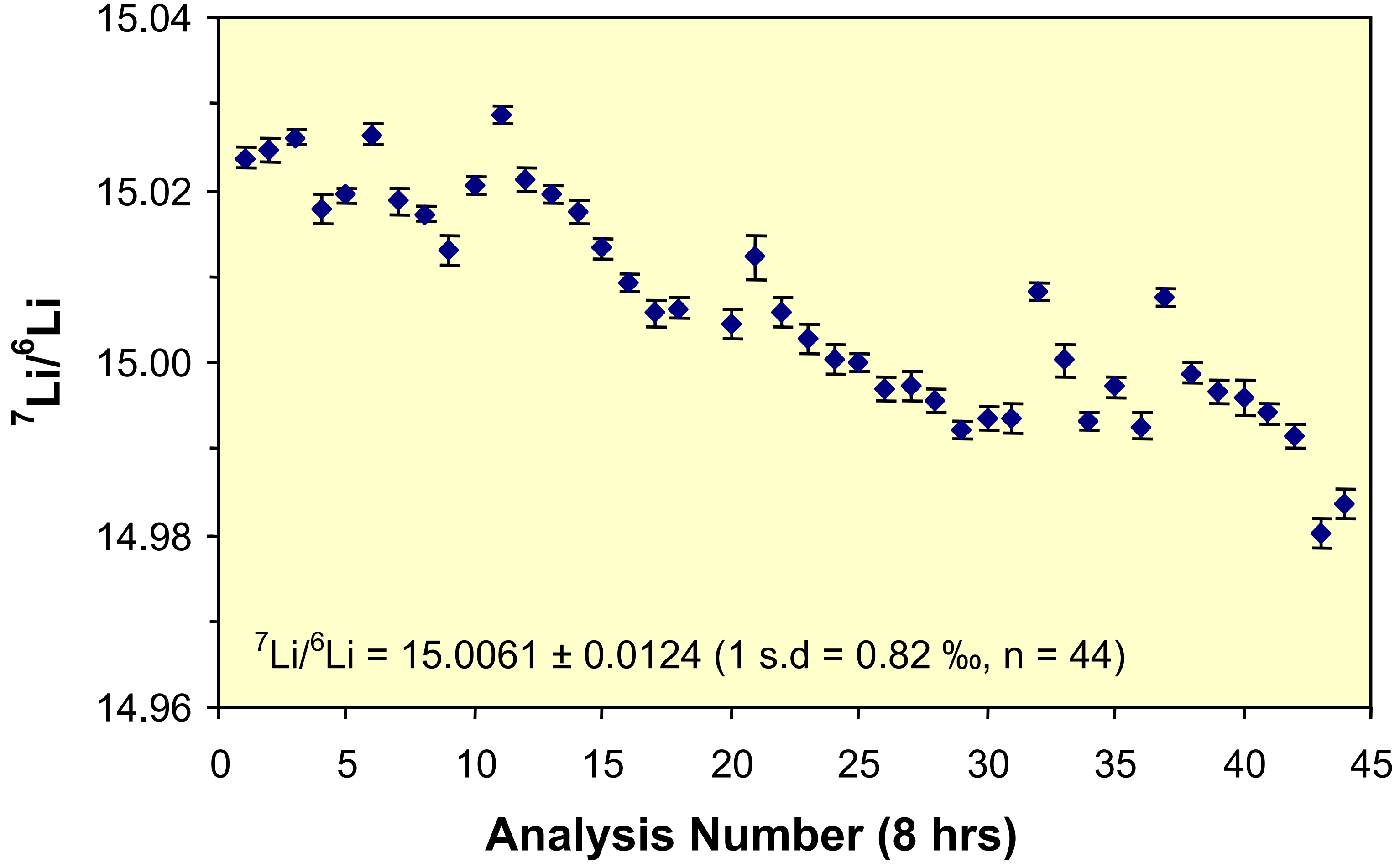
→ $$\delta = \left(\frac{R_{sample}}{R_{standard}} - 1 \right) \times 1000 \text{ ‰}$$

Mass bias

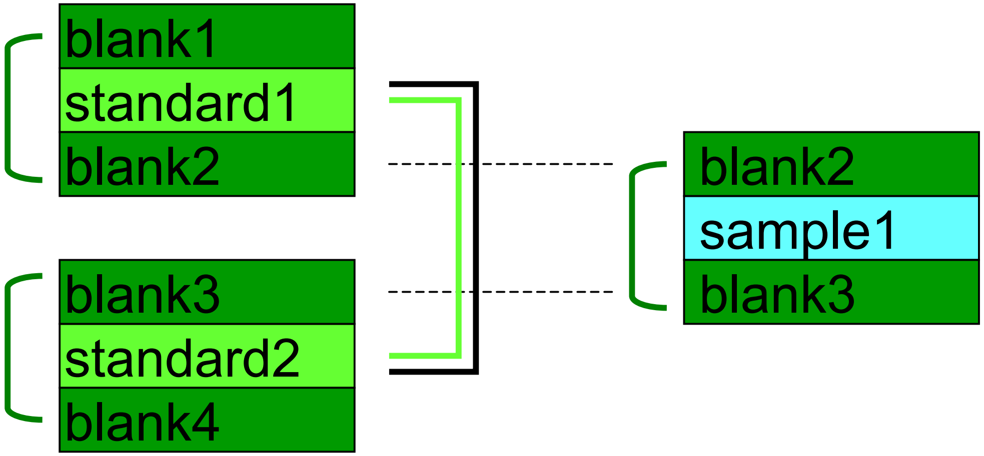


$^{7}Li/^{6}Li$ = 14.8309 ± 0.0033 (1 s.d., n = 14)
(0.022 % RSD)

