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

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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?

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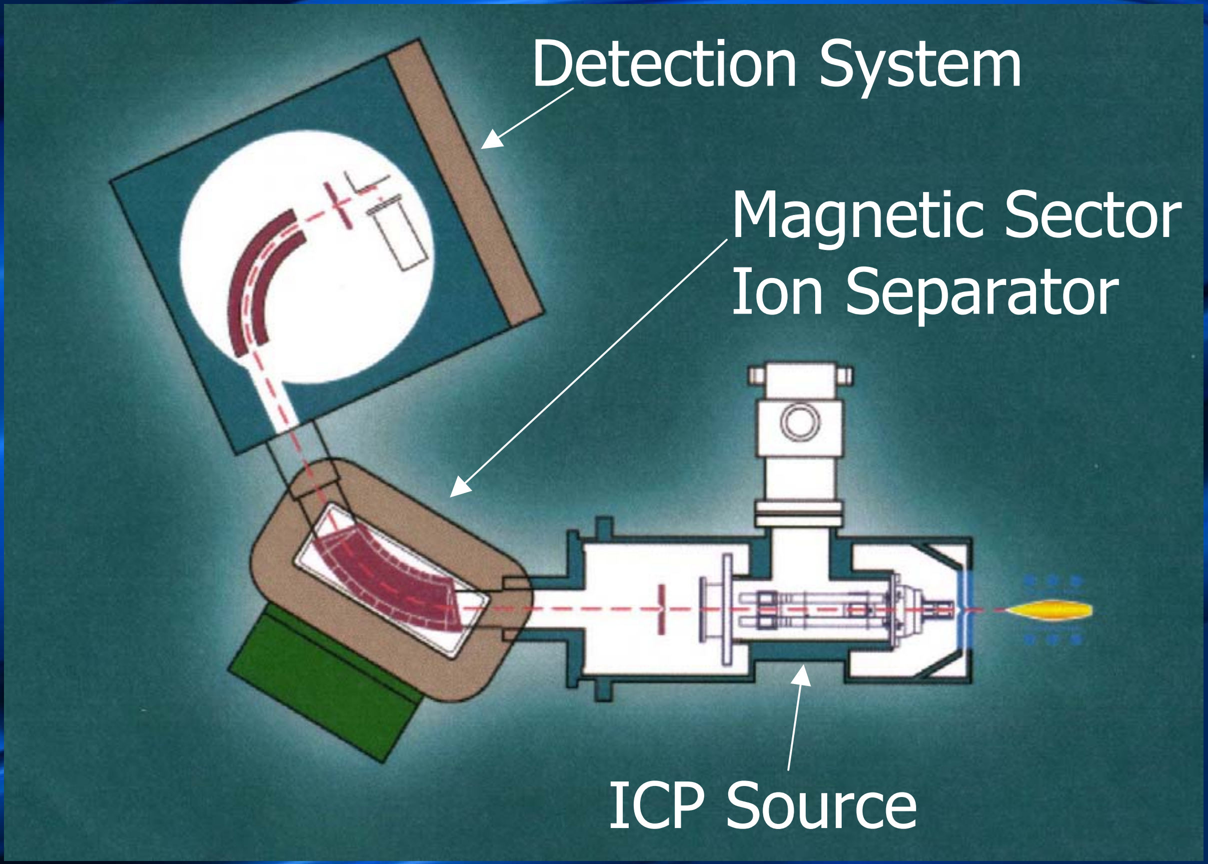
High Resolution ICP-MS



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

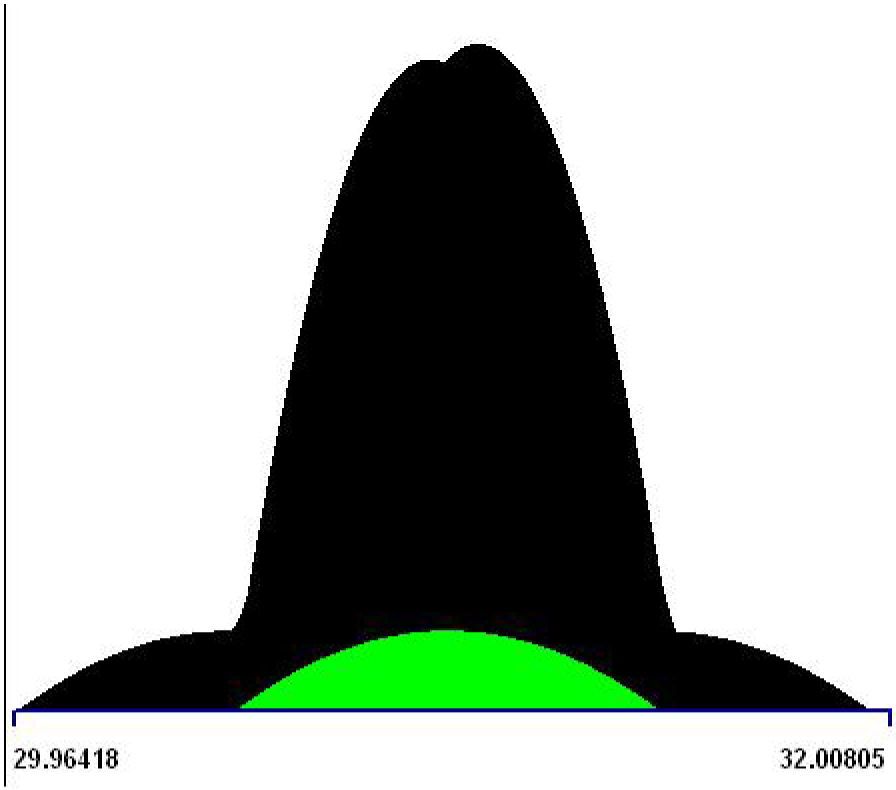
Element	HR-ICP-MS	ICP-MS
As	3 ng/L	30 ng/L
Se	20 ng/L	200 ng/L
Au	0.05 ng/L	5 ng/L
Pt	0.5 ng/L	10 ng/L

Resolution Improvements:

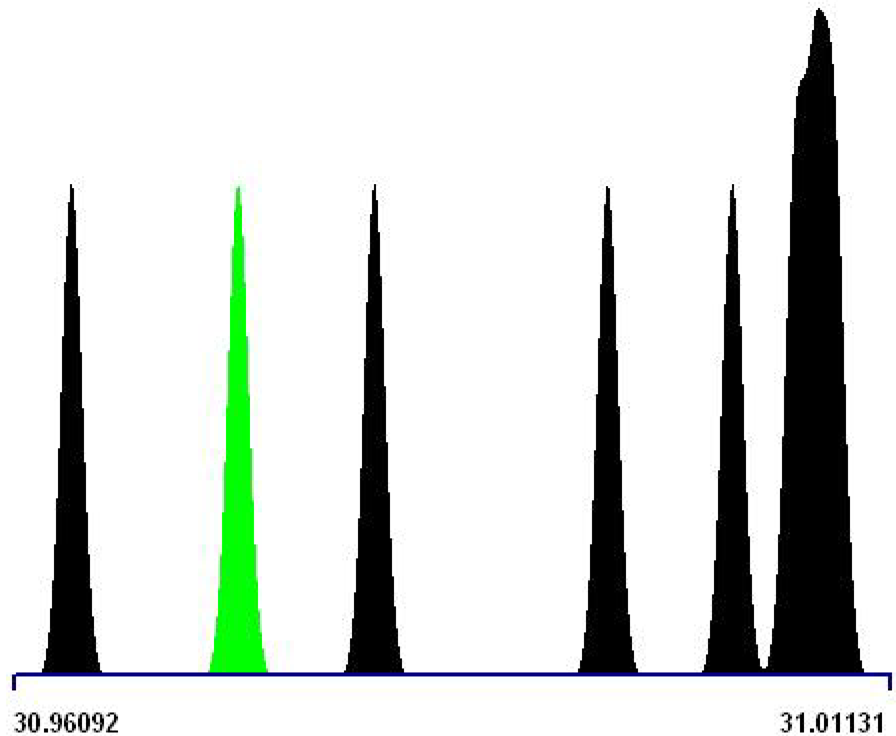
Resolves Many Interferences Using Quadrupole ICP-MS

Nominal Mass	Accurate Mass	Abundance [%]
31	30.97376	100.00

P
15



Quadruple Resolution



10,000 HR Resolution

Some Interferences:

$^{61}Ni^{++}$ $^{62}Ni^{++}$

$^{15}N^{16}O$ $^{14}N^{16}O^{1}H$

$^{12}C^{18}O^{1}H$ $^{63}Cu^{++}$

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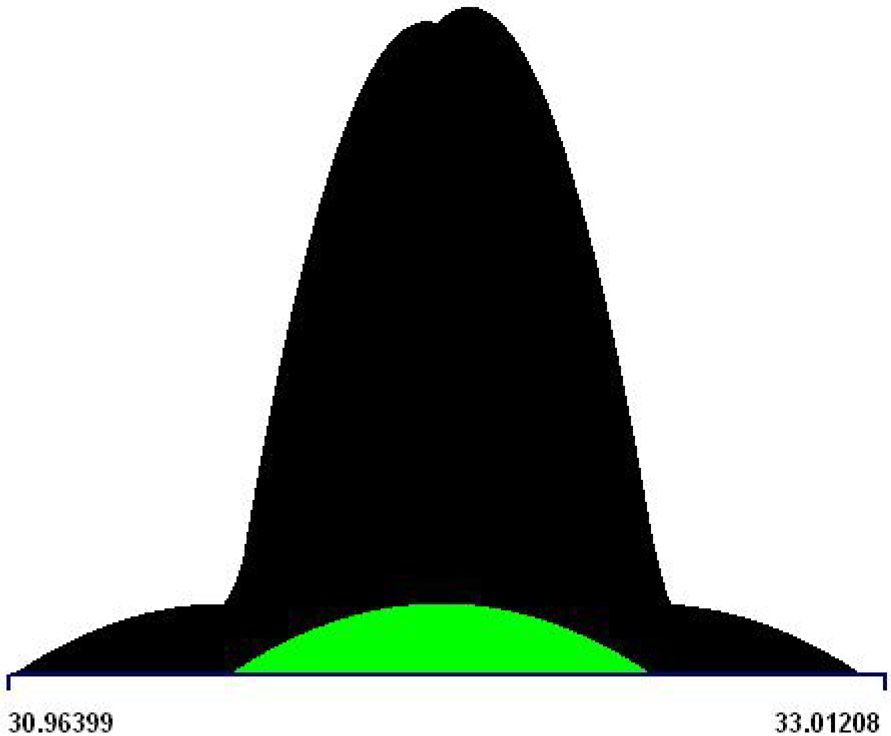
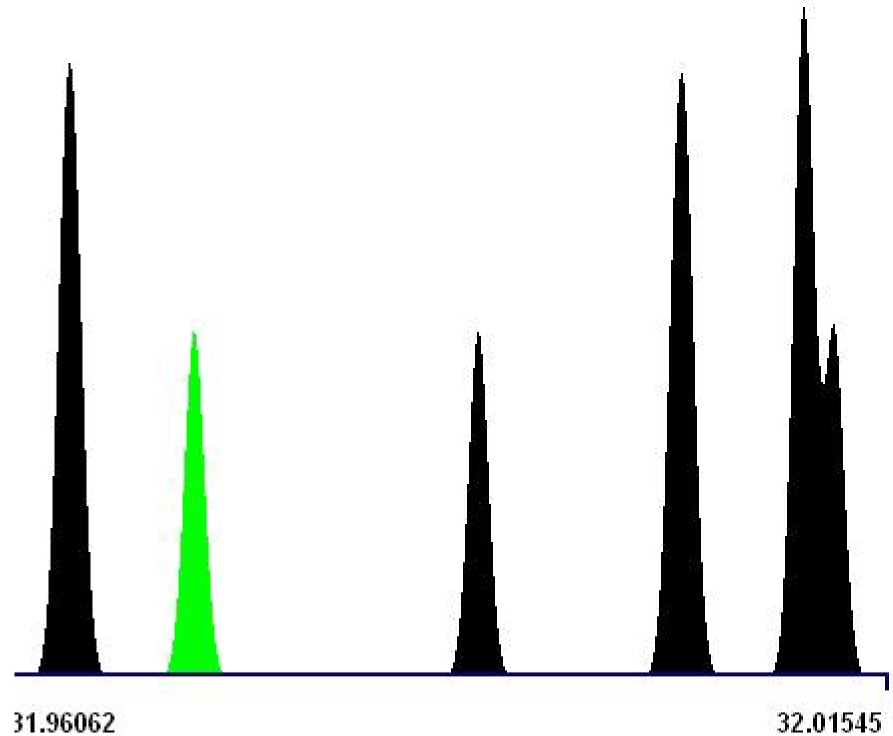
Nominal Mass	Accurate Mass	Abundance [%]	S 16
32	31.97207	95.02	



