Implications for Exploration With The Use of High Resolution ICP-MS Technology

Eric L. Hoffman, Yakov Kapusta and M. Dzierzgowska
Introduction:

• What is HR-ICP/MS?
• Advantages and Disadvantages
• Applications:
  * Hydrogeochemistry (Au+PGE)
  * Biogeochemistry (Au+PGE)
  * Lithogeochemistry (REE)
  * Pb Isotopes
  * Metal Speciation
• Conclusions
What is the difference between High Resolution ICP-MS (HR-ICP/MS) and Quadrupole ICP-MS Technology?
High Resolution ICP-MS

Detection System
Magnetic Sector Ion Separator
ICP Source
Advantages of HR/ICP-MS vs. Quadrupole ICP-MS

Resolution — to separate interferences

Detection Limit — to detect metals at their natural levels which are typically very low
### High Resolution ICP-MS vs. Quadrupole ICP-MS (Conventional) Limits of Detection

<table>
<thead>
<tr>
<th>Element</th>
<th>HR-ICP-MS</th>
<th>ICP-MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>3 ng/L</td>
<td>30 ng/L</td>
</tr>
<tr>
<td>Se</td>
<td>20 ng/L</td>
<td>200 ng/L</td>
</tr>
<tr>
<td>Au</td>
<td>0.05 ng/L</td>
<td>5 ng/L</td>
</tr>
<tr>
<td>Pt</td>
<td>0.5 ng/L</td>
<td>10 ng/L</td>
</tr>
</tbody>
</table>
Resolution Improvements:

Resolves Many Interferences Using Quadrupole ICP-MS
Quadruple Resolution 10,000 HR Resolution

Some Interferences:
- $^{61}\text{Ni}^{++}$
- $^{62}\text{Ni}^{++}$
- $^{15}\text{N}^{16}\text{O}$
- $^{14}\text{N}^{16}\text{O}^{1}\text{H}$
- $^{12}\text{C}^{18}\text{O}^{1}\text{H}$
- $^{63}\text{Cu}^{++}$

Nominal Mass | Accurate Mass | Abundance [%]
--- | --- | ---
31 | 30.97376 | 100.00

P 15

Quadruple Resolution

10,000 HR Resolution

Actlabs
### Quadruple Resolution

<table>
<thead>
<tr>
<th>Nominal Mass</th>
<th>Accurate Mass</th>
<th>Abundance [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>31.97207</td>
<td>95.02</td>
</tr>
</tbody>
</table>

#### Some Interferences:
- $^{16}\text{O}^{16}\text{O}$
- $^{14}\text{N}^{18}\text{O}$
- $^{15}\text{N}^{16}\text{O}^\text{H}$
- $^{65}\text{Cu}^{++}$
- $^{64}\text{Ni}^{++}$
- $^{63}\text{Cu}^{++}$
- $^{64}\text{Zn}^{++}$

### 10,000 HR Resolution

![Graph showing Quadruple Resolution and 10,000 HR Resolution]
<table>
<thead>
<tr>
<th>Nominal Mass</th>
<th>Accurate Mass</th>
<th>Abundance [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>34</td>
<td>33.96787</td>
<td>4.21</td>
</tr>
</tbody>
</table>

Some Interferences:

- $^{67}\text{Zn}^{++}$
- $^{68}\text{Zn}^{++}$
- $^{16}\text{O}^{16}\text{O}^{1H}^{1H}$
- $^{18}\text{O}^{16}\text{O}$
- $^{69}\text{Ga}^{++}$

Quadruple Resolution

10,000 HR Resolution
**Quadruple Resolution 10,000 HR Resolution**

<table>
<thead>
<tr>
<th>Nominal Mass</th>
<th>Accurate Mass</th>
<th>Abundance [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>74.92160</td>
<td>100.00</td>
</tr>
</tbody>
</table>

**Some Interferences:**

- $^{149}$Sm$^{++}$
- $^{35}$Cl$^{40}$Ar
- $^{150}$Nd$^{++}$
- $^{39}$K$^{36}$Ar
- $^{151}$Eu$^{++}$
- $^{59}$Co$^{16}$O
- $^{150}$Sm$^{++}$