Long-term reproducibility of ^{7}Li/^{6}Li



Li isotopes – analysis sequence

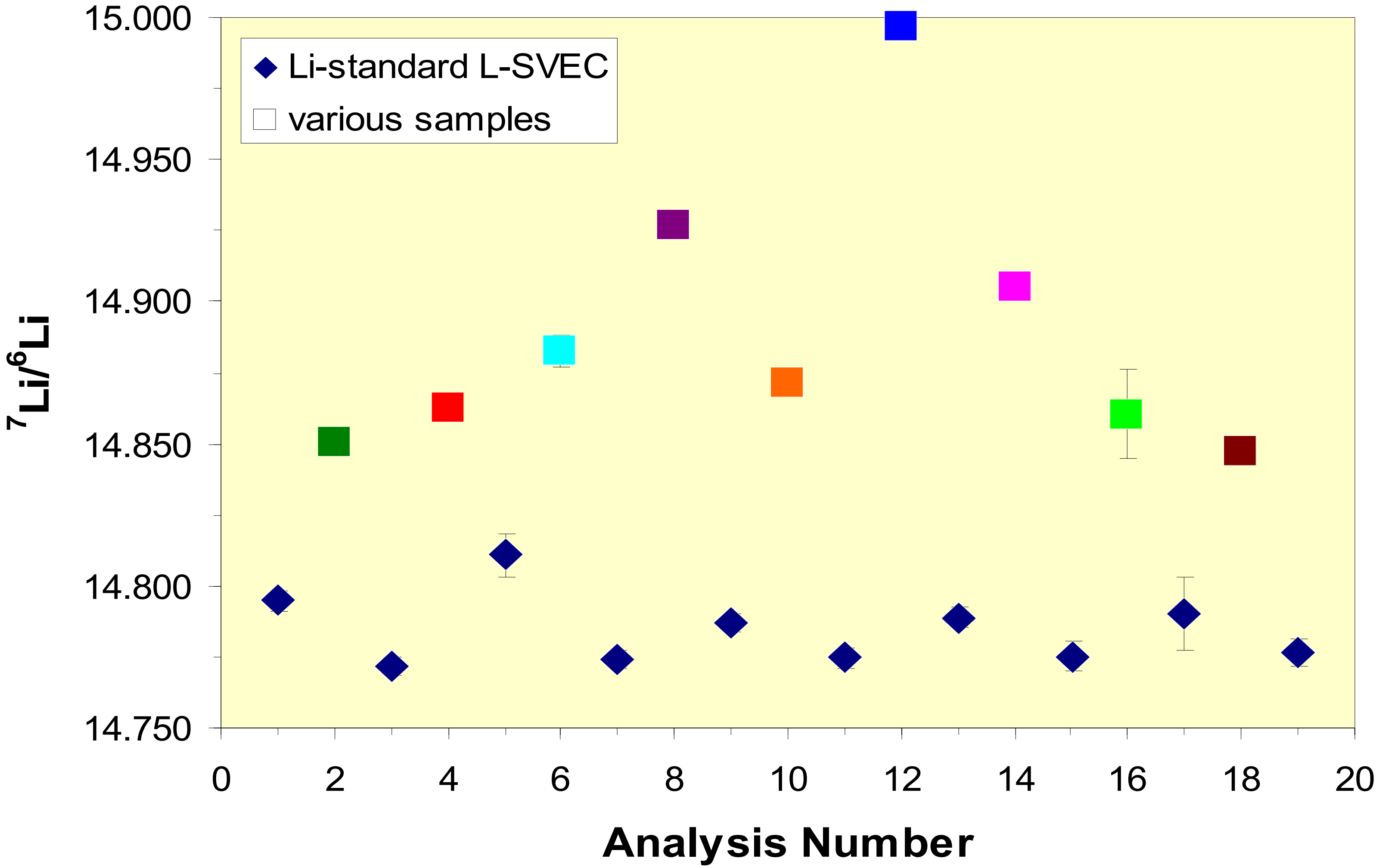


Blank correction $I_{st}-I_{bl}$

$I_{sa}-I_{bl}$

Sample normalisation (delta-values) $\delta = (R_{sa}/R_{st}-1)x1000$

Li isotopes – example sample/standard



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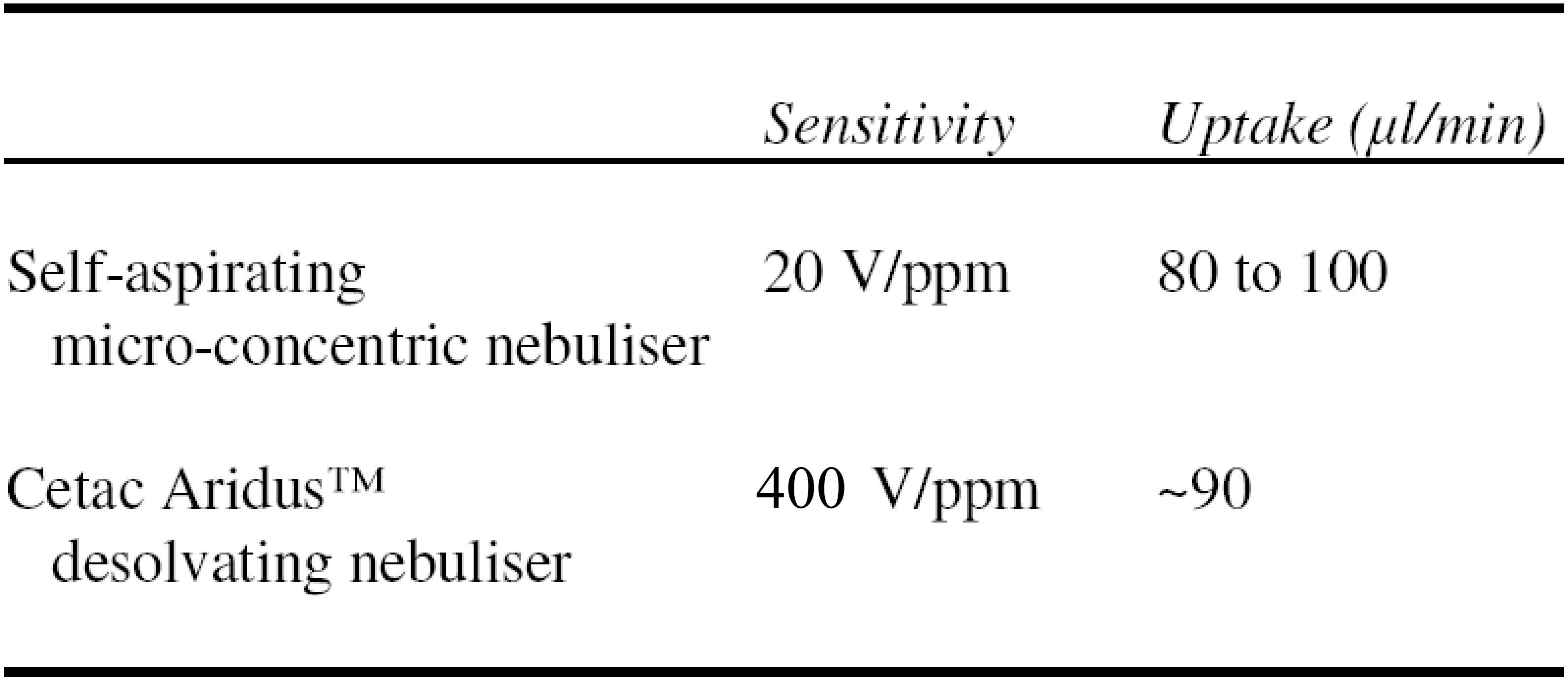
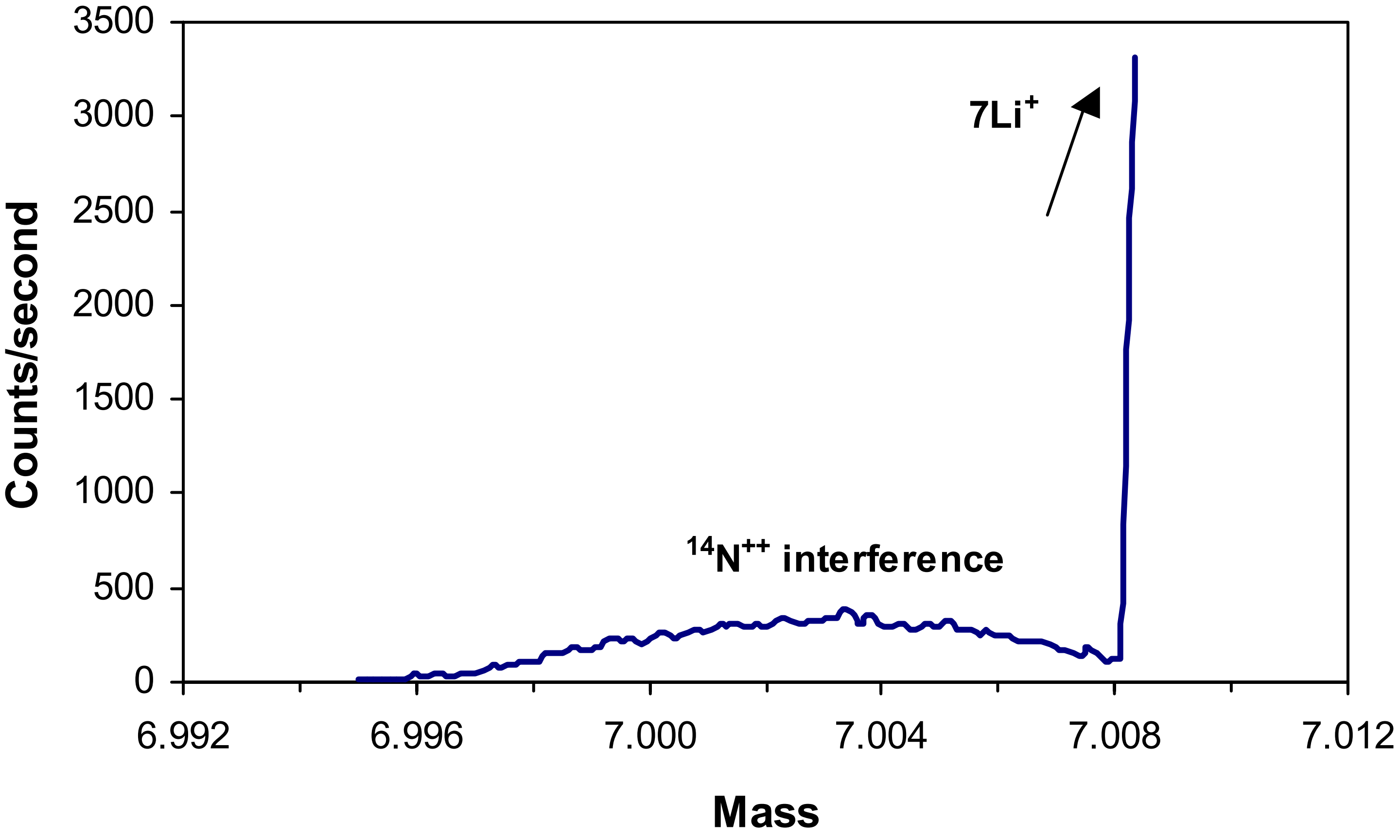
Li - Sensitivity

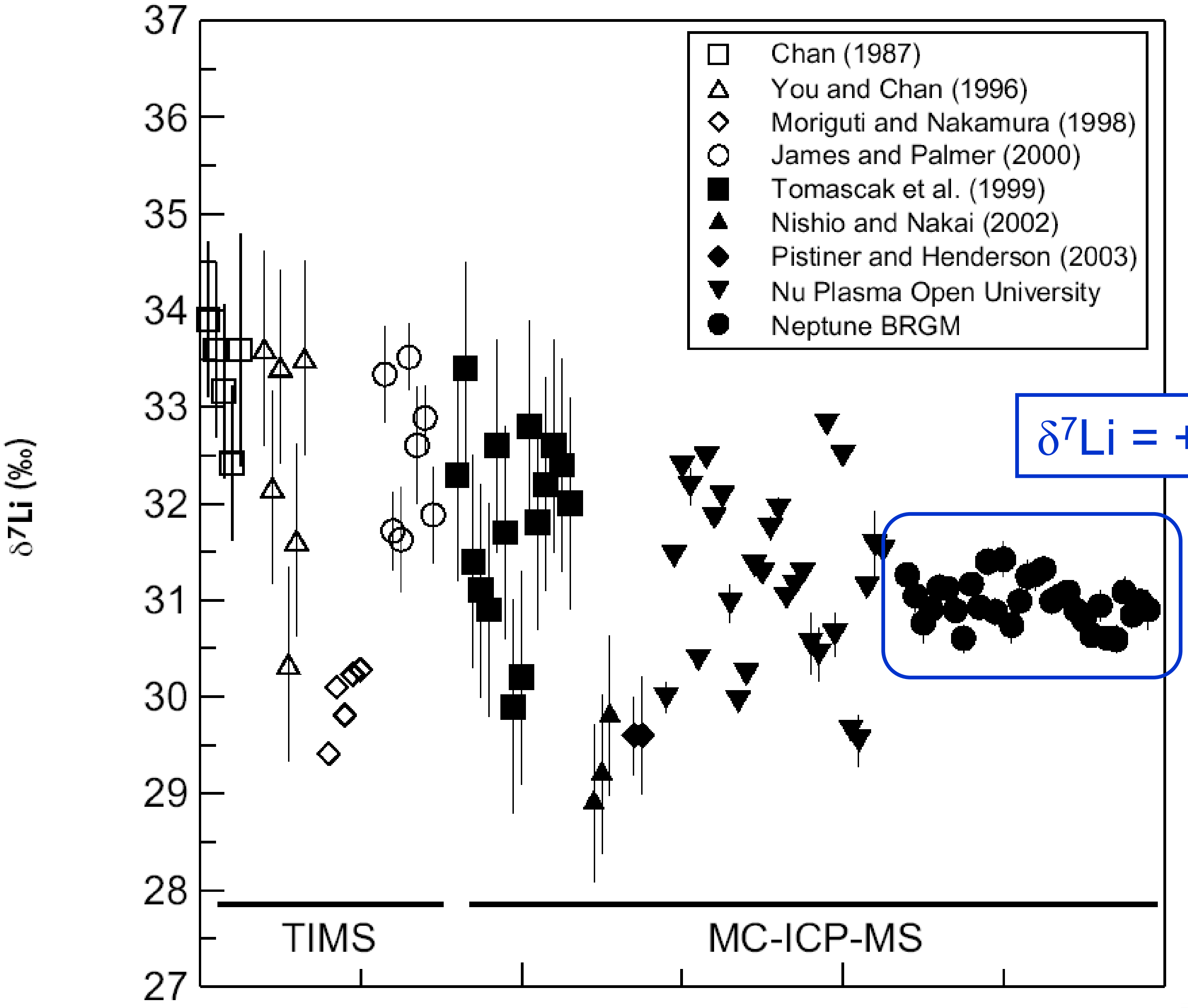


	Sensitivity	*Uptake (μl/min)*
Self-aspirating micro-concentric nebuliser	20 V/ppm	80 to 100
Cetac Aridus™ desolvating nebuliser	400 V/ppm	~90