Quadruple Resolution



10,000 HR Resolution

Some Interferences:

$^{16}O^{16}O$ $^{65}Cu^{++}$

$^{14}N^{18}O$ $^{64}Ni^{++}$ $^{63}Cu^{++}$

$^{15}N^{16}O^{1}H$ $^{64}Zn^{++}$

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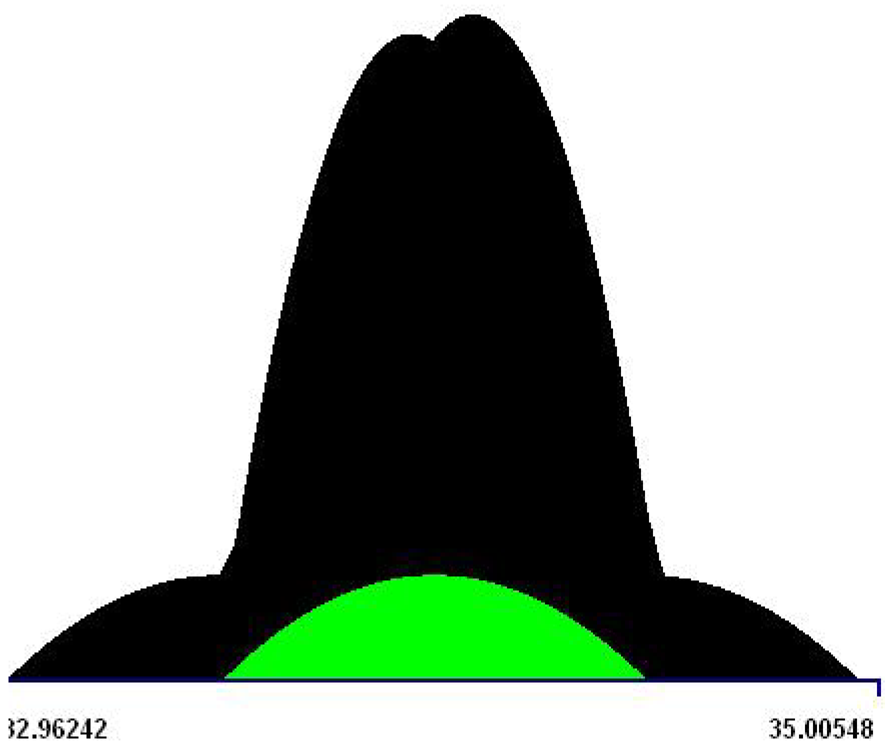
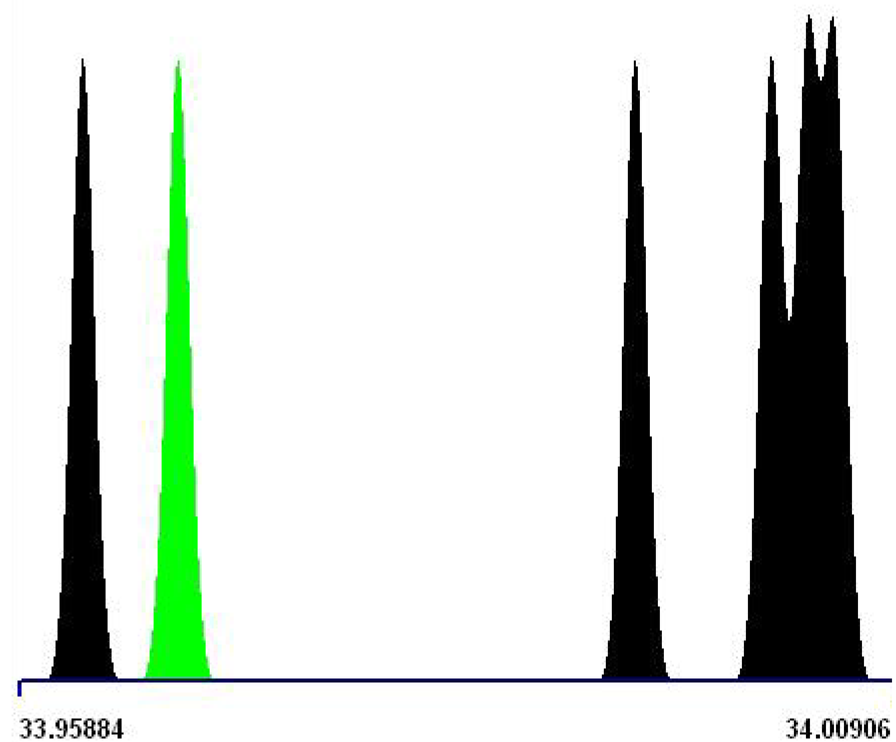
Nominal Mass	Accurate Mass	Abundance [%]	S 16
34	33.96787	4.21	



Quadruple Resolution



10,000 HR Resolution

Some Interferences:

$^{67}Zn^{++}$ $^{16}O^{16}O^{1}H^{1}H$

$^{68}Zn^{++}$ $^{69}Ga^{++}$

$^{18}O^{16}O$

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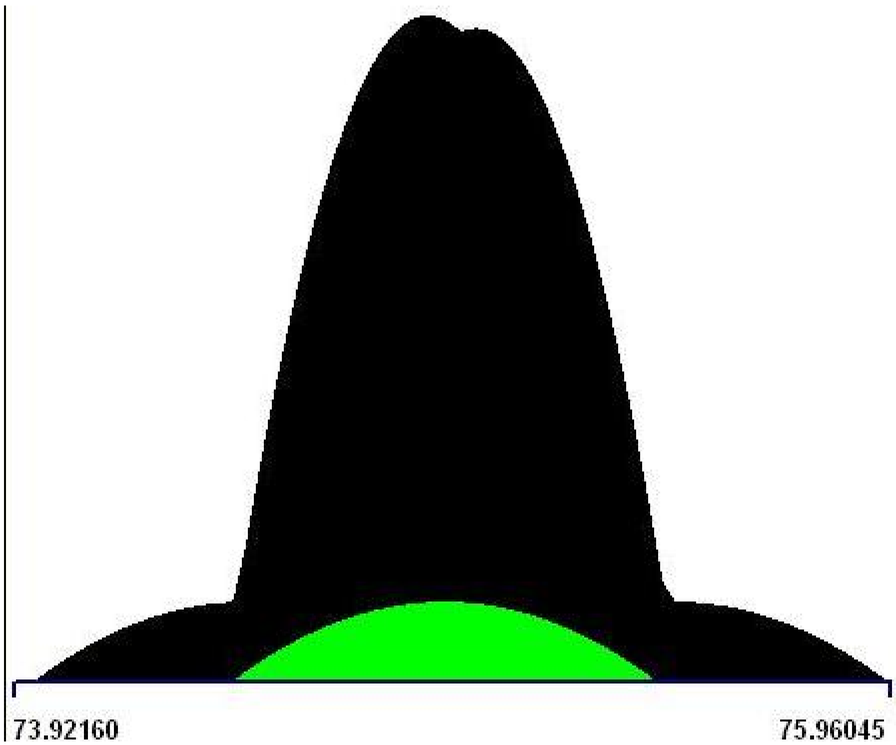
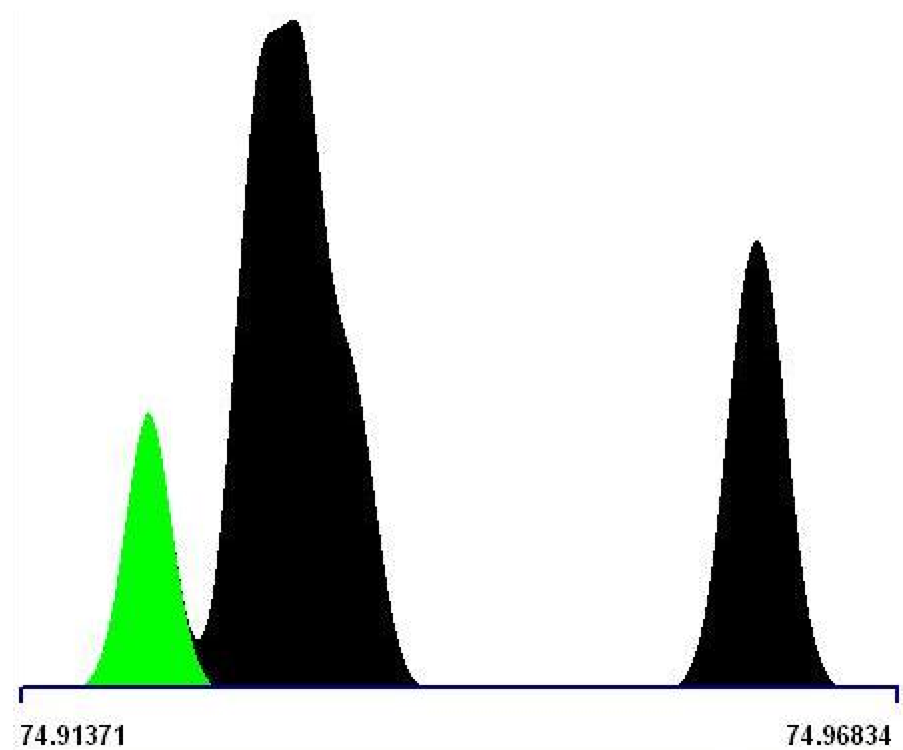
Nominal Mass	Accurate Mass	Abundance [%]	As 33
75	74.92160	100.00	



Quadruple Resolution



10,000 HR Resolution

Some Interferences:

$^{149}Sm^{++}$ $^{35}Cl^{40}Ar$ $^{150}Nd^{++}$

$^{39}K^{36}Ar$ $^{151}Eu^{++}$

$^{59}Co^{16}O$ $^{150}Sm^{++}$

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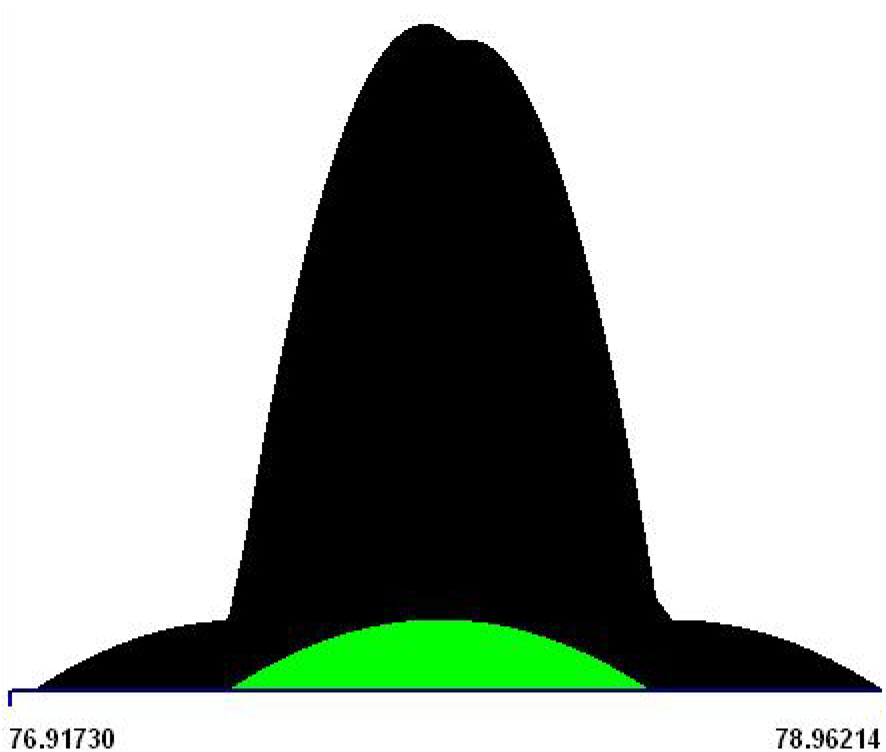
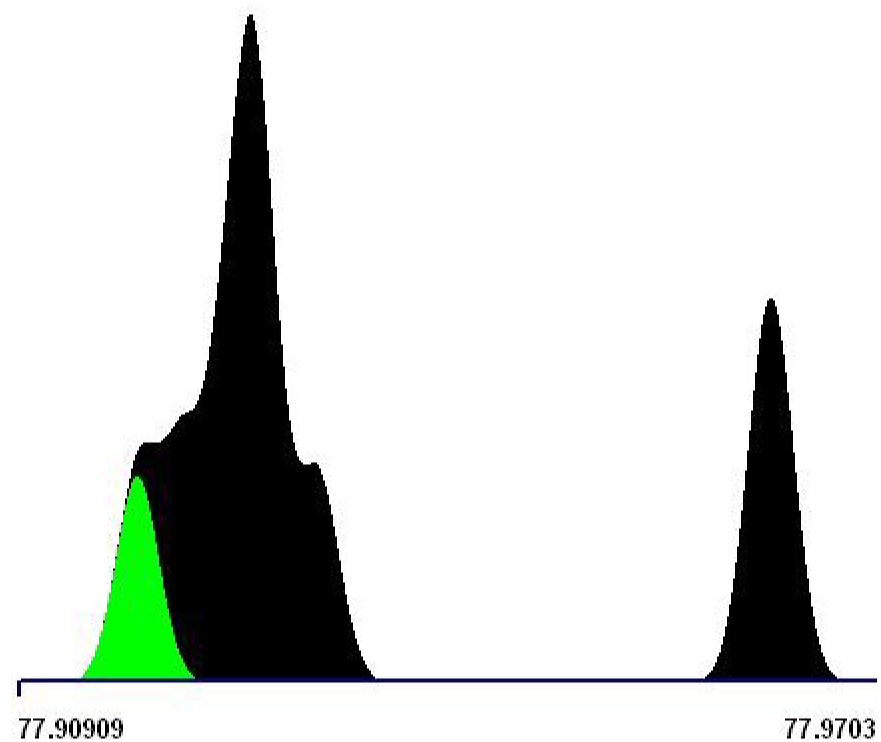
Nominal Mass	Accurate Mass	Abundance [%]
78	77.91730	23.60

Se
34



Quadruple Resolution



10,000 HR Resolution

Some Interferences:

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

Interference:

Kr

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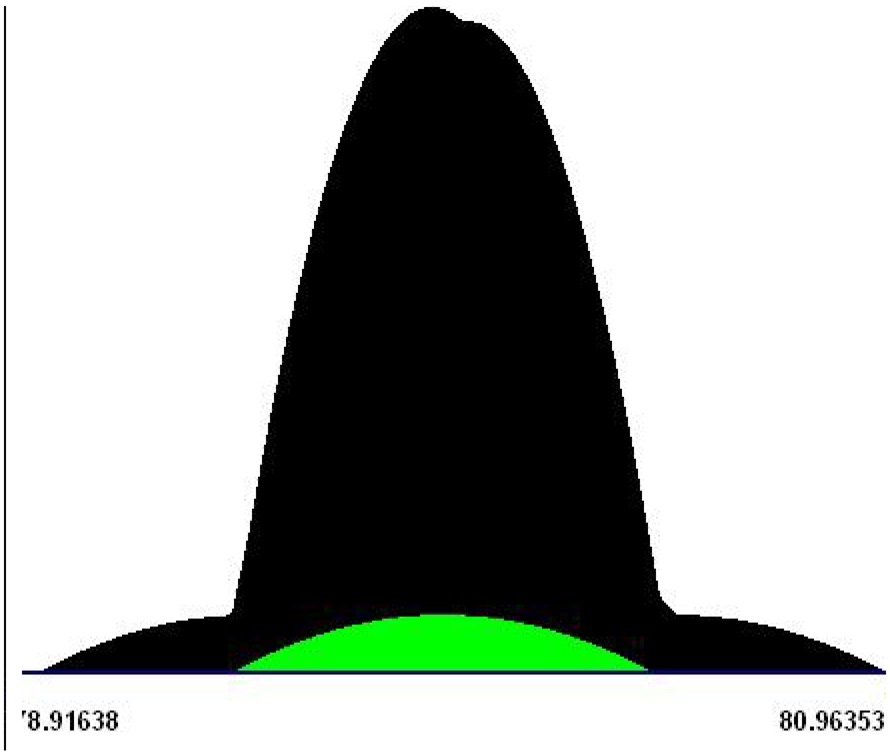
Nominal Mass	Accurate Mass	Abundance [%]
80	79.91652	49.70

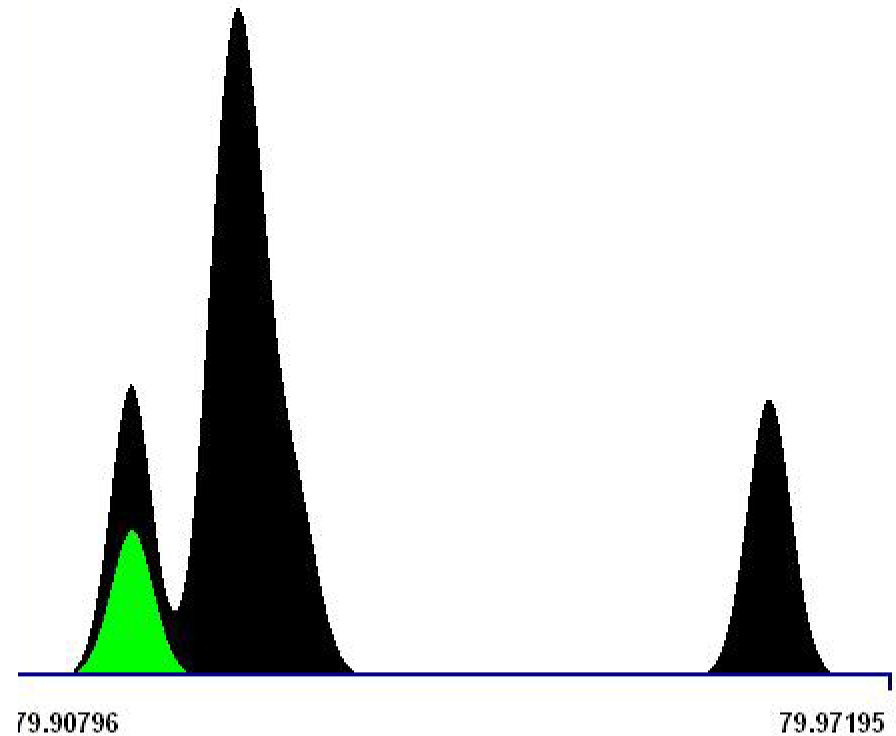
Se
34



Quadruple Resolution

Some Interferences:

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

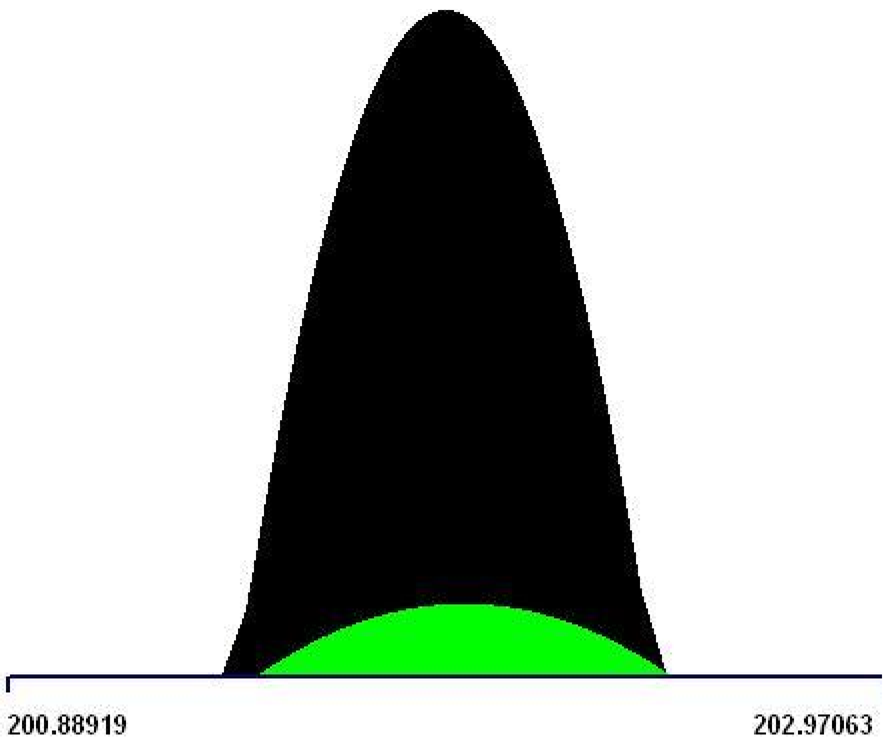


10,000 HR Resolution

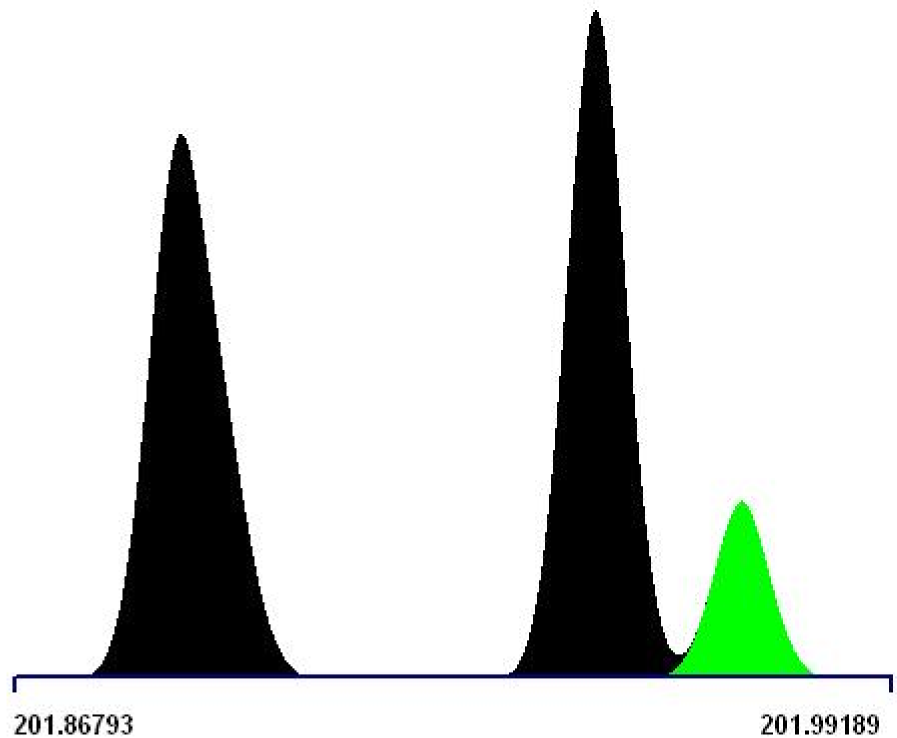
Interference:

