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

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The NEPTUNE

Introduced 2000
Multicollection vs. 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 NEPTUNE is an evolution of the TRITON multicollector combined with the proven ELEMENT2 ICP source.
A Family of Instruments for High Resolution Isotopic and Elemental Analysis

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?

- Magnet
- Electric sector
- Transfer lenses
- Plasma
- Ion source
- Detector system
Detector system
Variable Multicollector

Variable in position
Variable in detector type (Faraday/MIC)
Precise positioning (<10 µm) by in-situ position readout

17 % relative mass range
Multicollector with Multi Ion Counting

- “plug-in” MIC detectors identical in size and interchangeable with Faraday cups

- up to 8 MIC channels plus 9 Faraday cups can be installed simultaneously
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: $^{48}\text{Ti}^+$ interferes on $^{48}\text{Ca}^+$

Isobaric *doubly- (or multiply-) charged* ion interferences:
- caused by ions consisting of more than one charge

example: $^{86}\text{Sr}^{++}$ interferes in $^{43}\text{Ca}^{+}$
Isobaric *molecular* (or poly-atomic) interferences:
  → caused by ions consisting of more than one atom

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

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

example: $^{238}\text{U}^+$ tails on $^{236}\text{U}^+$
How to deal with interferences?

Example 1:
Interference of $^{48}\text{Ti}^+$ on $^{48}\text{Ca}^+$

Measure an interference-free Ti isotope, i.e. $^{47}\text{Ti}^+$.
Determine the amount of $^{48}\text{Ti}^+$ using the natural relative abundances.

$$^{48}\text{Ca}^+_{\text{corrected for Ti interference}} = ^{48}\text{Ca}^+_{\text{measured}} - ^{48}\text{Ti}^+$$

$$^{47}\text{Ti}^+_{\text{measured}} \times \left( ^{48}\text{Ti}^{}/^{47}\text{Ti}^{}\right)_{\text{natural}}$$

Example 2:
Interference of $^{86}\text{Sr}^{++}$ interferes in $^{43}\text{Ca}^+$

Measure $^{87}\text{Sr}^{++}$ on mass 43.5 (87/2).
Determine the amount of $^{86}\text{Sr}^{++}$ using the natural relative abundances.

$$^{43}\text{Ca}^+_{\text{corrected for Sr interference}} = ^{43}\text{Ca}^+_{\text{measured}} - ^{86}\text{Sr}^{++}$$

$$^{87}\text{Sr}^{++}_{\text{measured}} \times \left( ^{86}\text{Sr}^{}/^{87}\text{Sr}^{}\right)_{\text{natural}}$$
Example: Lithium isotopes

Solution containing Li
Lithium isotopes: challenges

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

• Li-standard NIST L-SVEC:

  measured $^{7}\text{Li}/^{6}\text{Li}$ ratio $\sim15$
  true $^{7}\text{Li}/^{6}\text{Li}$ ratio $\sim12.15$ (Qi et al. 1997)
  $\rightarrow$ mass bias $\sim 25\%$ !!

• No internal correction possible

• External correction by “sample-standard bracketing”

  $\rightarrow \delta = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} \right) - 1 \times 1000 \ \%$
Mass bias

$^{7}\text{Li}/^{6}\text{Li} = 14.8309 \pm 0.0033$ (1 s.d., n = 14)
(0.022 % RSD)
Long-term reproducibility of $^{7}\text{Li}/^{6}\text{Li}$

$^{7}\text{Li}/^{6}\text{Li} = 15.0061 \pm 0.0124$ (1 s.d = 0.82 ‰, n = 44)
Li isotopes – analysis sequence

Blank correction

\[ \frac{I_{st}}{I_{bl}} - \frac{I_{sa}}{I_{bl}} \]

Sample normalisation (delta-values)

\[ \delta = \left( \frac{R_{sa}}{R_{st}} - 1 \right) \times 1000 \]
Li isotopes – example sample/standard

![Graph showing Li isotopes with analysis number and ratio of $^{7}\text{Li}/^{6}\text{Li}$](image)

- **Li-standard L-SVEC**
- **Various samples**

The graph illustrates the analysis numbers (0-20) on the x-axis and the ratio of $^{7}\text{Li}/^{6}\text{Li}$ on the y-axis. Different colors represent different samples.
<table>
<thead>
<tr>
<th></th>
<th>Sensitivity</th>
<th>Uptake (µl/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Self-aspirating</td>
<td>20 V/ppm</td>
<td>80 to 100</td>
</tr>
<tr>
<td>micro-concentric nebuliser</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cetac Aridus™</td>
<td>400 V/ppm</td>
<td>~90</td>
</tr>
<tr>
<td>desolvating nebuliser</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Interference of doubly charged species: $^{14}\text{N}^{++}$
Seawater $\delta^7\text{Li}$ reported from a customer’s lab (BRGM France)

$\delta^7\text{Li} = +31.0 \, \text{‰} \pm 0.1 \, (2\sigma, \, n=31)$

Example: Iron isotopes

Solution containing Fe
Iron isotopes: challenges

Molecular Interferences

\[ ^{54}\text{Fe}: \ ^{40}\text{Ar}^{14}\text{N} \]
\[ ^{56}\text{Fe}: \ ^{40}\text{Ar}^{16}\text{O} \]
\[ ^{57}\text{Fe}: \ ^{40}\text{Ar}^{16}\text{O}^{1}\text{H} \]
\[ ^{58}\text{Fe}: \ ^{40}\text{Ar}^{18}\text{O} \]