Interference of doubly charged species: $^{14}N^{++}$



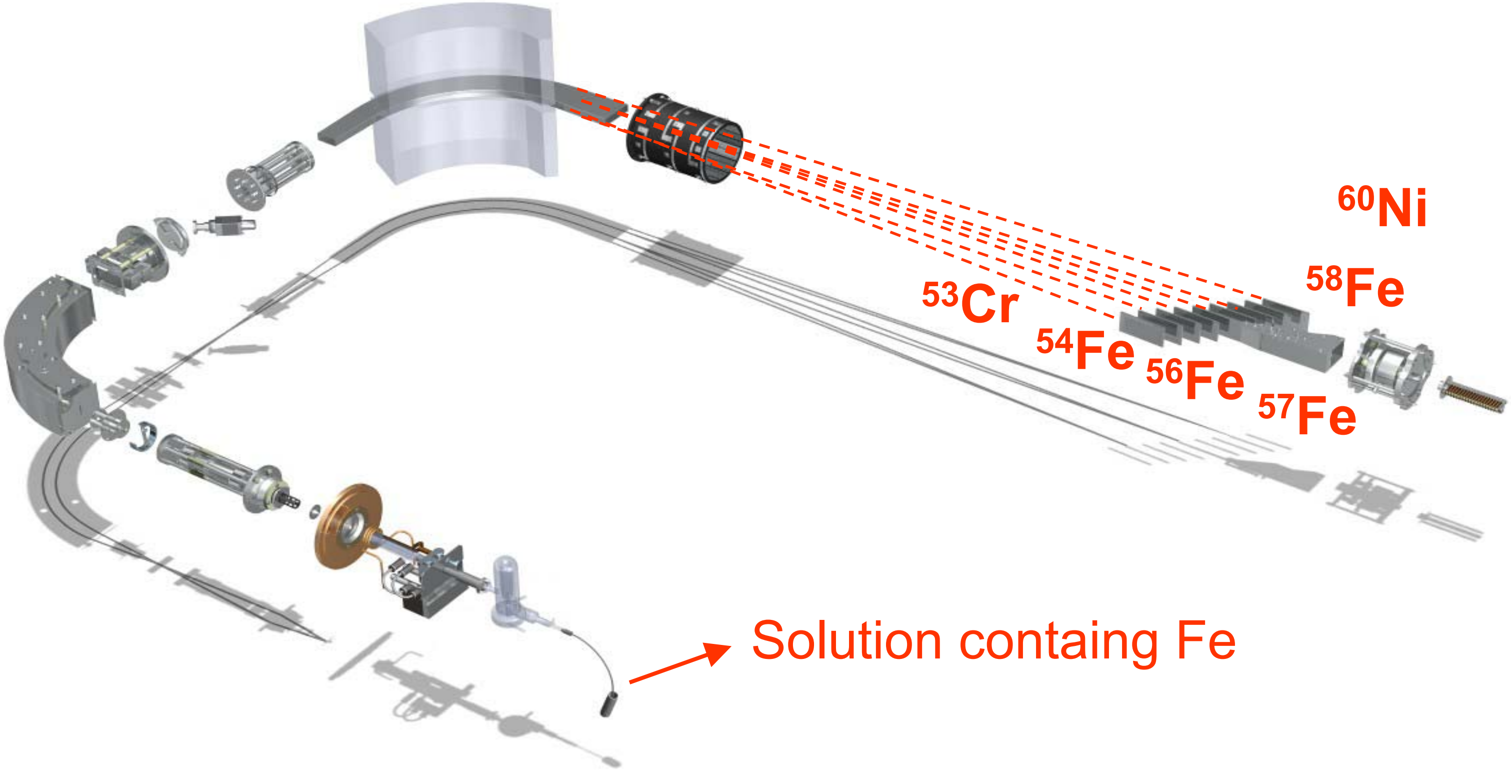
Seawater δ^7Li reported from a customer's lab (BRGM France)



δ^7Li = +31.0 ‰ ± **0.1** (2σ, n=31)

Millot et al. (2004) Geostandard Newsletter V28, 153-159.

Example: Iron isotopes



Iron isotopes: challenges

Molecular Interferences

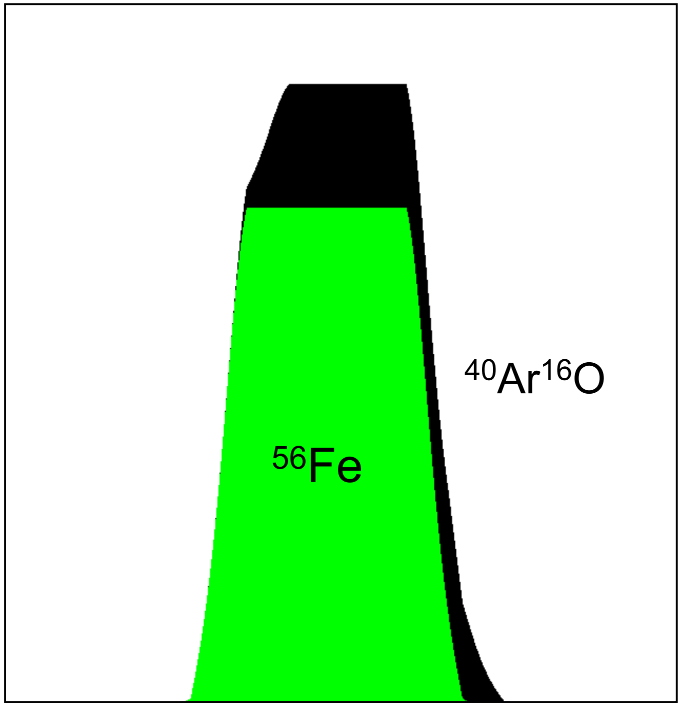
^{54}Fe: $^{40}Ar^{14}N$
^{56}Fe: $^{40}Ar^{16}O$
^{57}Fe: $^{40}Ar^{16}O^{1}H$
^{58}Fe: $^{40}Ar^{18}O$

Atomic Interferences

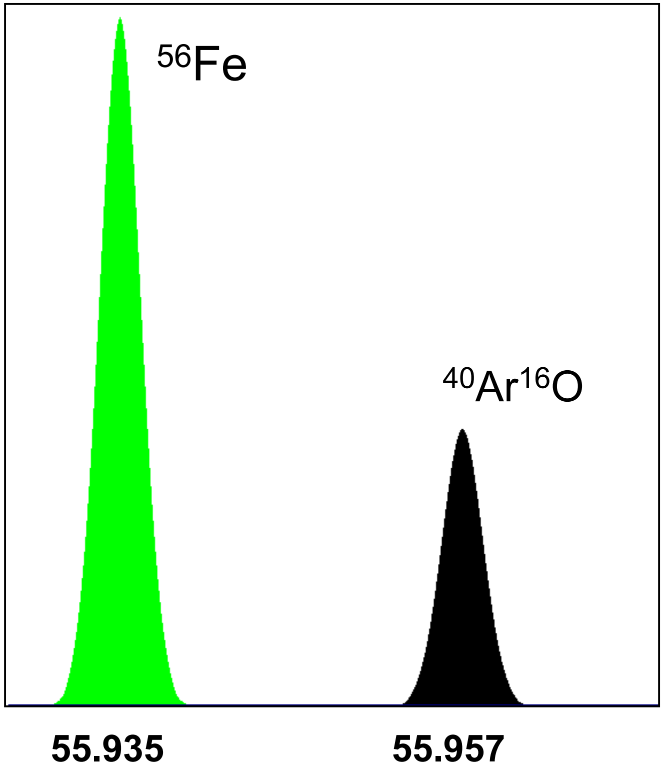
^{54}Fe: ^{54}Cr
^{58}Fe: ^{58}Ni

How to deal with interferences ?

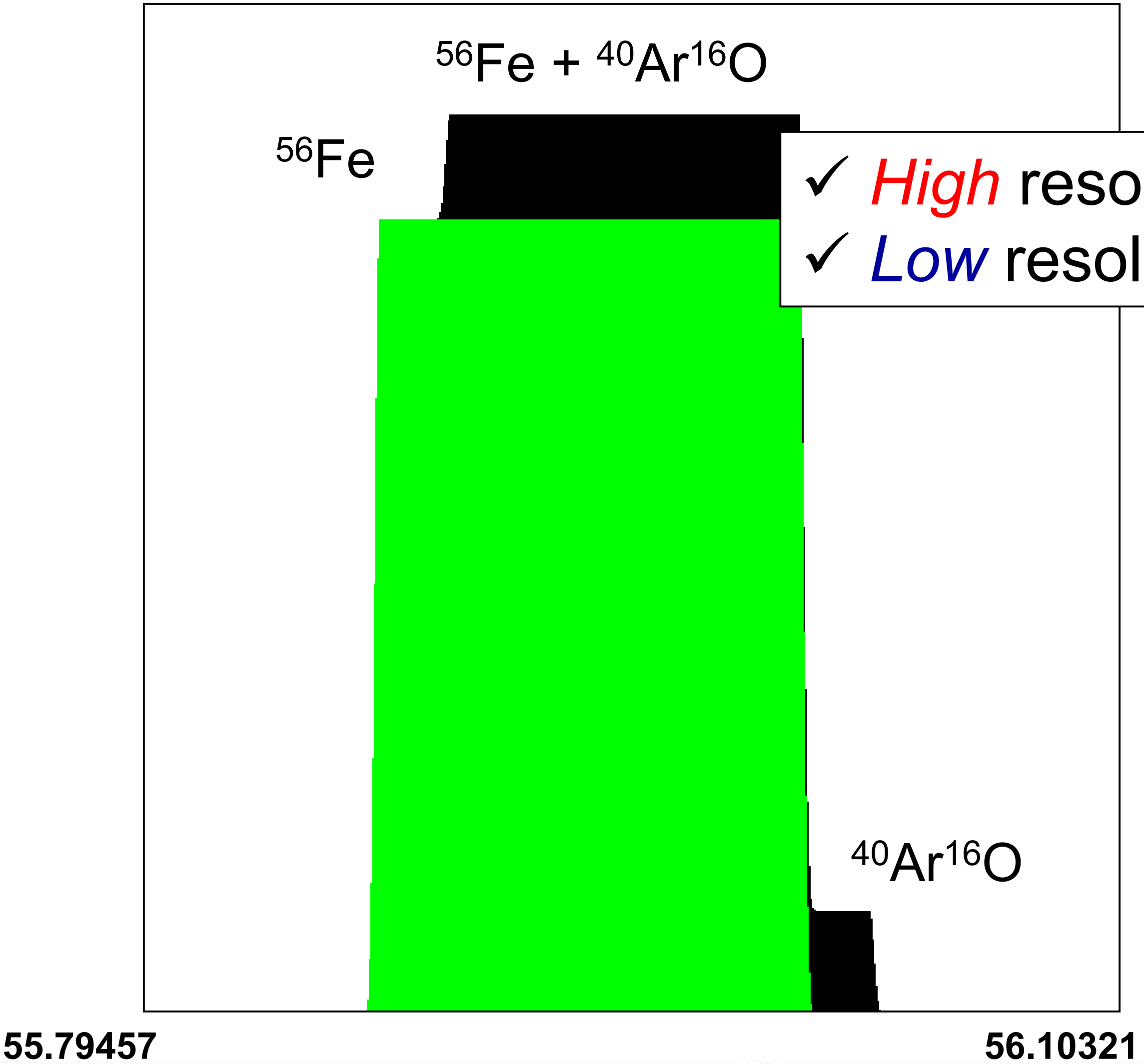
Low resolution (“normal” mode)