---

**10,000 HR Resolution**
<table>
<thead>
<tr>
<th>Nominal Mass</th>
<th>Accurate Mass</th>
<th>Abundance [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>78</td>
<td>77.91730</td>
<td>23.60</td>
</tr>
</tbody>
</table>

Some Interferences:

- $^{159}\text{Tb}^{++}$
- $^{64}\text{Zn}^{16}\text{O}$
- $^{160}\text{Dy}^{++}$
- $^{40}\text{Kr}$
- $^{40}\text{Ar}^{40}\text{Ar}$
- $^{160}\text{Gd}^{++}$
- $^{64}\text{Ni}^{16}\text{O}$
- $^{40}\text{Ca}^{40}\text{Ar}$
- $^{161}\text{Dy}^{++}$

Quadruple Resolution

10,000 HR Resolution

Interference:

- Kr
Quadruple Resolution 10,000 HR Resolution

Some Interferences:

\[ ^{159}\text{Tb}^{++} \quad ^{64}\text{Zn}^{16}\text{O} \quad ^{160}\text{Dy}^{++} \]
\[ \text{Kr} \quad ^{40}\text{Ar}^{40}\text{Ar} \quad ^{160}\text{Gd}^{++} \]
\[ ^{64}\text{Ni}^{16}\text{O} \quad ^{40}\text{Ca}^{40}\text{Ar} \quad ^{161}\text{Dy}^{++} \]

Interference:

Kr
Nominal Mass | Accurate Mass | Abundance [%]
--- | --- | ---
202 | 201.97063 | 29.80

**Quadruple Resolution**

Some Interferences:

$^{162}\text{Dy}^{40}\text{Ar}$  $^{186}\text{Os}^{16}\text{O}$

$^{162}\text{Er}^{40}\text{Ar}$  $^{186}\text{W}^{16}\text{O}$

$^{166}\text{Er}^{36}\text{Ar}$

**10,000 HR Resolution**
New Elements Can Be Done By HR-ICP/MS

- Fluorine
<table>
<thead>
<tr>
<th>Nominal Mass</th>
<th>Accurate Mass</th>
<th>Abundance [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>18.99840</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Quadruple Resolution

Some Interferences:

- $^{37}$Cl$^{+} + ^{16}$O$^{+}$
- $^{38}$Ar$^{+}$
- $^{1}H^{+}^{18}$O

4,000 MR Resolution

[Actlabs Logo]
Rare Earth Elements

• Barite rich samples have always created an analytical problem with BaO interference on Eu
Methods for the Analysis of Gold in Water

- Carbon sachet – INAA (CSIRO Method)
- Direct ICP-MS
- Evaporation ICP-MS
- Evaporation in baby bottle liners - INAA
Method:
• Carbon sachet is placed in a 1 L bottle of water and it is assumed that the carbon sachet will adsorb all of the gold.

Problem:
• Our experiments indicate that most of the gold is adsorbed by the carbon sachet mesh with only ~40% of the gold being adsorbed on the activated charcoal. Gold is also adsorbed on the walls of the polyethylene bottle.
• INAA cannot determine PGE at this level instrumentally at a reasonable cost.
ICP-MS Analysis

**Method:**
- Gold is analysed directly by ICP-MS or by preconcentration ICP-MS.

**Problems:**
- Direct ICP-MS does not give enough sensitivity
  - Natural levels of PGE and Au are below detection limits
- Preconcentration is prone to contamination
- Problem of adsorption on bottles is present
Evaporation and INAA

**Method:**
- 100 mL of water is collected and evaporated in baby bottle liners and analysed by INAA

**Problems:**
- Slow process and baby bottle liner blank can vary
- Cannot determine PGE by this method
Direct Analysis and HR-ICP/MS

Method:
- Samples are collected in polyethylene bottles without preservation required.
- Acidification and complexing agent is added in the laboratory under tightly controlled conditions.
- Analysis performed by HR-ICP/MS.