Atomic Interferences

\[ ^{54}\text{Fe}: \ ^{54}\text{Cr} \]
\[ ^{58}\text{Fe}: \ ^{58}\text{Ni} \]
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

$^{56}\text{Fe} + ^{40}\text{Ar}^{16}\text{O}$

55.79457  56.10321
Peakscan of Fe
(wet plasma, 1 ppm Fe, medium resolution slit)

[Graph showing the mass-signal relationship for isotopes of iron and interferences from argon species]

- $^{54}$Fe (L2)
- $^{56}$Fe (C)
- $^{57}$Fe (H1)
- $^{58}$Fe (H2)

Interferences:
- $^{40}$Ar$^{16}$O
- $^{40}$Ar$^{16}$OH
- $^{40}$Ar$^{18}$O
- $^{40}$Ar$^{14}$N

56Fe

Collector slit
Faraday cup
Peakscan of Fe
(wet plasma, 1 ppm Fe, medium resolution slit)

![Graph showing mass spectrum with signal peaks for 54Fe (L2), 56Fe (C), 57Fe (H1), and 58Fe (H2) along with interferences such as 40Ar16O, 40Ar16OH, 40Ar18O, and 40Ar14N. The signal is normalized to 56Fe.]

- 54Fe (L2)
- 56Fe (C)
- 57Fe (H1)
- 58Fe (H2)

Interferences:
- 40Ar16O
- 40Ar16OH
- 40Ar18O
- 40Ar14N

Signal (V) normalized to 56Fe

mass

55.85 55.90 55.95 56.00 56.05

signal (V) normalized to 56Fe

Collector slit
Faraday cup
Peakscan of Fe
(wet plasma, 1 ppm Fe, medium resolution slit)

![Graph showing peakscan of Fe with mass range 55.85 to 56.05 and signal normalized to 56Fe. The graph indicates interferences such as 40Ar16O and 40Ar14N, with 56Fe and 56Fe + Interferences highlighted. Collector slit and Faraday cup are also indicated.]
Fe isotopes - plateau scan

The diagram shows the signal [V] normalised to 56Fe as a function of mass for different iron isotopes: 
- 54Fe (L2)
- 56Fe (C)
- 57Fe (H1)
- 58Fe (H2)

The graph highlights the 56Fe/54Fe ratio with a vertical arrow pointing to the plateau region.
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)
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 $^{40}\text{Ar}^+$ 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

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Natural abundance (%)</th>
<th>Faraday cup</th>
<th>Interferences</th>
<th>Resolution required</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{40}\text{Ca}$</td>
<td>96.941</td>
<td>L4</td>
<td>$^{40}\text{Ar}^+$</td>
<td>192 500</td>
</tr>
<tr>
<td>$^{42}\text{Ca}$</td>
<td>0.647</td>
<td>L4</td>
<td>$^{40}\text{Ar}^{+}\text{H}_2^+$</td>
<td>2200</td>
</tr>
<tr>
<td>$^{43}\text{Ca}$</td>
<td>0.135</td>
<td>L2</td>
<td>$^{14}\text{N}_3^+$</td>
<td>830</td>
</tr>
<tr>
<td>$^{44}\text{Ca}$</td>
<td>2.086</td>
<td>L1</td>
<td>$^{14}\text{N}_3\text{H}^+$</td>
<td>740</td>
</tr>
<tr>
<td>$^{46}\text{Ca}$</td>
<td>0.004</td>
<td>H3</td>
<td>$^{12}\text{C}^{16}\text{O}_2^+$</td>
<td>1280</td>
</tr>
<tr>
<td>$^{48}\text{Ca}$</td>
<td>0.187</td>
<td>H4</td>
<td>$^{14}\text{N}_2^{16}\text{O}^+$</td>
<td>965</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$^{88}\text{Sr}^{2+}$</td>
<td>160 500</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$^{46}\text{Ti}^+$</td>
<td>43 400</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$^{48}\text{Ti}^+$</td>
<td>10 500</td>
</tr>
</tbody>
</table>

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

5 ppm SRM915a in 3% HNO₃
Background (3% HNO$_3$)
IAPSO Ca isotope compositions reported from a customer’s lab (Ruhr University Bochum)

SRM915a vs. IAPSO Ca standards

\[ \delta^{44}\text{Ca}/^{42}\text{Ca} = -0.88 \pm 0.11 \ (2\sigma) \]

\[ \delta^{48}\text{Ca}/^{42}\text{Ca} = -2.70 \pm 0.33 \ (2\sigma) \]

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 $\delta^{34}$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)

![Graph showing peak scan for Si isotopes]

- 28Si
- 29Si
- 30Si

Isotopes of interest:
- $^{14}\text{N}^{16}\text{O}$
- $^{14}\text{N}_2$
- $^{15}\text{N}^{14}\text{N}$, $^{14}\text{N}_2^{1}\text{H}$
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 (sildenafil) provides a case study for the application of laser ablated measurements of $\delta^{34}$S.

Counterfeit Viagra 1
Counterfeit Viagra ‘plus’
Genuine Pfizer Viagra

$\delta^{34}$S relative to Pfizer Viagra

$\delta^{15}$N

$\delta^{13}$C

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).