High resolution (narrow slits)



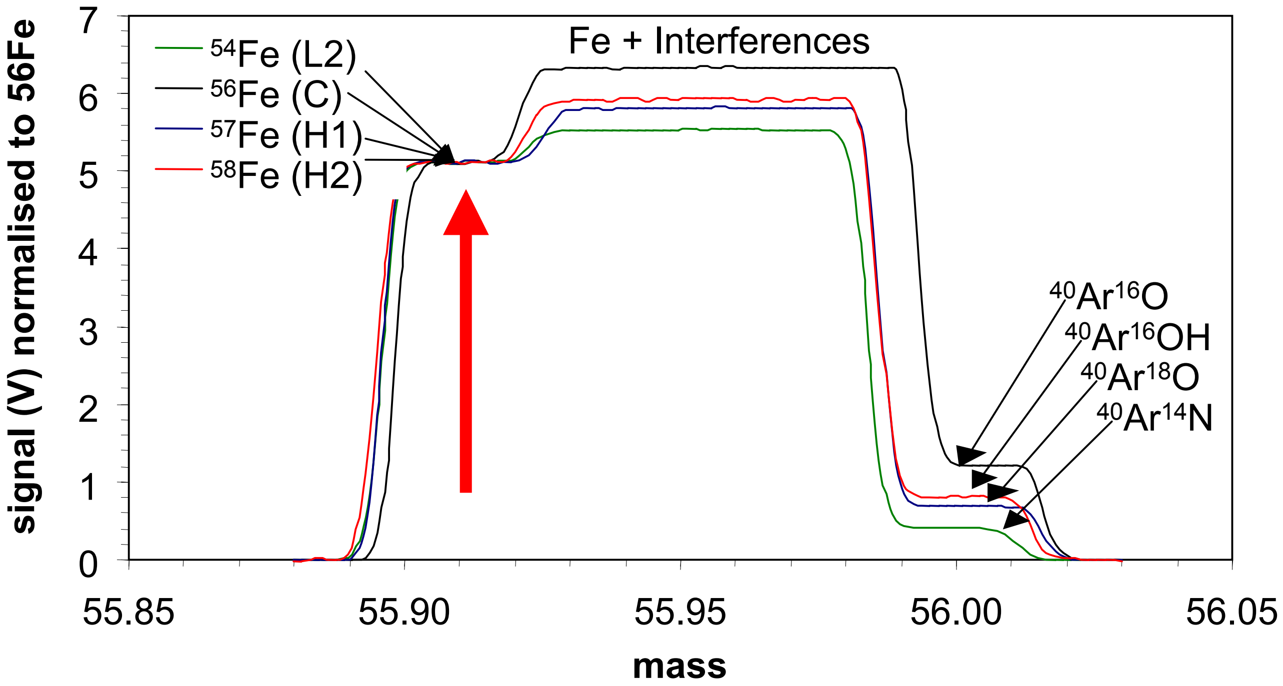
Fe isotopes – high resolution

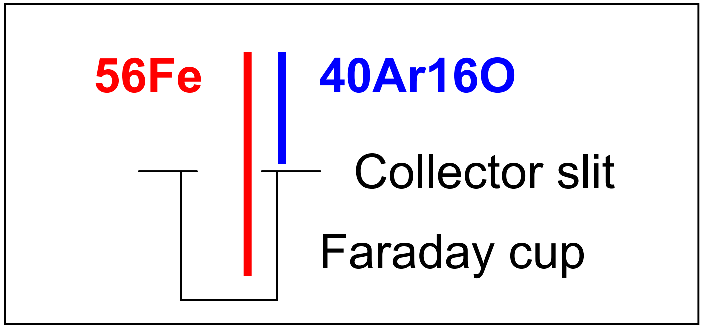


- ✓ *High* resolution entrance slit
- ✓ *Low* resolution exit slit

Peakscan of Fe

(wet plasma, 1 ppm Fe, medium resolution slit)





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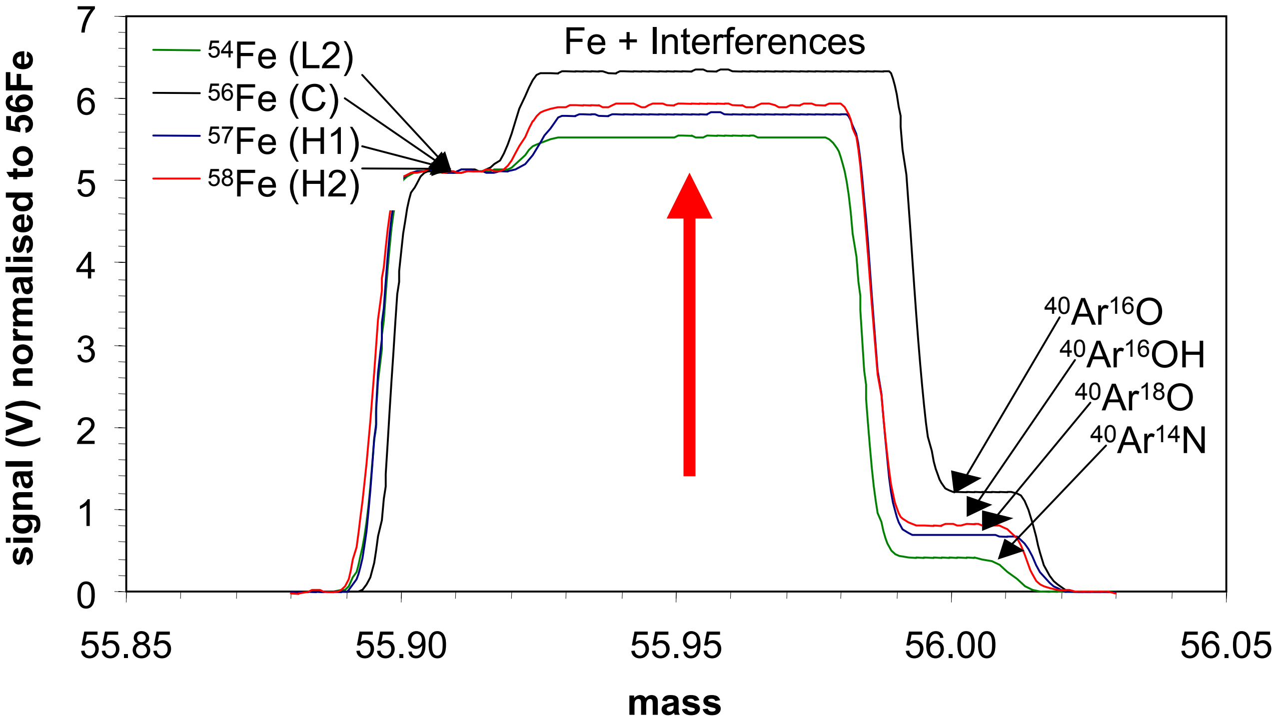
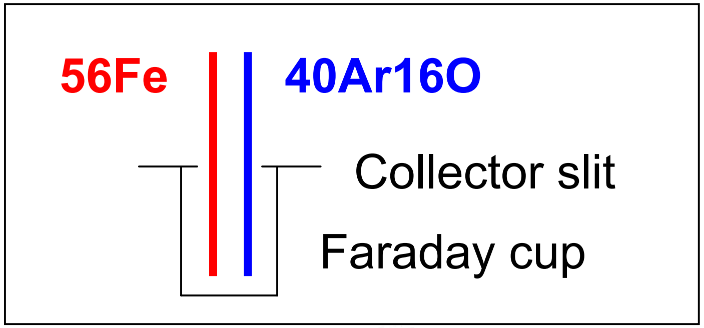
Peakscan of Fe

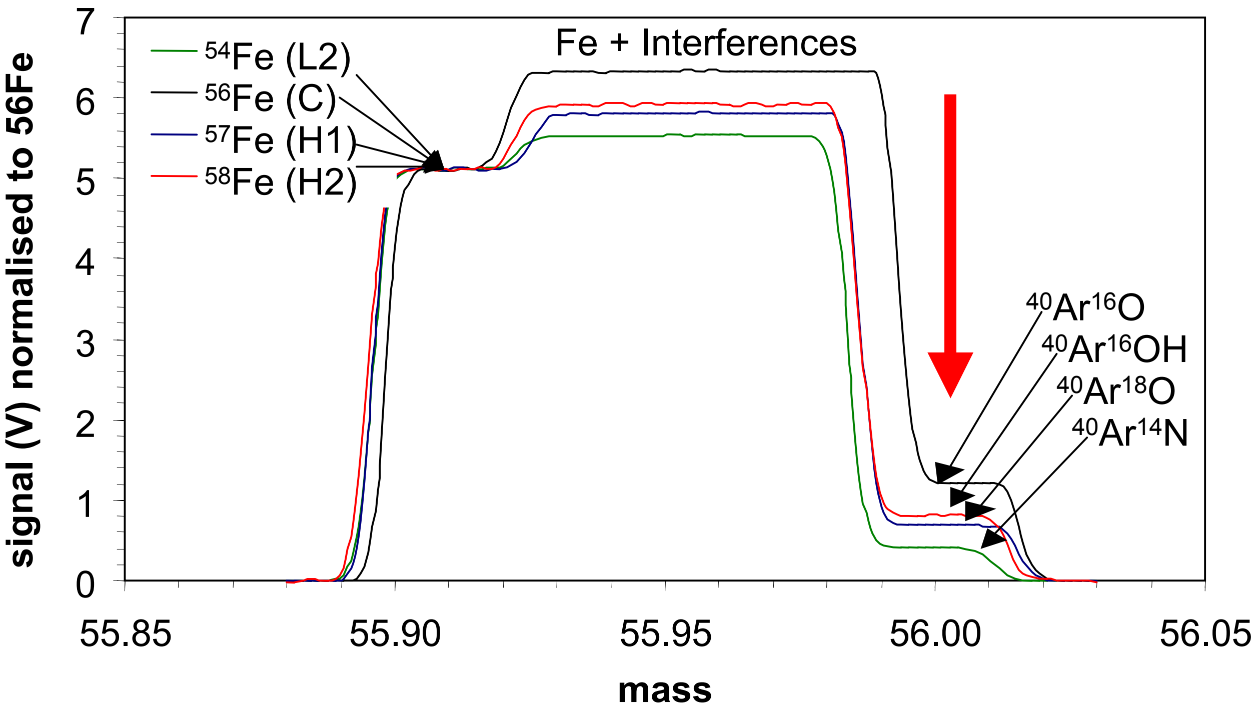
(wet plasma, 1 ppm Fe, medium resolution slit)