Problems:
- PGE background may still require preconcentration depending on local geology.
Quadruple Resolution 10,000 HR Resolution

Some Interferences:

$^{157}$Gd$^{40}$Ar
$^{181}$Ta$^{16}$O
<table>
<thead>
<tr>
<th>Nominal Mass</th>
<th>Accurate Mass</th>
<th>Abundance [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>195</td>
<td>194.96479</td>
<td>33.80</td>
</tr>
</tbody>
</table>

Some Interferences:
- $^{155}\text{Gd}^{40}\text{Ar}$
- $^{159}\text{Tb}^{36}\text{Ar}$
- $^{179}\text{Hf}^{16}\text{O}$
Quadruple Resolution

<table>
<thead>
<tr>
<th>Nominal Mass</th>
<th>Accurate Mass</th>
<th>Abundance [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>104</td>
<td>103.90403</td>
<td>11.14</td>
</tr>
</tbody>
</table>

Some Interferences:
- $^{207}\text{Pb}^{++}$
- $^{88}\text{Sr}^{16}\text{O}$
- $^{208}\text{Pb}^{++}$
- $^{64}\text{Ni}^{40}\text{Ar}$
- $^{209}\text{Bi}^{++}$
- $^{64}\text{Zn}^{40}\text{Ar}$
- Ru

10,000 HR Resolution

Interference:
- Ru
- $^{88}\text{Sr}^{16}\text{O}$
Quadruple Resolution

Some Interferences:
- $^{209}\text{Bi}^{++}$
- $^{89}\text{Y}^{16}\text{O}$
- $^{65}\text{Cu}^{40}\text{Ar}$
- $^{69}\text{Ga}^{36}\text{Ar}$

10,000 HR Resolution

Interference:
- $^{89}\text{Y}^{16}\text{O}$
Some Interferences:

\[ ^{66}\text{Zn}^{40}\text{Ar} \]
\[ ^{90}\text{Zr}^{16}\text{O} \]
\[ ^{88}\text{Sr}^{18}\text{O} \]

Interference:

\[ ^{88}\text{Sr}^{18}\text{O} \]
\[ ^{90}\text{Zr}^{16}\text{O} \]
\[ \text{Cd} \]
<table>
<thead>
<tr>
<th>Nominal Mass</th>
<th>Accurate Mass</th>
<th>Abundance [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>108</td>
<td>107.90389</td>
<td>26.46</td>
</tr>
</tbody>
</table>

**Quadruple Resolution**

**Some Interferences:**
- $^{68}\text{Zn}^{40}\text{Ar}$
- $^{92}\text{Zr}^{16}\text{O}$
- $^{92}\text{Mo}^{16}\text{O}$
- $^{90}\text{Zr}^{18}\text{O}$

**10,000 HR Resolution**

**Some Interferences:**
- $^{90}\text{Zr}^{18}\text{O}$
- Cd
- $^{92}\text{Zr}^{16}\text{O}$
- $^{92}\text{Mo}^{16}\text{O}$
Quadruple Resolution

Some Interferences:

- $^{70}\text{Ge}^{40}\text{Ar}$
- $^{70}\text{Zn}^{40}\text{Ar}$
- $^{74}\text{Ge}^{36}\text{Ar}$

Accurate Mass: 109.90517
Abundance [%]: 11.72

Pd

10,000 HR Resolution

Some Interferences:

- $^{94}\text{Mo}^{16}\text{O}$
- $^{94}\text{Zr}^{16}\text{O}$
- $\text{Cd}$
Clean Sample Preparation Areas

- HEPA filtered laminar flow hoods
- Room air HEPA filtered
- Polypropylene workbenches (Metal free work stations)
Platinum Group Elements and Gold in Water

- Detection limits in parts per trillion (ng/L)

<table>
<thead>
<tr>
<th></th>
<th>ICP-MS</th>
<th>HR-ICP/MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>5</td>
<td>0.05</td>
</tr>
<tr>
<td>Pt</td>
<td>10</td>
<td>0.5</td>
</tr>
<tr>
<td>Pd</td>
<td>20</td>
<td>varies</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 varies (Cd, Sr, Zr, Mo, Y interferes)</td>
</tr>
<tr>
<td>Rh</td>
<td>20</td>
<td>0.5</td>
</tr>
<tr>
<td>Ru</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>Ir</td>
<td>5</td>
<td>1</td>
</tr>
</tbody>
</table>
• Plant material can be analysed directly by HR-ICP/MS for PGE+Au plus many other analytes
• Losses resulting from ashing are eliminated through direct analysis of macerated material

• Background levels can now be reached for most metals
### HR-ICP/MS Biogeochemistry

**Selected Detection Limits on Dried Vegetation in ppb**

<table>
<thead>
<tr>
<th>Element</th>
<th>Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>0.01</td>
</tr>
<tr>
<td>Ag</td>
<td>1</td>
</tr>
<tr>
<td>Pt</td>
<td>0.1</td>
</tr>
<tr>
<td>Pd</td>
<td>0.2</td>
</tr>
<tr>
<td>Cu</td>
<td>15</td>
</tr>
<tr>
<td>Mo</td>
<td>1</td>
</tr>
<tr>
<td>Co</td>
<td>0.5</td>
</tr>
<tr>
<td>Re</td>
<td>0.1</td>
</tr>
<tr>
<td>Ni</td>
<td>100</td>
</tr>
<tr>
<td>Pb</td>
<td>6</td>
</tr>
<tr>
<td>Ru</td>
<td>0.5</td>
</tr>
<tr>
<td>Sb</td>
<td>0.2</td>
</tr>
<tr>
<td>As</td>
<td>5</td>
</tr>
<tr>
<td>Bi</td>
<td>1</td>
</tr>
<tr>
<td>Te</td>
<td>1</td>
</tr>
<tr>
<td>Hg</td>
<td>5</td>
</tr>
</tbody>
</table>
Rare Earth Elements

- Some rock types such as very low REE ultramafics could not have the REE determined by quadrupole ICP-MS due to detection limit problems

- Barium interferes on some REE in high barite samples
### Quadruple Resolution

Some Interferences:

- $^{111}\text{Cd}^{40}\text{Ar}$
- $^{133}\text{Cs}^{18}\text{O}$
- $^{115}\text{In}^{36}\text{Ar}$
- $^{135}\text{Ba}^{16}\text{O}$

### 10,000 HR Resolution

[Graph showing mass resolution improvement]
<table>
<thead>
<tr>
<th>Nominal Mass</th>
<th>Accurate Mass</th>
<th>Abundance [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>153</td>
<td>152.92124</td>
<td>52.20</td>
</tr>
</tbody>
</table>

Some Interferences:
- $^{113}\text{In}^{40}\text{Ar}$
- $^{113}\text{Cd}^{40}\text{Ar}$
- $^{137}\text{Ba}^{16}\text{O}$
# Rare Earth Elements: Detection Limits by Lithium Metaborate/Tetraborate Fusion HR-ICP/MS

<table>
<thead>
<tr>
<th>Analyte</th>
<th>ICP-MS</th>
<th>HR-ICP/MS</th>
<th>Analyte</th>
<th>ICP-MS</th>
<th>HR-ICP/MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>50</td>
<td>5</td>
<td>Tb</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>Ce</td>
<td>50</td>
<td>5</td>
<td>Dy</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>Pr</td>
<td>10</td>
<td>1</td>
<td>Ho</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>Nd</td>
<td>50</td>
<td>5</td>
<td>Er</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>Sm</td>
<td>10</td>
<td>1</td>
<td>Tm</td>
<td>5</td>
<td>0.5</td>
</tr>
<tr>
<td>Eu</td>
<td>5</td>
<td>0.5</td>
<td>Yb</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>Gd</td>
<td>10</td>
<td>1</td>
<td>Lu</td>
<td>2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Detection limits in ppb
Pb Isotopes: Precision

ICP-MS  
0.5%

HR-ICP/MS  
0.1%

TIMS  
<0.1%

increasing cost
Pb Isotopes: Exploration Potential

(Modified from K. Fletcher, 2003 GAC Abstract)

Comparison of Pb-isotope ratios for the Swim deposit to ratios for the anomalies might:

(i) corroborate the relation between them
(ii) allow the ability of different extractions to preferentially “see” Pb from the deposit.
(iii) TIMS anomaly and HR-ICP/MS anomalies showed similar patterns
(iv) relatively rapid, inexpensive Pb isotopic fingerprinting of geochemical anomalies may become possible with HR-ICP/MS
Example: Arsenic Speciation

As(III) - arsenite
As(V) - arsenate
MMA – monomethylarsonic acid
DMA – dimethylarsinic acid
Arsenosugars, etc.