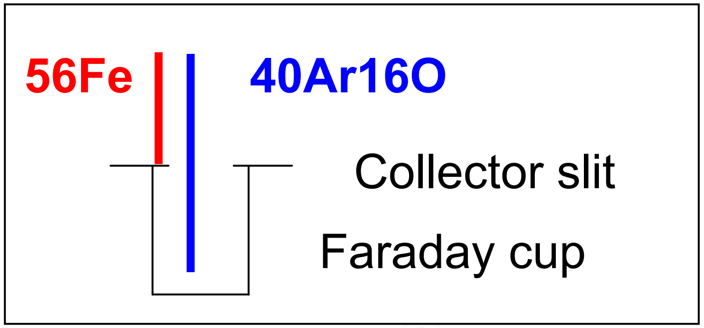




Peakscan of Fe

(wet plasma, 1 ppm Fe, medium resolution slit)

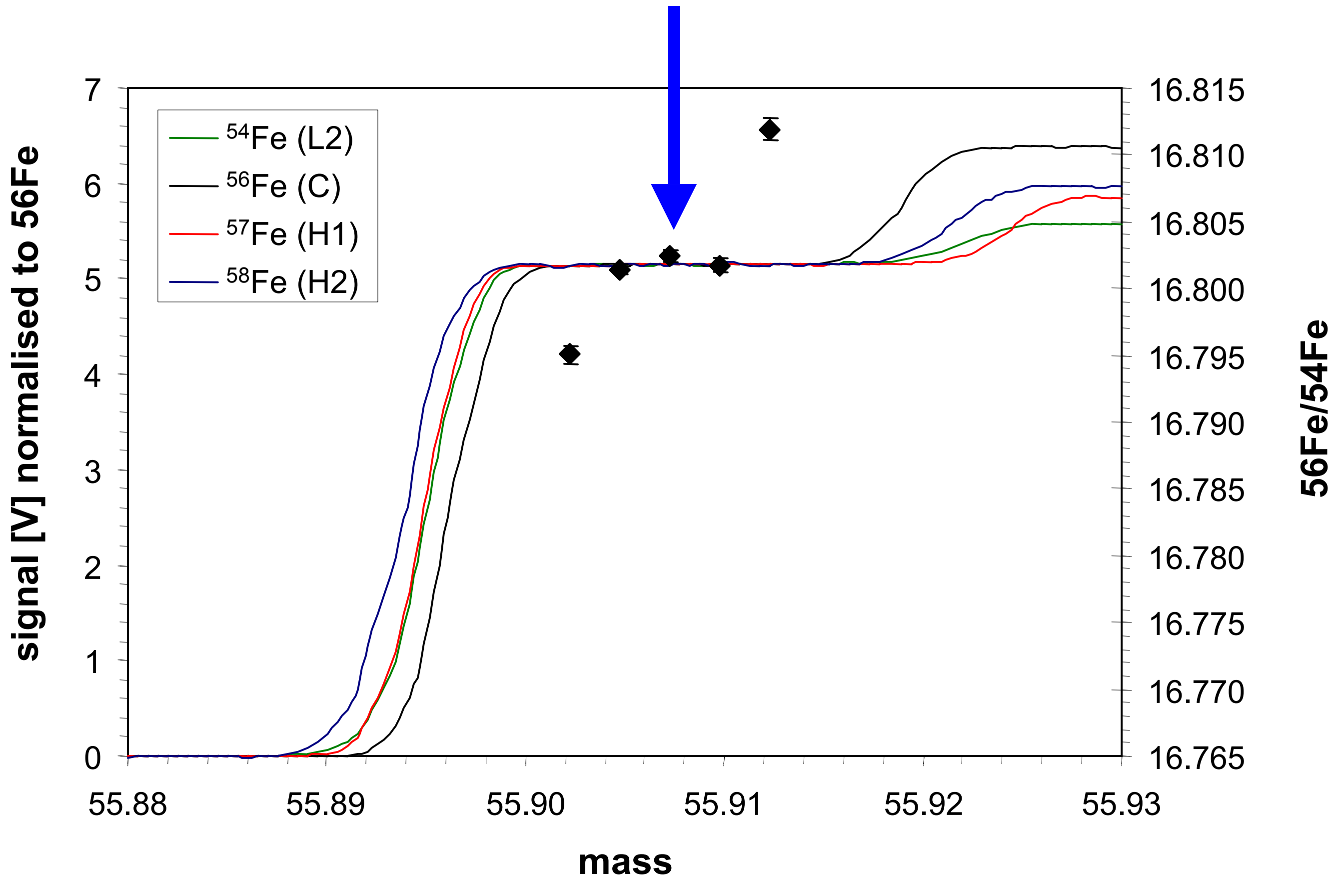




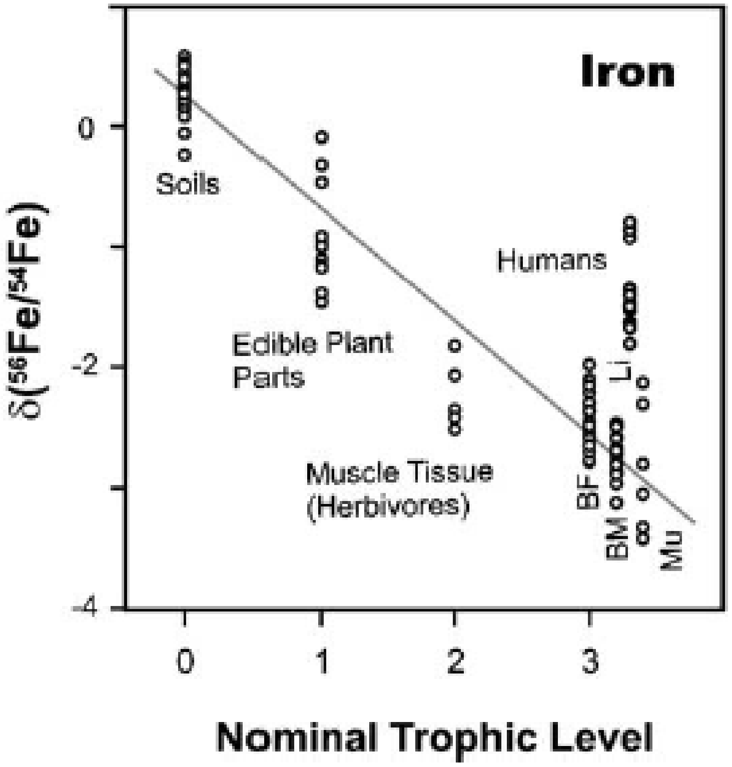
Collector slit

Faraday cup

Fe isotopes - plateau scan



Fe isotopic fractionation along food chain

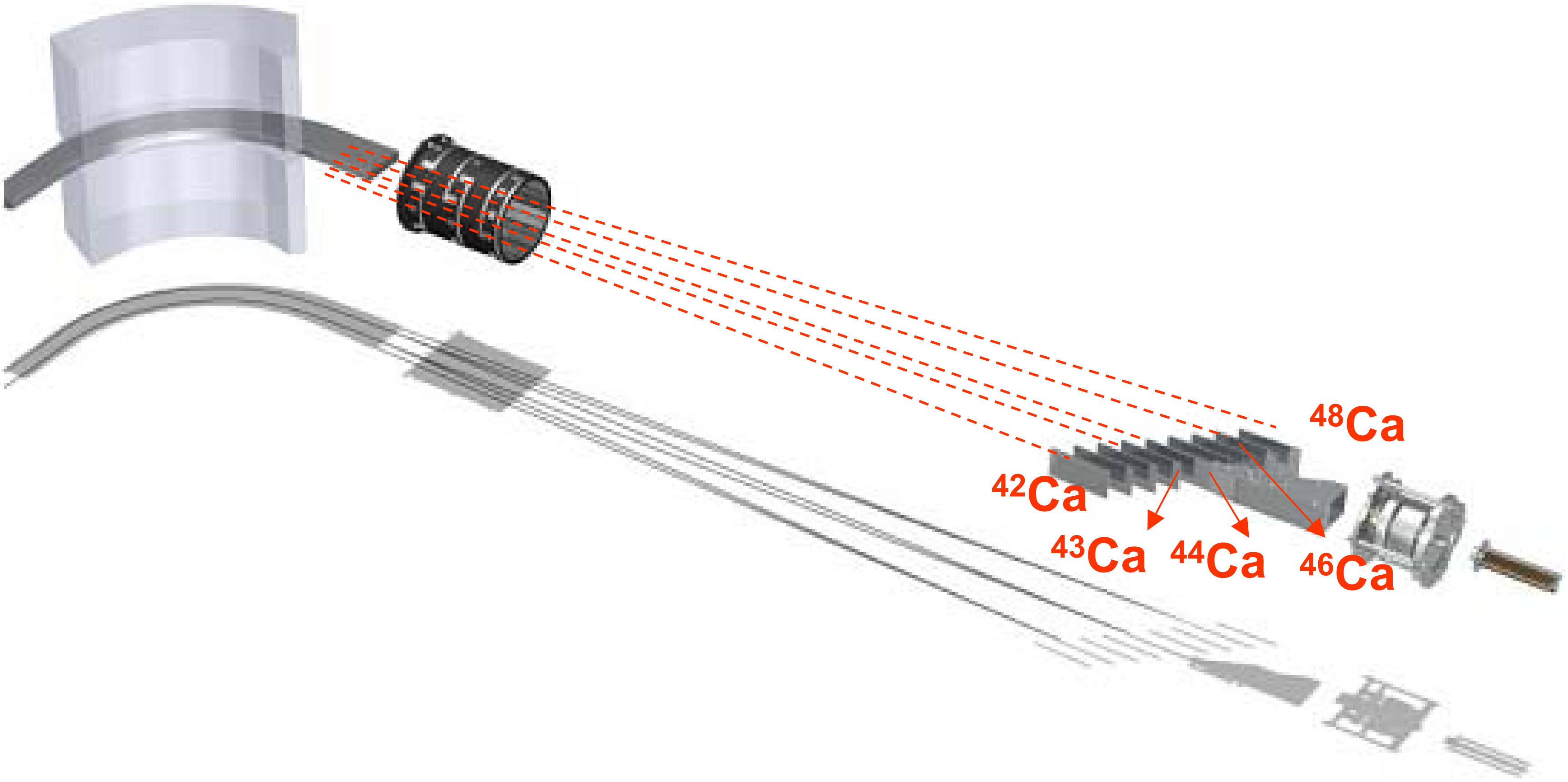


Potential use of Fe isotopes:
- Study Fe redox cycle
- Trace microbial activity
- Study Fe metabolism in humans

→ Fractionation effects in higher organisms

Walczyk and von Blanckenburg (2005) Int. Journal of Mass Spectrometry V242, 117-134.

Example: Calcium isotopes



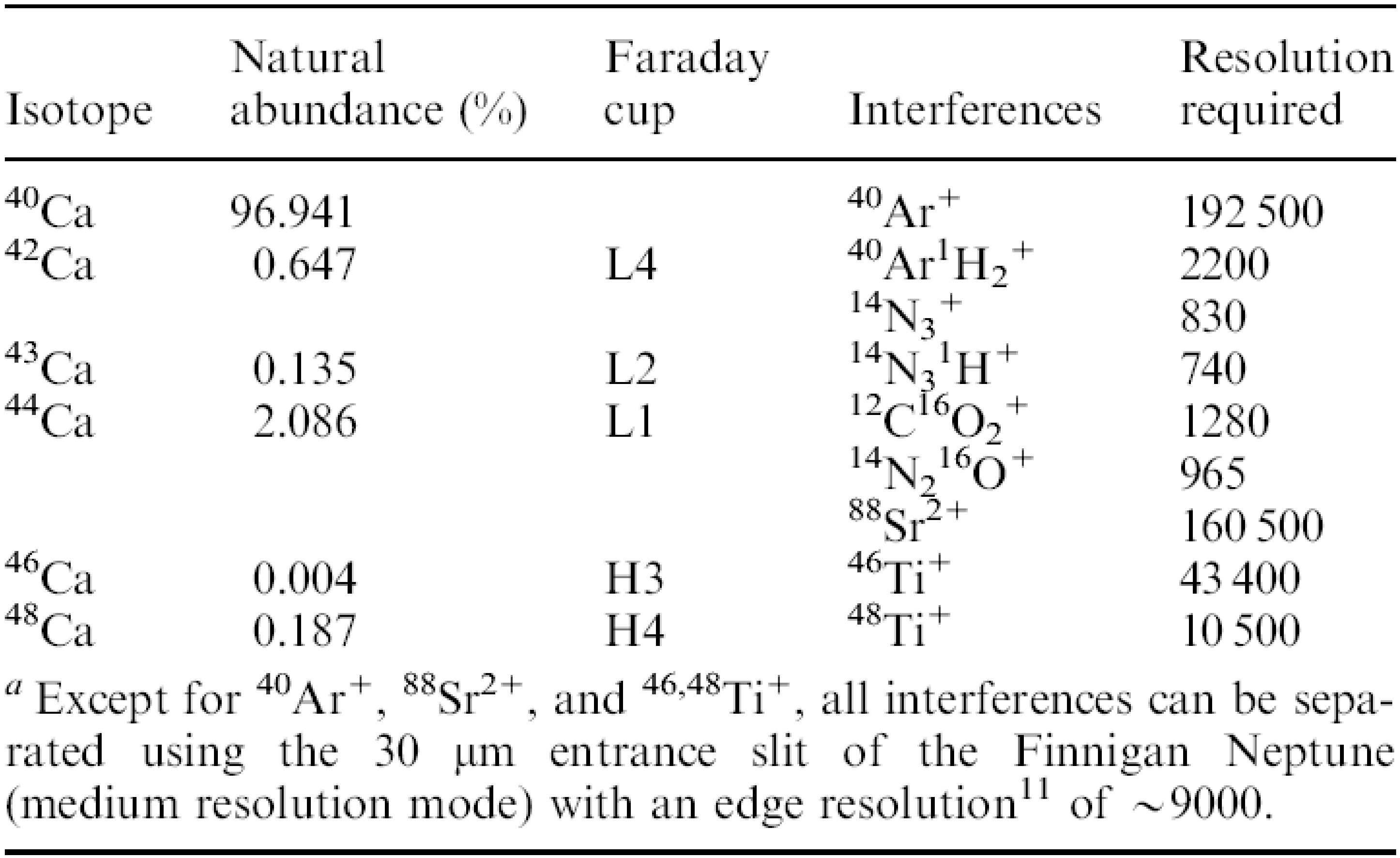
Calcium isotopes: challenges

- the extent of isotopic variations are small, so high precision data are required in order to resolve isotopic effects.

- the intense $^{40}Ar^+$ ion beam produced by the inductively coupled plasma source cause interferences across the entire Ca mass range.

→ High mass resolution is needed

Calcium isotopes: interferences

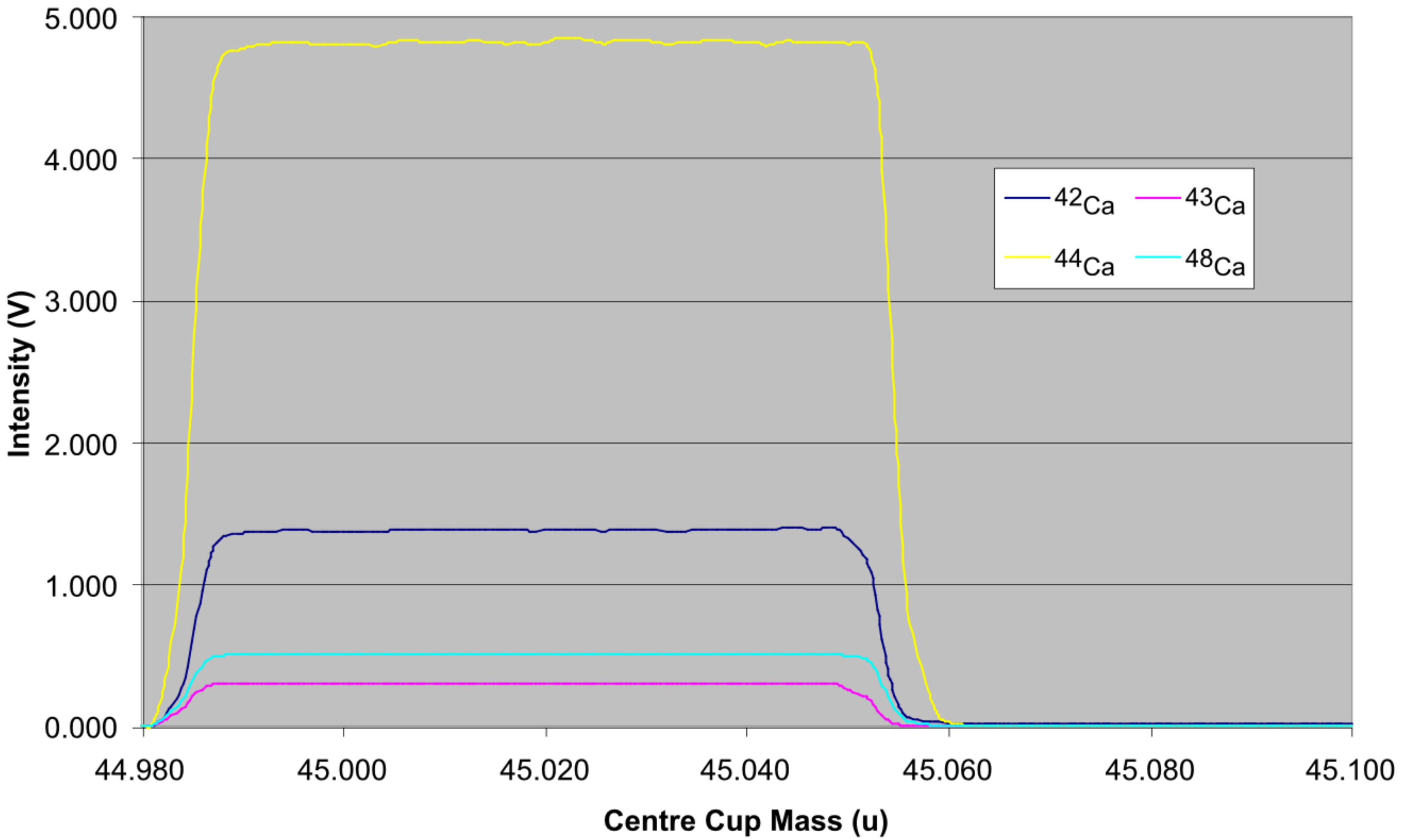


Isotope	Natural abundance (%)	Faraday cup	Interferences	Resolution required
^{40}Ca	96.941		$^{40}Ar^+$	192 500
^{42}Ca	0.647	L4	$^{40}Ar^1H_2{}^+$	2200
			$^{14}N_3{}^+$	830
^{43}Ca	0.135	L2	$^{14}N_3{}^1H^+$	740
^{44}Ca	2.086	L1	$^{12}C^{16}O_2{}^+$	1280
			$^{14}N_2{}^{16}O^+$	965
			$^{88}Sr^{2+}$	160 500
^{46}Ca	0.004	H3	$^{46}Ti^+$	43 400
^{48}Ca	0.187	H4	$^{48}Ti^+$	10 500