Increasing toxicity
Methods for measuring metal speciation?

Examples: HPLC (high pressure liquid chromatography + UV or MS detection)
GC (gas chromatography + UV or MS detection)
CE (capillary electrophoresis + UV or MS detection)

...plus many more methods!
How are we going to measure metal speciation?

Capillary Electrophoresis with High Resolution ICP-MS detection (CE-HR/ICP-MS)
How do we choose the appropriate method?

- High resolution on separation – CE promises the best resolution
- Natural systems contain very low levels of metals – HR ICP-MS provides the lowest detection limits
- Geological Applications may have very small sample sizes - CE-HR/ICP-MS can analyse samples in the µL range
What is CE-HR/ICP-MS?
Principle of Capillary Electrophoresis (CE)

Species are moving because of their size.
Principle of High Resolution Magnetic Sector ICP-MS

Detection System

Magnetic Sector Ion Separator

ICP Source
Coupling CE to HR/ICP-MS
Principle of MIRA Mist CE Nebuliser

- Aerosol of Makeup & Sample
- Induced Gas Flow
- Argon Gas Flow
- Mira Mist CE Nebulizer Tip
- CE Sample Flow
- CE Capillary
- Make up Solution
CE-HR/ICP-MS Interface

- CE Capillary to CE Instrument
- Pt Electrode
- Argon
- Make UP Solution @ 3 - 10 ul/min Run through Pt Electrode for positive contact.

Detail of Nebulizer Assembly

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Capillary Electrophoresis and Interface

HR-ICP/MS

interface

capillary electrophoresis
CE-HR/ICP-MS is a multi-element speciation technique.
Pore Water Squeezing Apparatus
(courtesy of Dr. Dave Blowes, Waterloo)
Pore water from mine tailings

Se(VI)
As(V)
organoarsenic
As(III)

Se(VI)
As(V)
As(III)
Water Well Sample Near Arsenopyrite Stockpile

Sample SLW17

As\textsuperscript{5+}

As\textsuperscript{3+}
Metal Speciation Application to Exploration?

- Mapping redox potential
- Unique metal species associated with ore deposits? Can we use these unique species to differentiate good anomalies from bad?

Linda Bloom in 3D Geochemistry CAMIRO Project is proposing to test this hypothesis
<table>
<thead>
<tr>
<th>Sample</th>
<th>As(^{3+})</th>
<th>As(^{5+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLW17</td>
<td>0.6</td>
<td>0.2</td>
</tr>
<tr>
<td>SLTP</td>
<td>&lt;0.1</td>
<td>2.6</td>
</tr>
<tr>
<td>SLLP2</td>
<td>&lt;0.1</td>
<td>0.6</td>
</tr>
<tr>
<td>SLLP1</td>
<td>&lt;0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>SLCC</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

Gold Mine in Canada

(Map and dataCourtesy of Dr. Barbara Sheriff and Kristin Salzsauler, University of Manitoba)
Gold Mine in Canada

(Map and data Courtesy of Dr. Barbara Sheriff and Kristin Salzsauler, University of Manitoba)
Conclusions:

- HR-ICP/MS offers one to two orders of magnitude better detection limits than quadrupole ICP-MS
- Resolves most but not all interferences
- Expanded element capability (ie: F)
- Direct vegetation analysis
- PGE and Au in water
- REE in rocks at sub-ppb levels
- Improves precision for Pb isotopic analysis
- Metal speciation for a variety of metals at natural levels is possible by CE-HR-ICP/MS