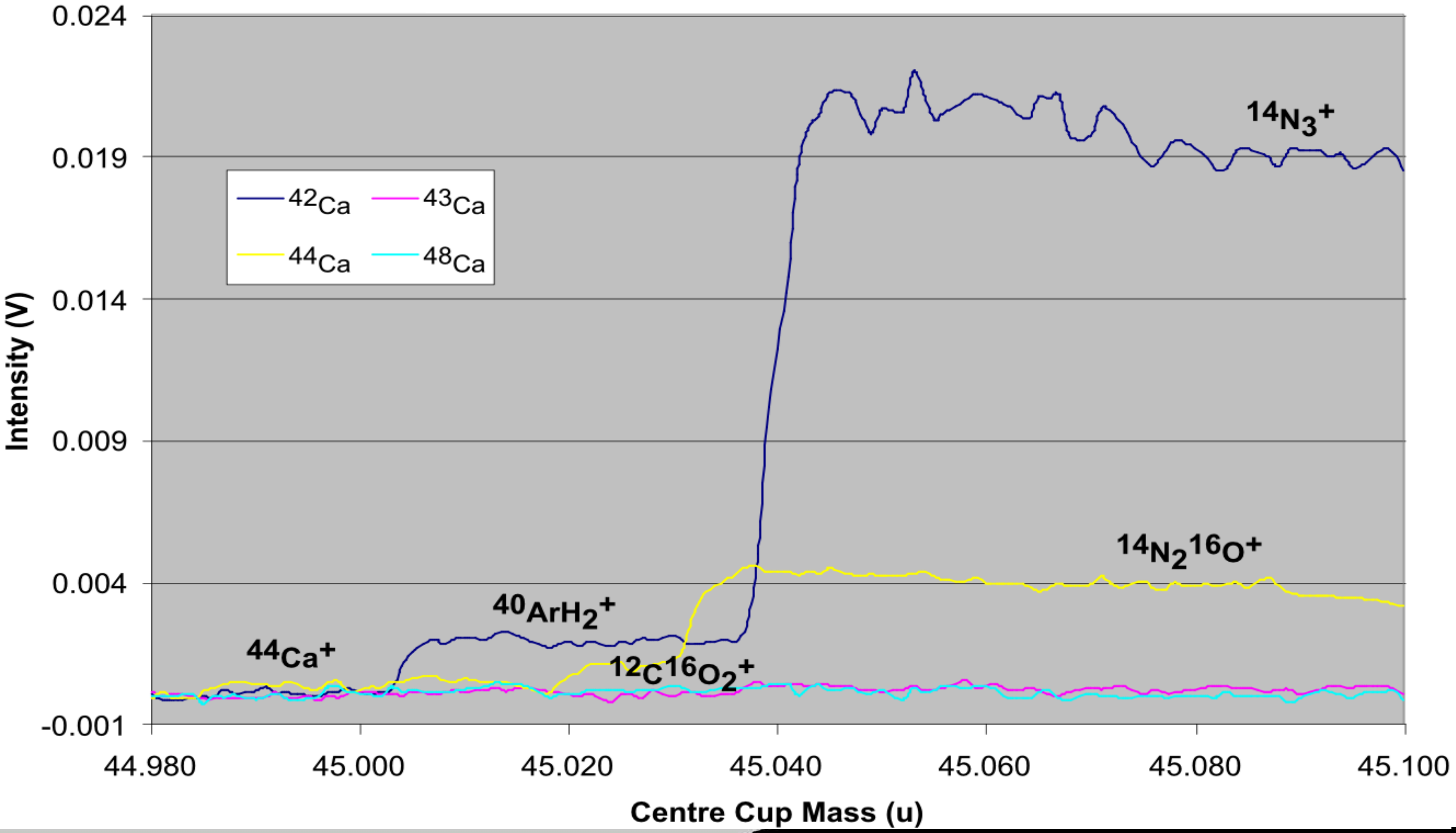
[a] Except for $^{40}Ar^+$, $^{88}Sr^{2+}$, and $^{46,48}Ti^+$, all interferences can be separated using the 30 μm entrance slit of the Finnigan Neptune (medium resolution mode) with an edge resolution[11] of ~9000.

Wieser et al. (2004) Journal of Analytical Atomic Spectrometry V19, 844-851

5 ppm SRM915a in 3% HNO_3



Background (3% HNO_3)



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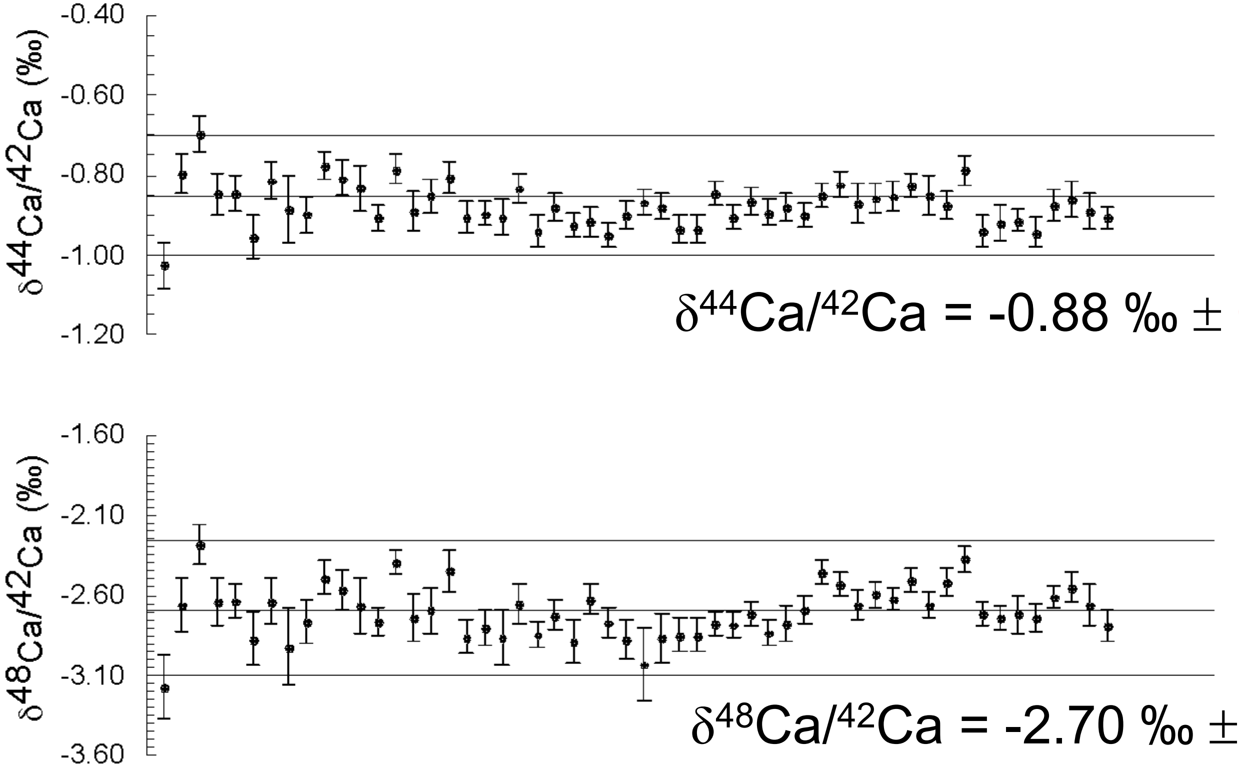
IAPSO Ca isotope compositions reported from a customer's lab (Ruhr University Bochum)

SRM915a vs. IAPSO Ca standards

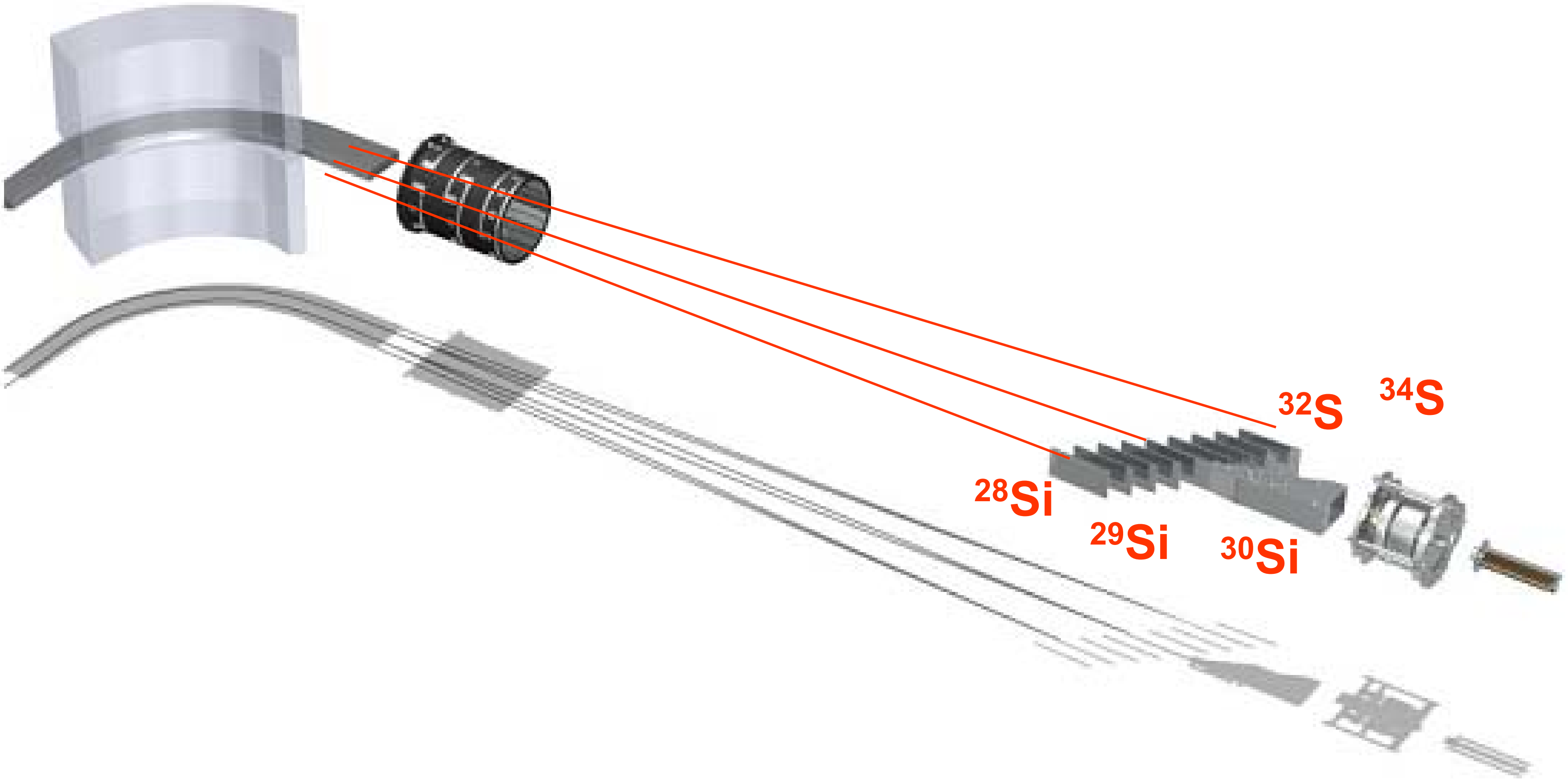


$\delta^{44}Ca/^{42}Ca = -0.88$ ‰ ± **0.11** (2σ)

$\delta^{48}Ca/^{42}Ca = -2.70$ ‰ ± **0.33** (2σ)

Wieser et al. (2004) Journal of Analytical Atomic Spectrometry V19, 844-851

Example: Sulfur (and silicon) isotopes



Sulfur isotopes: challenges

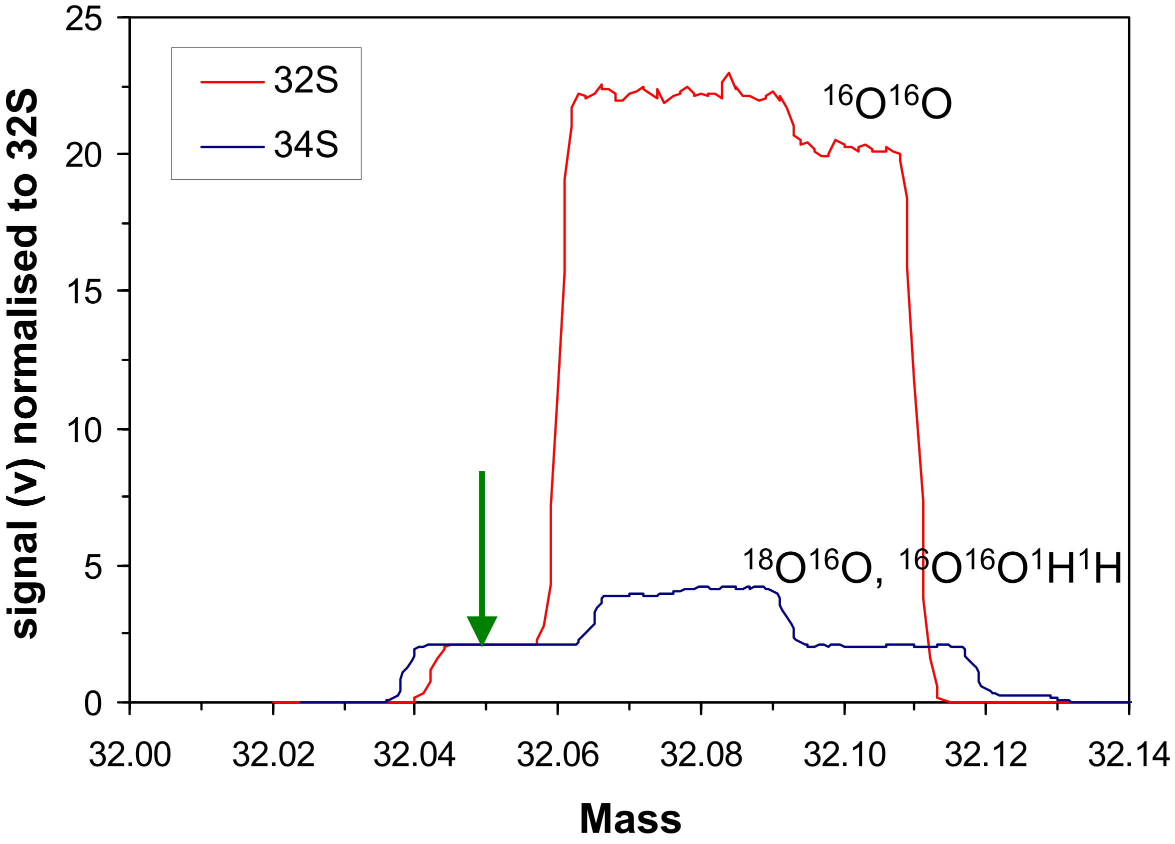
Classical technique to measure S isotopes is by Stable Isotope Mass Spectrometry (like C,N and O isotopes) (e.g., Finnigan Delta series, Finnigan MAT253)

Peter Evans et al. (2004), LGC, Teddington, UK:

“The thermoFinnigan Neptune high resolution multi-collector ICPMS can provide precise, reliable δ^{34}S values in **aqueous** and **solid** samples.”

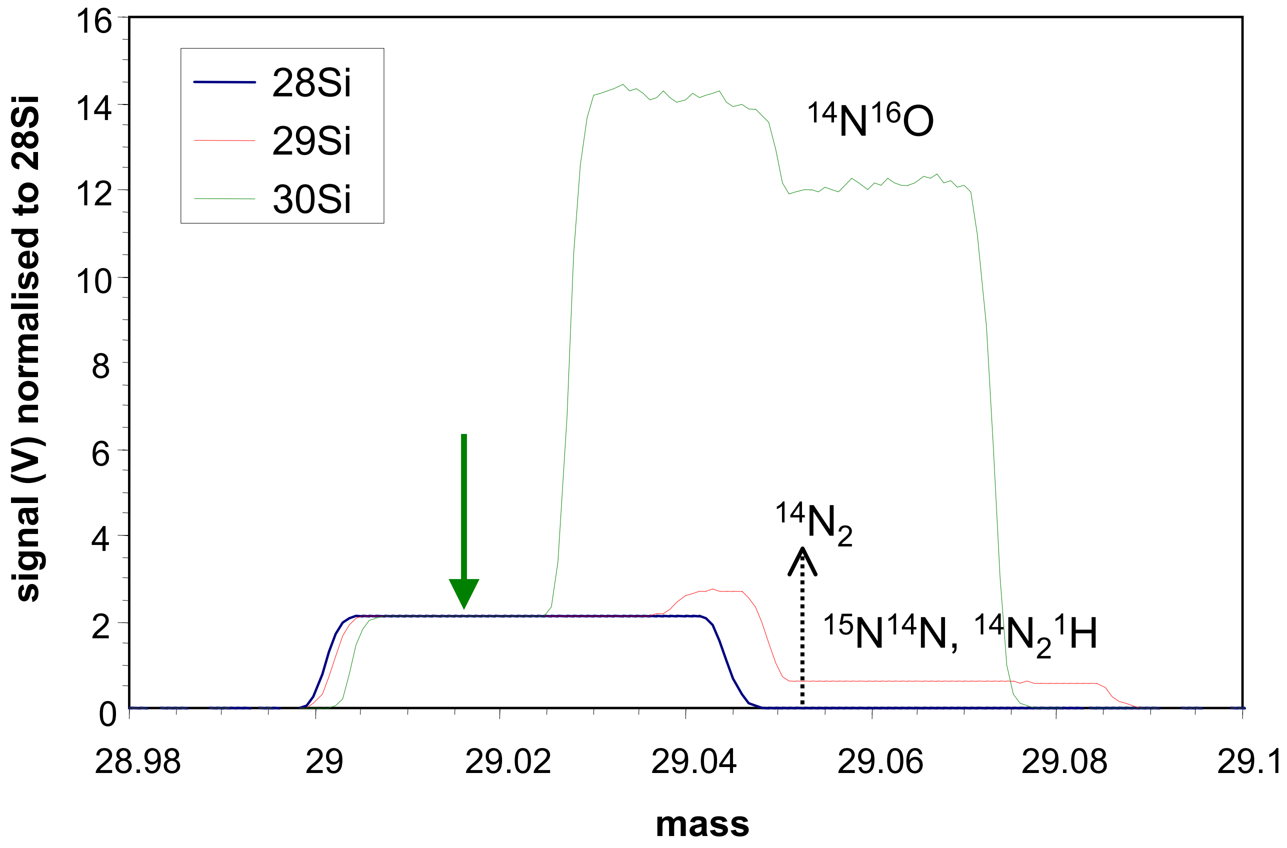
“Internal precision < 0.2 ‰ is routinely achievable.”

Peak scan for S isotopes
(wet plasma, 10ppm S, medium resolution slit)



Peak scan for Si isotopes

(wet plasma, 2ppm Si, medium resolution slit)



Internal correction using Si isotopes

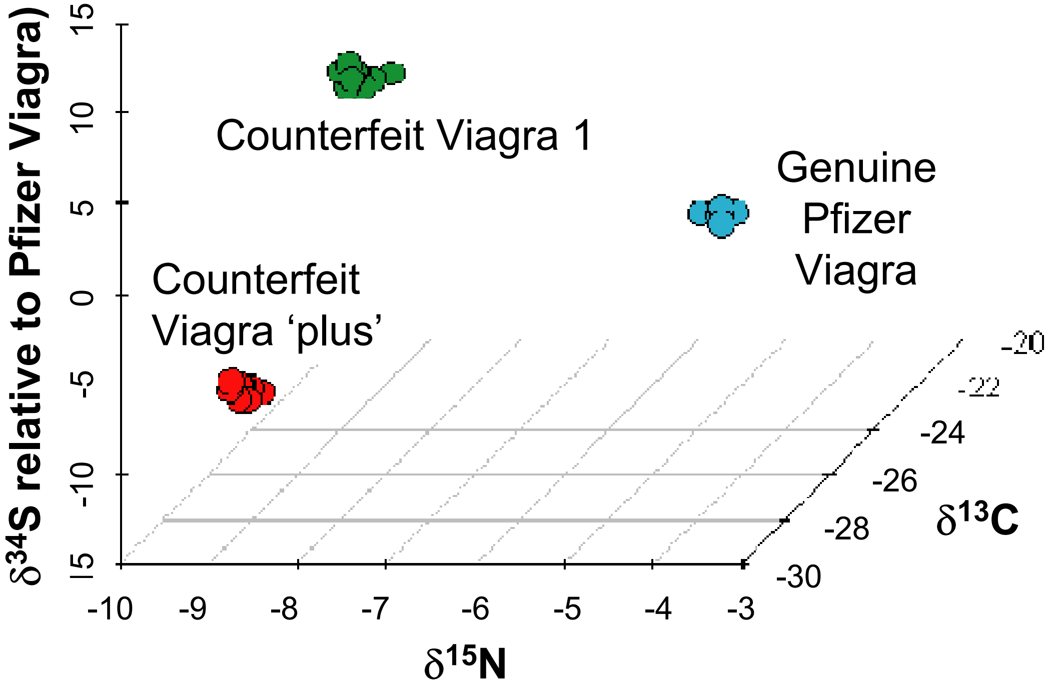
The uses of silicon to internally correct for drift in instrumental mass discrimination has two benefits:

1. It reduces the need to bracket samples with standards, significantly increasing sample throughput.

2. Internal correction compensates for matrix induced changes to mass discrimination reducing the need for sample pre-treatment.

Viagra: S isotope composition reported from a customer's lab (LGC, UK)

Viagra (sildenafil) provides a case study for the application of **laser ablated** measurements of $\delta^{34}S$.



Peter Evans et al. (2004), LGC, Teddington, UK.

Summary

- The Finnigan NEPTUNE is a high precision multicollector ICPMS based on a proven ICP-source (ELEMENT2) and an ultimate precision MC-analyzer (TRITON).

- The Finnigan NEPTUNE enables high precise stable isotope measurements due to stable mass bias (e.g. Li).

- The Finnigan NEPTUNE is the first instrument capable of doing high mass resolution multicollector measurements (e.g. Fe, Ca, S, Si).