Kr

Nominal Mass	Accurate Mass	Abundance [%]	Hg 80
202	201.97063	29.80	



Quadruple Resolution



10,000 HR Resolution

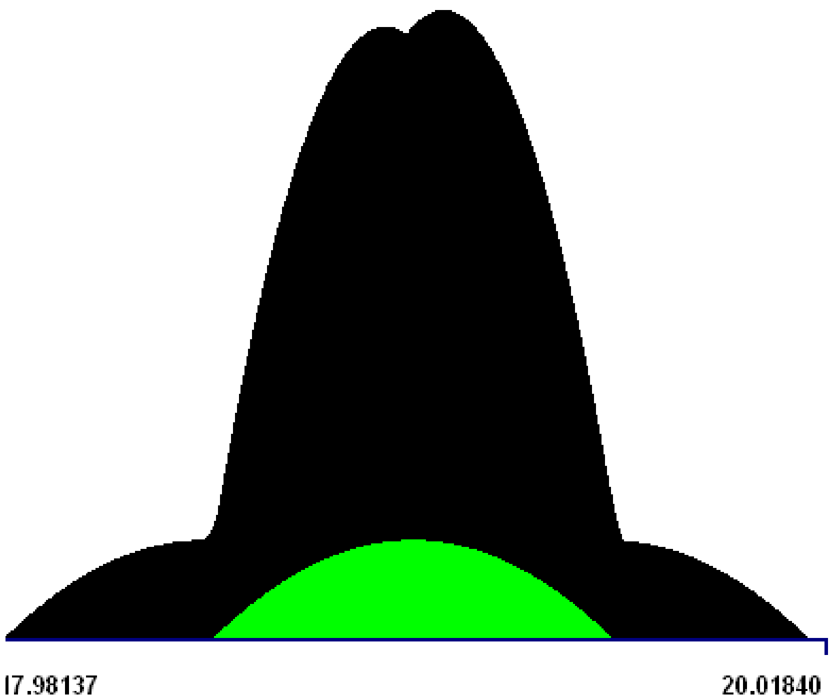
Some Interferences:

$^{162}Dy^{40}Ar$ $^{186}Os^{16}O$
$^{162}Er^{40}Ar$ $^{186}W^{16}O$
$^{166}Er^{36}Ar$

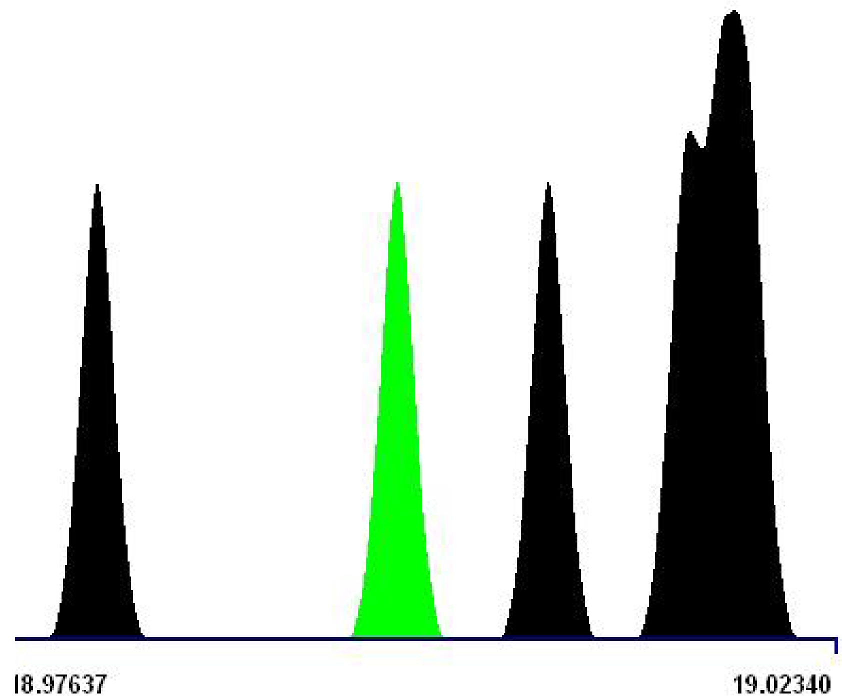
New Elements Can Be Done By HR-ICP/MS

- Fluorine

Nominal Mass	Accurate Mass	Abundance [%]	$_{9}F$
19	18.99840	100.00	



Quadruple Resolution



4,000 MR Resolution

Some Interferences:

$^{37}Cl^{++}$ $^{16}O^{1}H^{1}H^{1}H$

$^{38}Ar^{++}$ $^{39}K^{++}$

$^{1}H^{18}O$

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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

Carbon Sachet - 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

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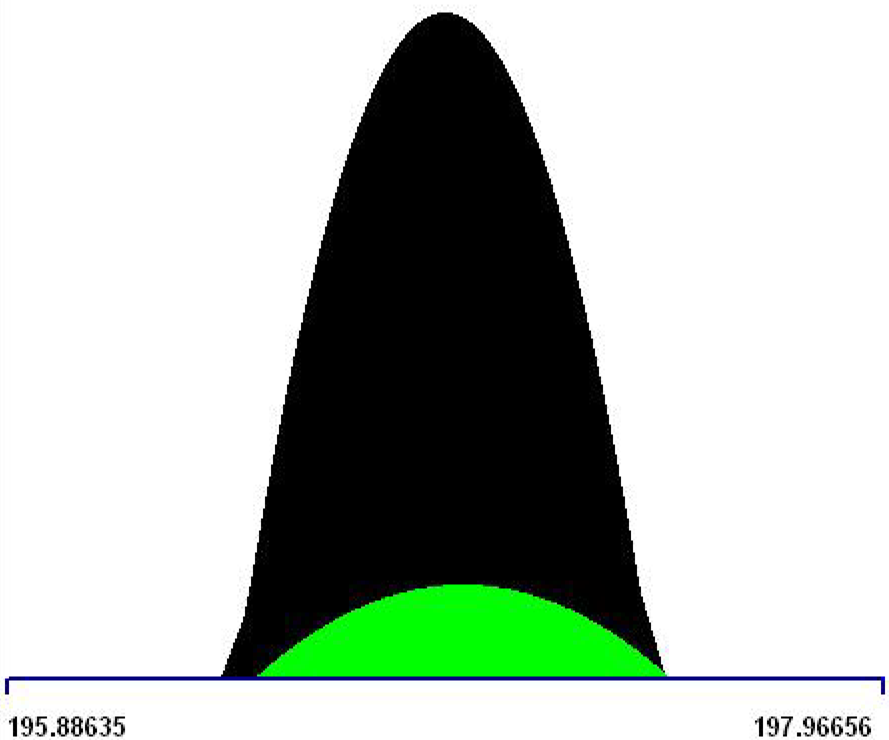
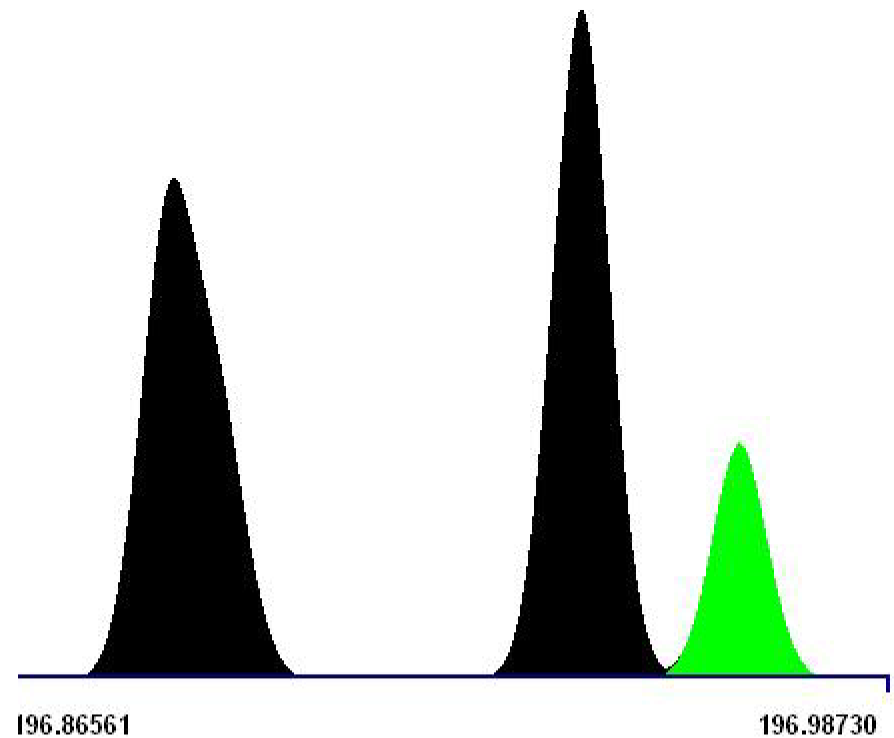
Nominal Mass	Accurate Mass	Abundance [%]	Au 79
197	196.96656	100.00	



Quadruple Resolution



10,000 HR Resolution

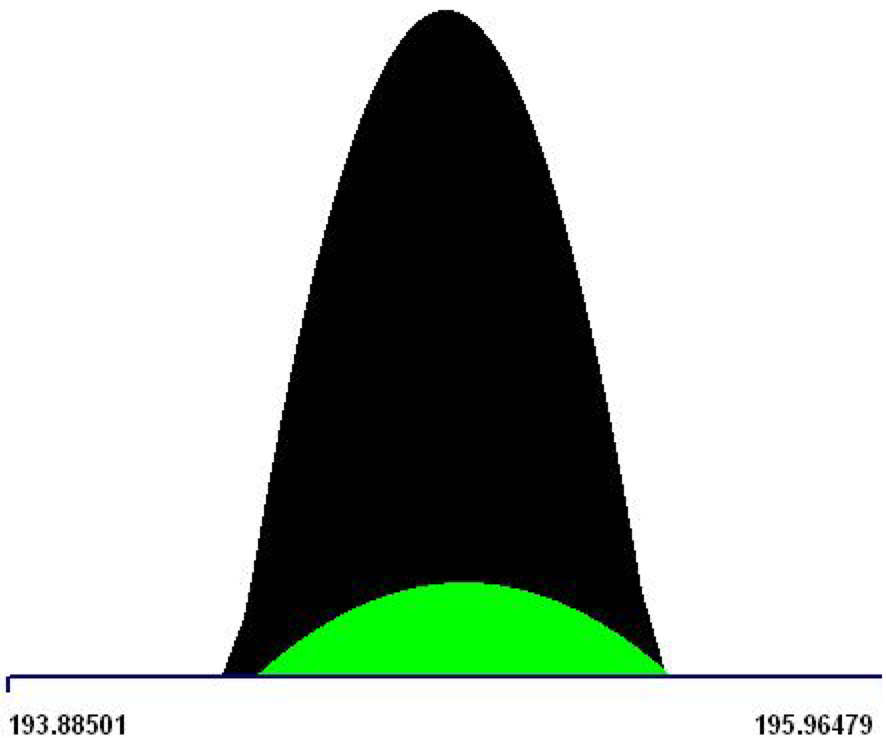
Some Interferences:

$^{157}Gd^{40}Ar$

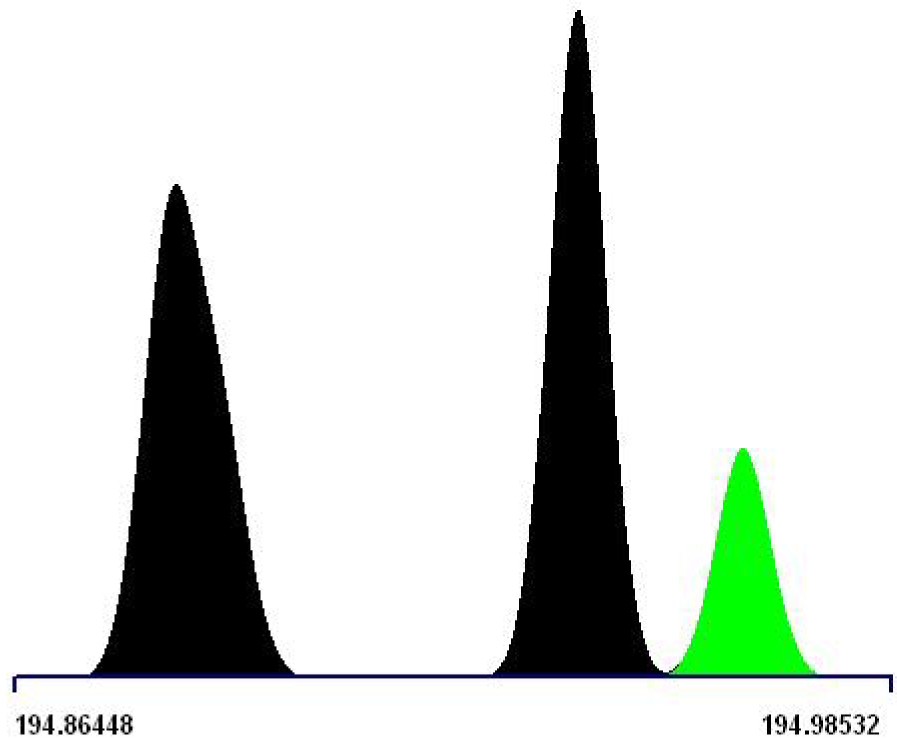
$^{181}Ta^{16}O$

Nominal Mass	Accurate Mass	Abundance [%]
195	194.96479	33.80

Pt
78



Quadruple Resolution



10,000 HR Resolution

Some Interferences:

$^{155}Gd^{40}Ar$

$^{159}Tb^{36}Ar$

$^{179}Hf^{16}O$

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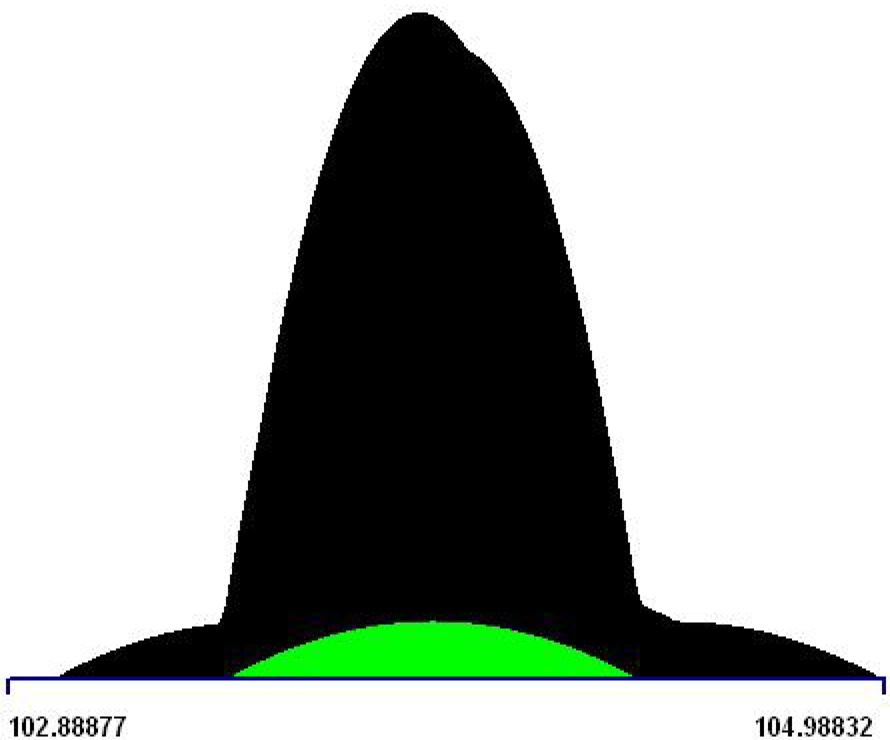
Nominal Mass	Accurate Mass	Abundance [%]	Pd 46
104	103.90403	11.14	



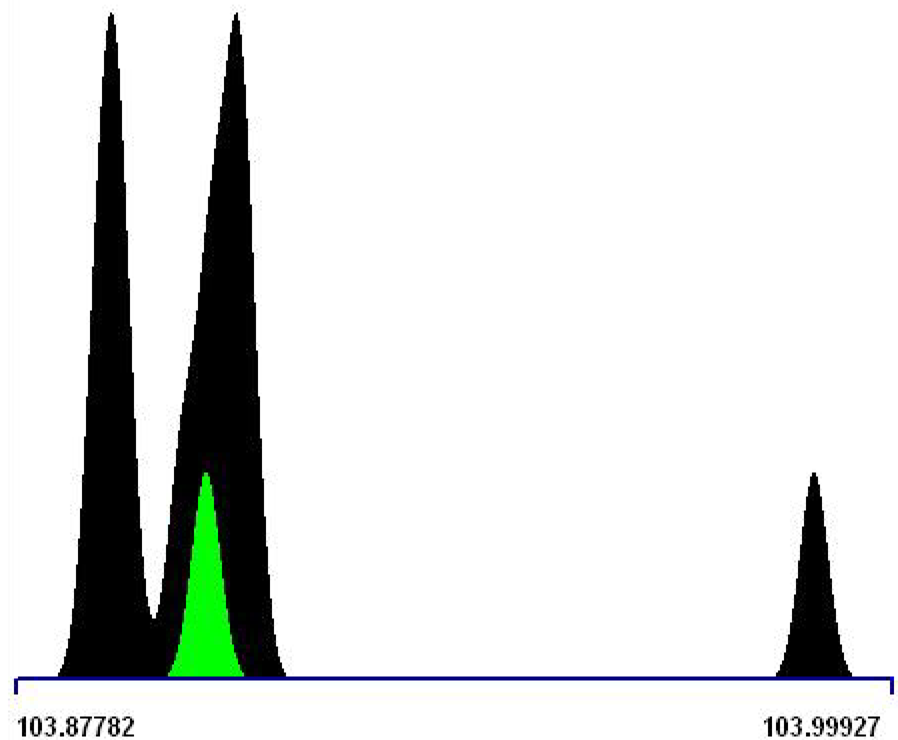
Quadruple Resolution

Some Interferences:

$^{207}Pb^{++}$ $^{88}Sr^{16}O$ $^{208}Pb^{++}$

$^{64}Ni^{40}Ar$ $^{209}Bi^{++}$

$^{64}Zn^{40}Ar$ Ru



10,000 HR Resolution

Interference:

Ru

$^{88}Sr^{16}O$

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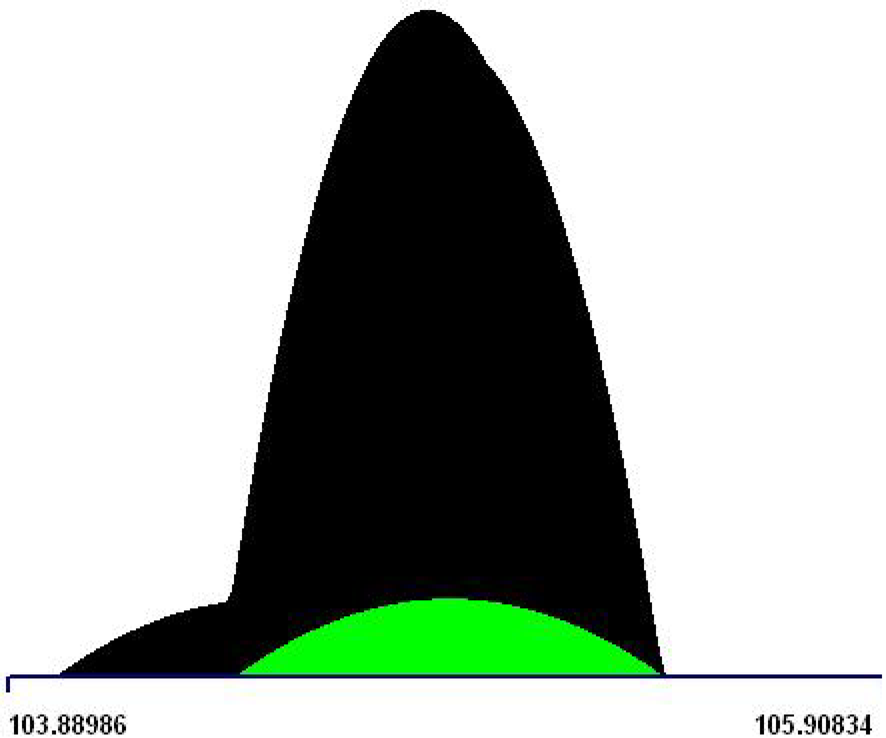
Nominal Mass	Accurate Mass	Abundance [%]
105	104.90508	22.33

Pd
46



Quadruple Resolution

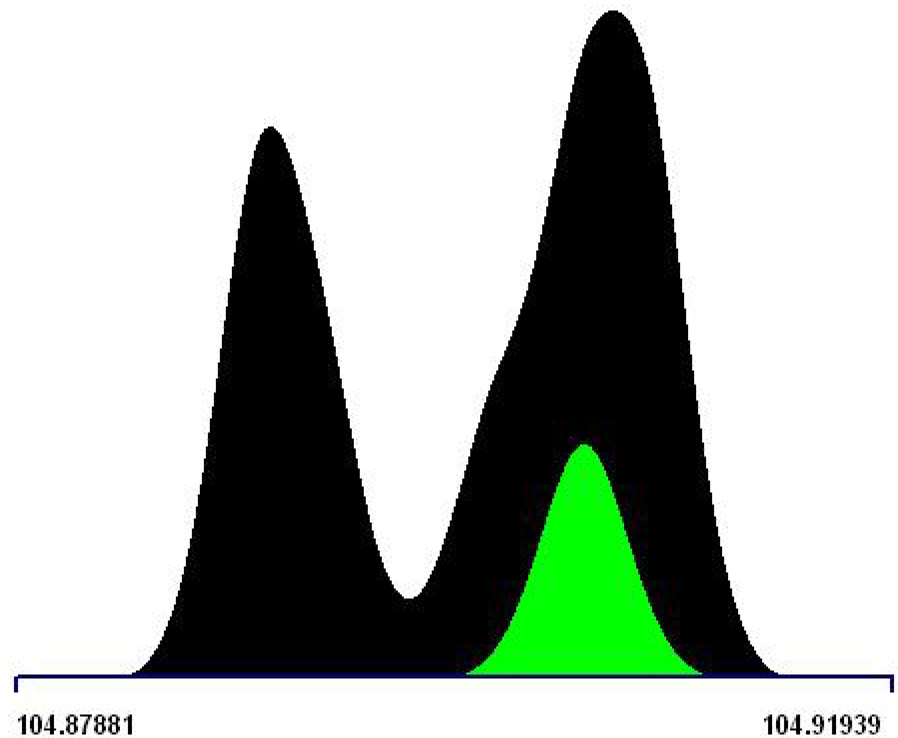
Some Interferences:

$^{209}Bi^{++}$

$^{89}Y^{16}O$

$^{65}Cu^{40}Ar$

$^{69}Ga^{36}Ar$



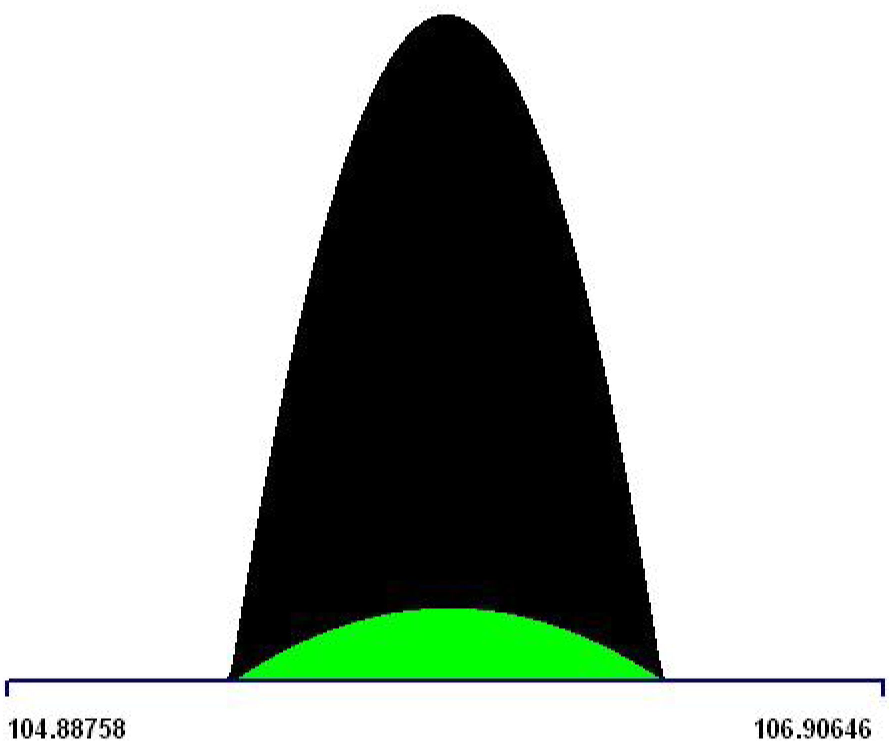
10,000 HR Resolution

Interference:

$^{89}Y^{16}O$

Nominal Mass	Accurate Mass	Abundance [%]
106	105.90348	27.33

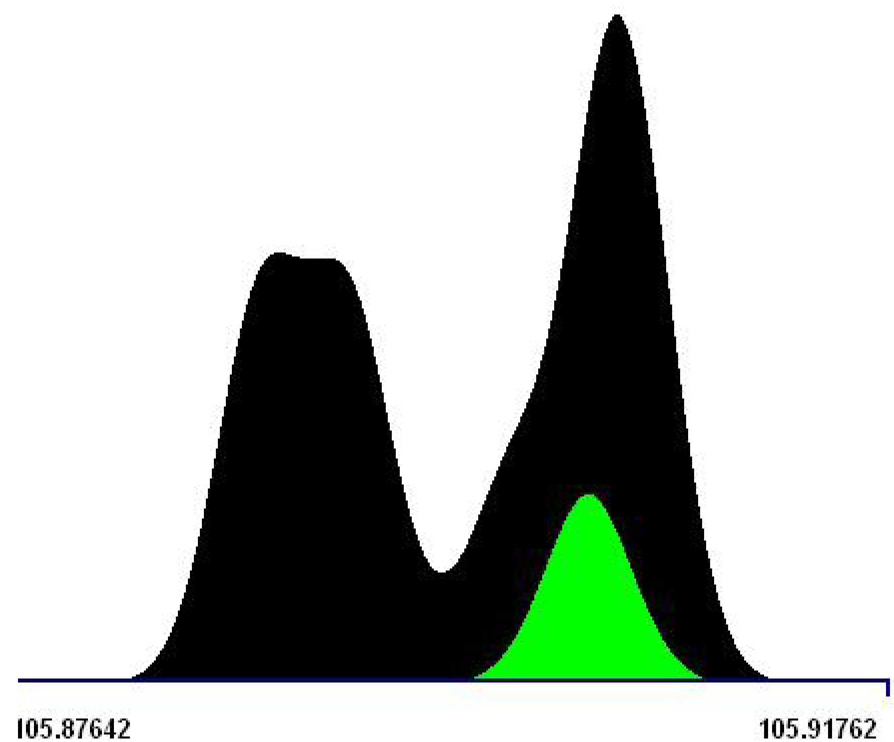
Pd
46



Quadruple Resolution

Some Interferences:

$^{66}Zn^{40}Ar$
$^{90}Zr^{16}O$ Cd
$^{88}Sr^{18}O$



10,000 HR Resolution

Interference:

$^{88}Sr^{18}O$
$^{90}Zr^{16}O$
Cd

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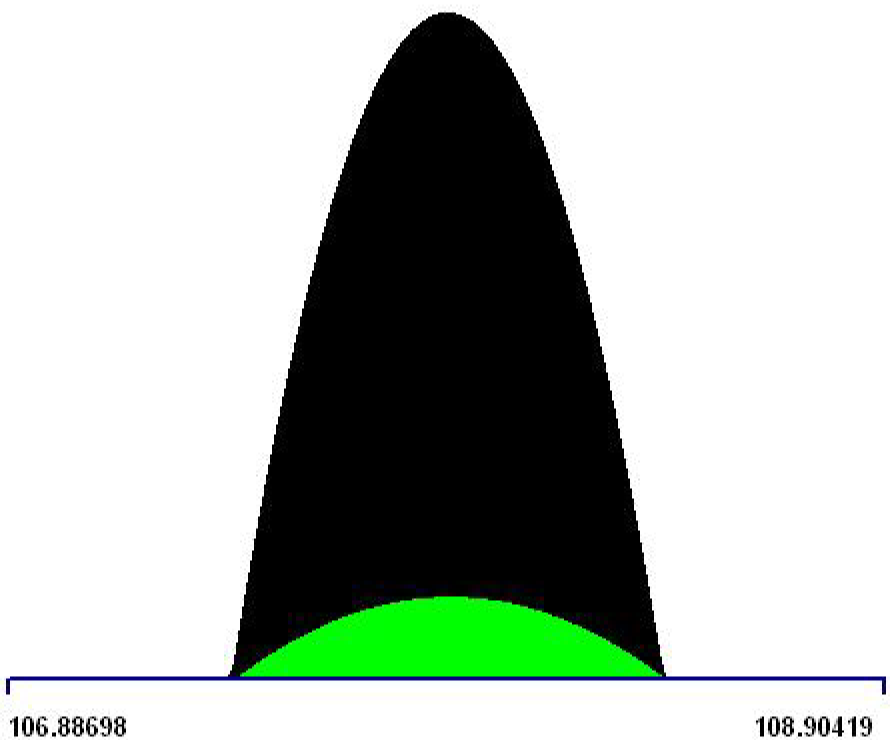
Nominal Mass	Accurate Mass	Abundance [%]	Pd 46
108	107.90389	26.46	



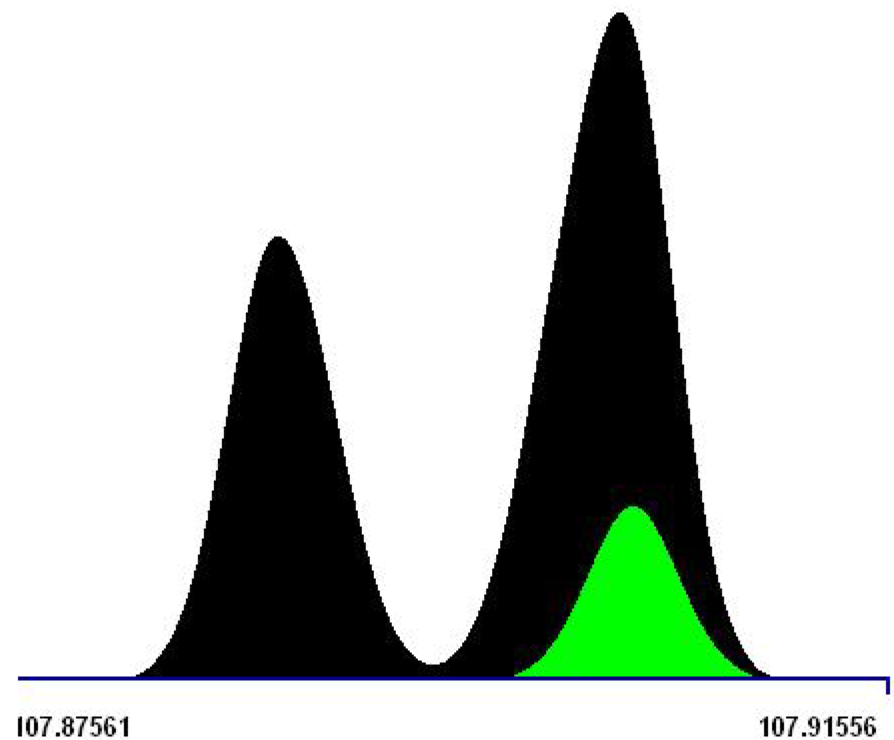
Quadruple Resolution

Some Interferences:

$^{68}Zn^{40}Ar$ $^{90}Zr^{18}O$

$^{92}Zr^{16}O$

$^{92}Mo^{16}O$ Cd



10,000 HR Resolution

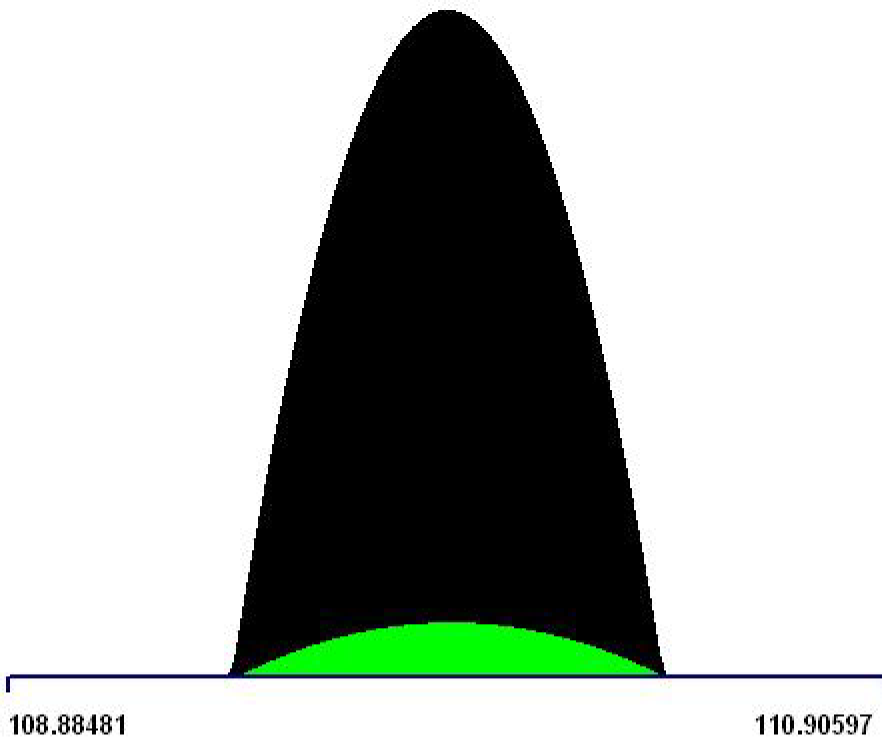
Some Interferences:

$^{90}Zr^{18}O$ Cd

$^{92}Zr^{16}O$

$^{92}Mo^{16}O$

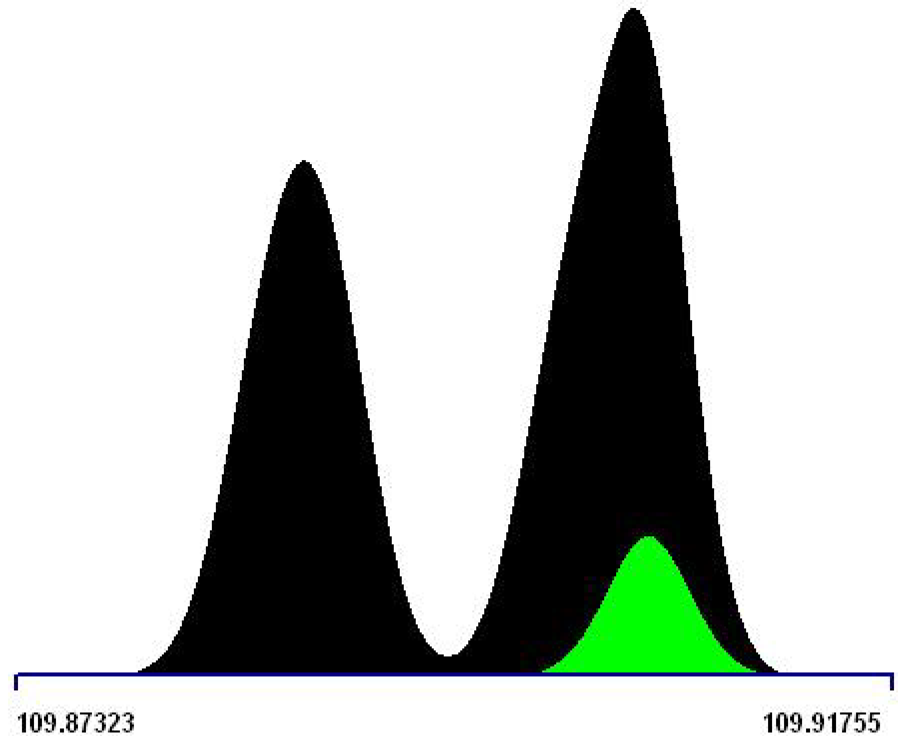
Nominal Mass	Accurate Mass	Abundance [%]	Pd 46
110	109.90517	11.72	



Quadruple Resolution

Some Interferences:

$^{70}Ge^{40}Ar$ $^{94}Mo^{16}O$
$^{70}Zn^{40}Ar$ $^{94}Zr^{16}O$
$^{74}Ge^{36}Ar$ Cd



10,000 HR Resolution

Some Interferences:

$^{94}Mo^{16}O$
$^{94}Zr^{16}O$
Cd

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Clean Sample Preparation Areas

HEPA filtered laminar flow hoods

Room air HEPA filtered

Polypropylene workbenches (Metal free work stations)

HEPA Filtered Air in ICP-MS Laboratory

Platinum Group Elements and Gold in Water

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

	ICP-MS	HR-ICP/MS
Au	5	0.05
Pt	10	0.5
Pd	20 varies	1 varies (Cd, Sr, Zr, Mo, Y interferes)
Rh	20	0.5
Ru	10	1
Ir	5	1

Biogeochemistry

- 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

Au 0.01	Ag 1	Pt 0.1	Pd 0.2
Cu 15	Mo 1	Co 0.5	Re 0.1
Ni 100	Pb 6	Ru 0.5	Sb 0.2
As 5	Bi 1	Te 1	Hg 5

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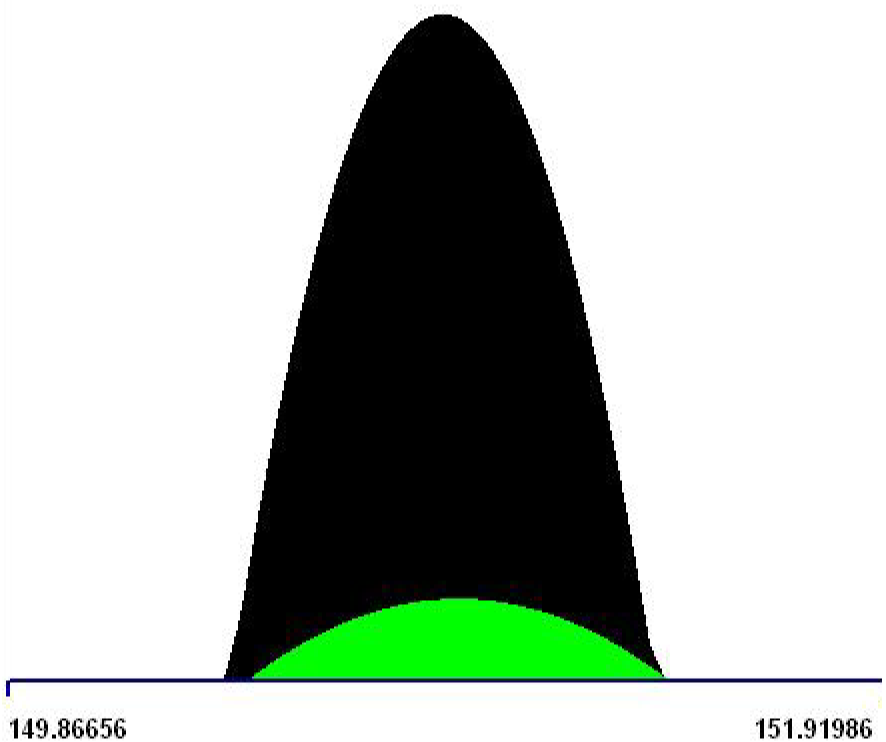
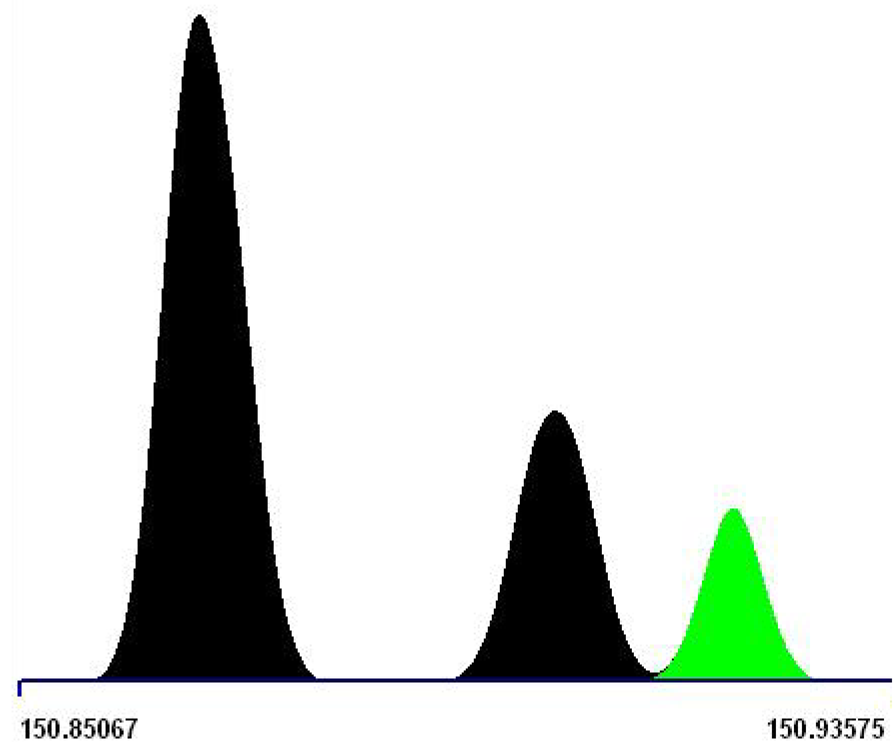
Rare Earth Elements

- 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

Nominal Mass	Accurate Mass	Abundance [%]	Eu 63
151	150.91986	47.80	



Quadruple Resolution



10,000 HR Resolution

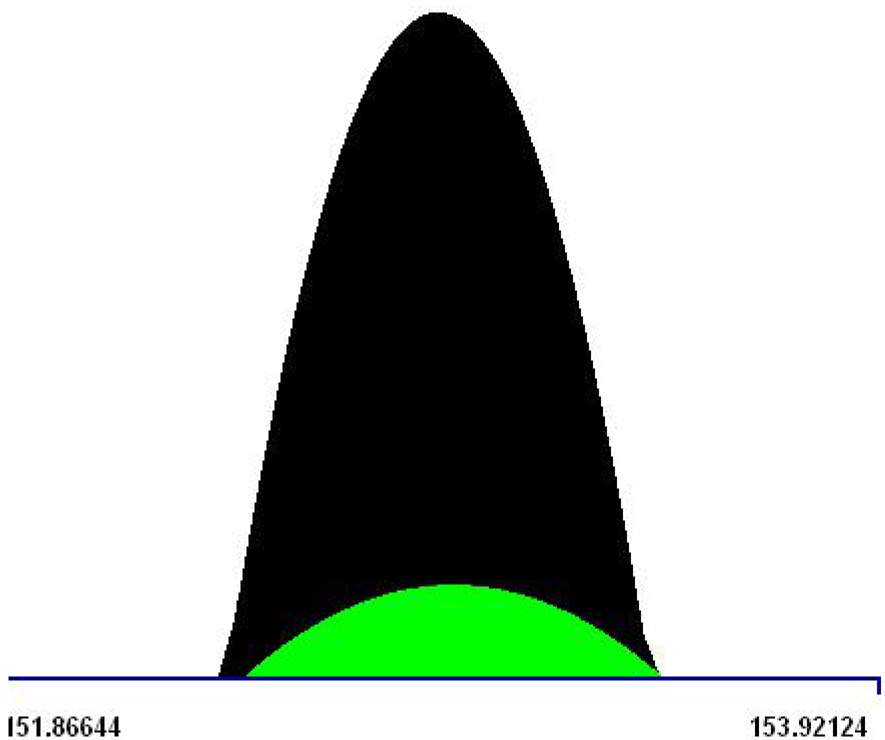
Some Interferences:

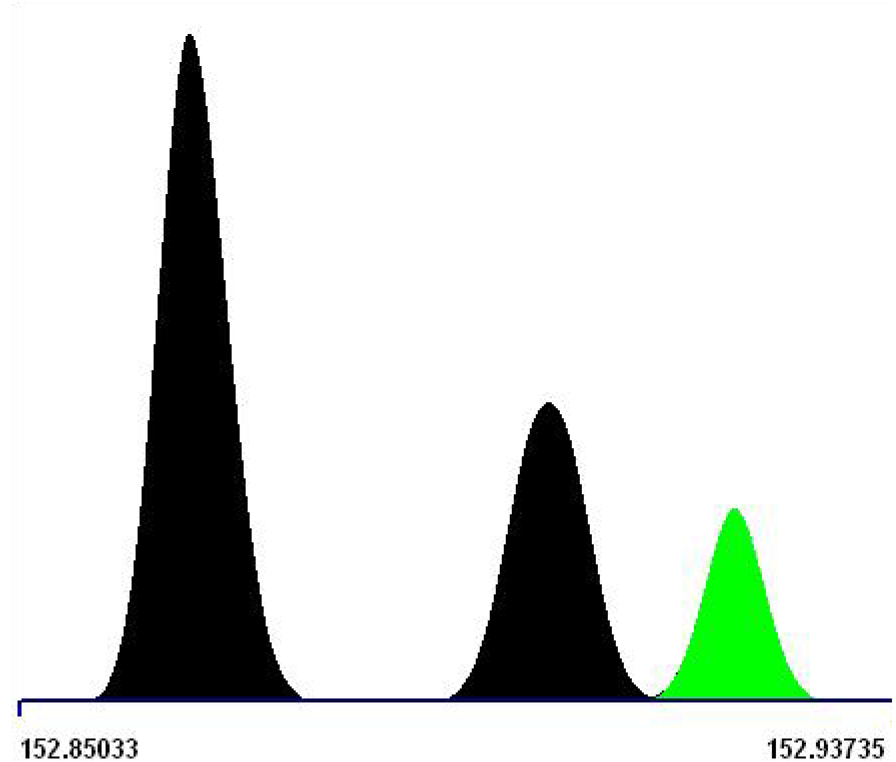
$^{111}Cd^{40}Ar$ $^{133}Cs^{18}O$

$^{115}In^{36}Ar$

$^{135}Ba^{16}O$

Nominal Mass	Accurate Mass	Abundance [%]	Eu 63
153	152.92124	52.20	





Quadruple Resolution

10,000 HR Resolution

Some Interferences:

$^{113}In^{40}Ar$

$^{113}Cd^{40}Ar$

$^{137}Ba^{16}O$

Rare Earth Elements: Detection Limits by Lithium Metaborate/Tetraborate Fusion HR-ICP/MS

Analyte	ICP-MS	HR-ICP/MS	Analyte	ICP-MS	HR-ICP/MS
La	50	5	**Tb**	10	1
Ce	50	5	**Dy**	10	1
Pr	10	1	**Ho**	10	1
Nd	50	5	**Er**	10	1
Sm	10	1	**Tm**	5	0.5
Eu	5	0.5	**Yb**	10	1
Gd	10	1	**Lu**	2	0.2

Detection limits in ppb

Pb Isotopes: Precision

ICP-MS	HR-ICP/MS	TIMS
0.5%	0.1%	<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.
(i) 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

Metal Speciation

Example: Arsenic Speciation

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

Increasing toxicity

Methods for measuring metal speciation?

Chromatography (for separation) + Spectrometry (for detection)

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!

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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

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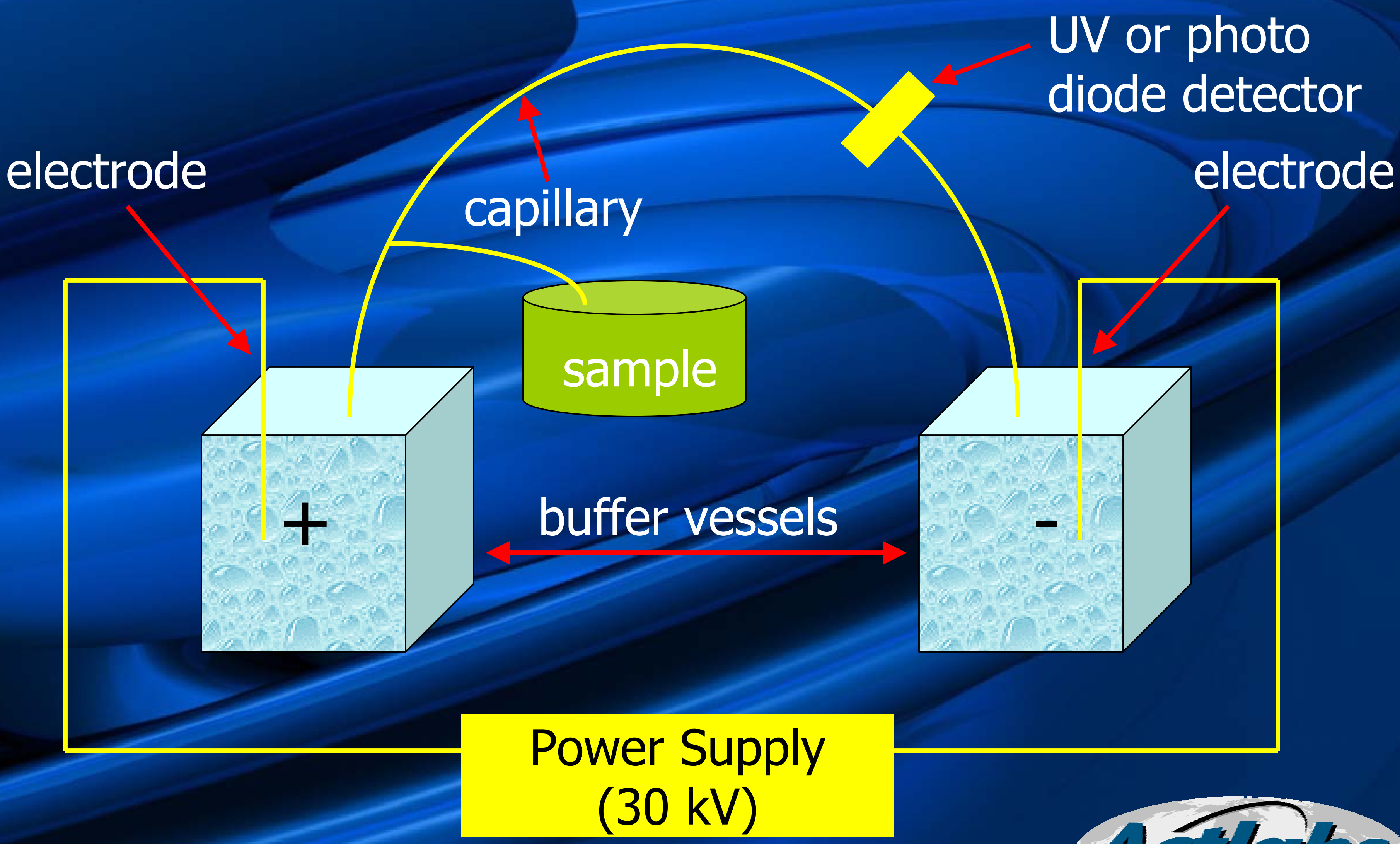
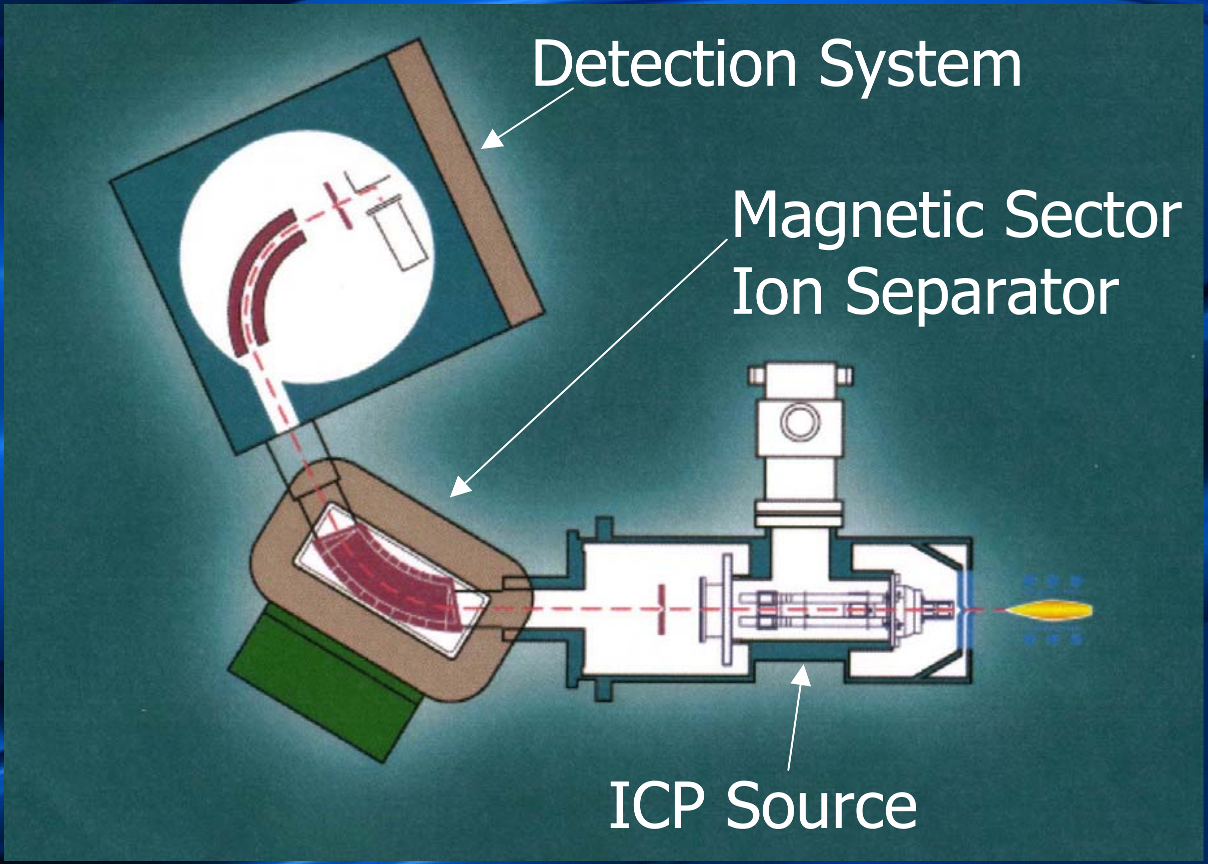
What is CE-HR/ICP-MS?

Principle of Capillary Electrophoresis (CE)

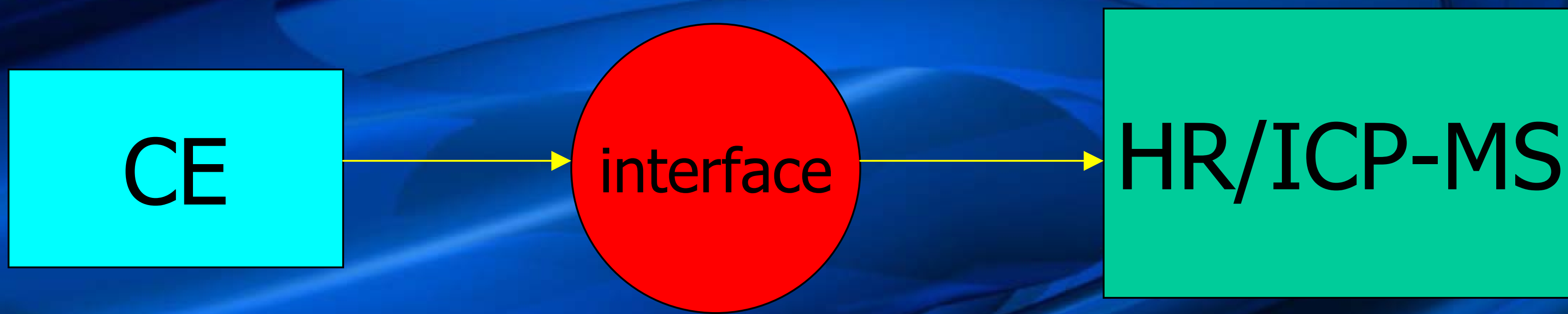


Species are moving because of their size

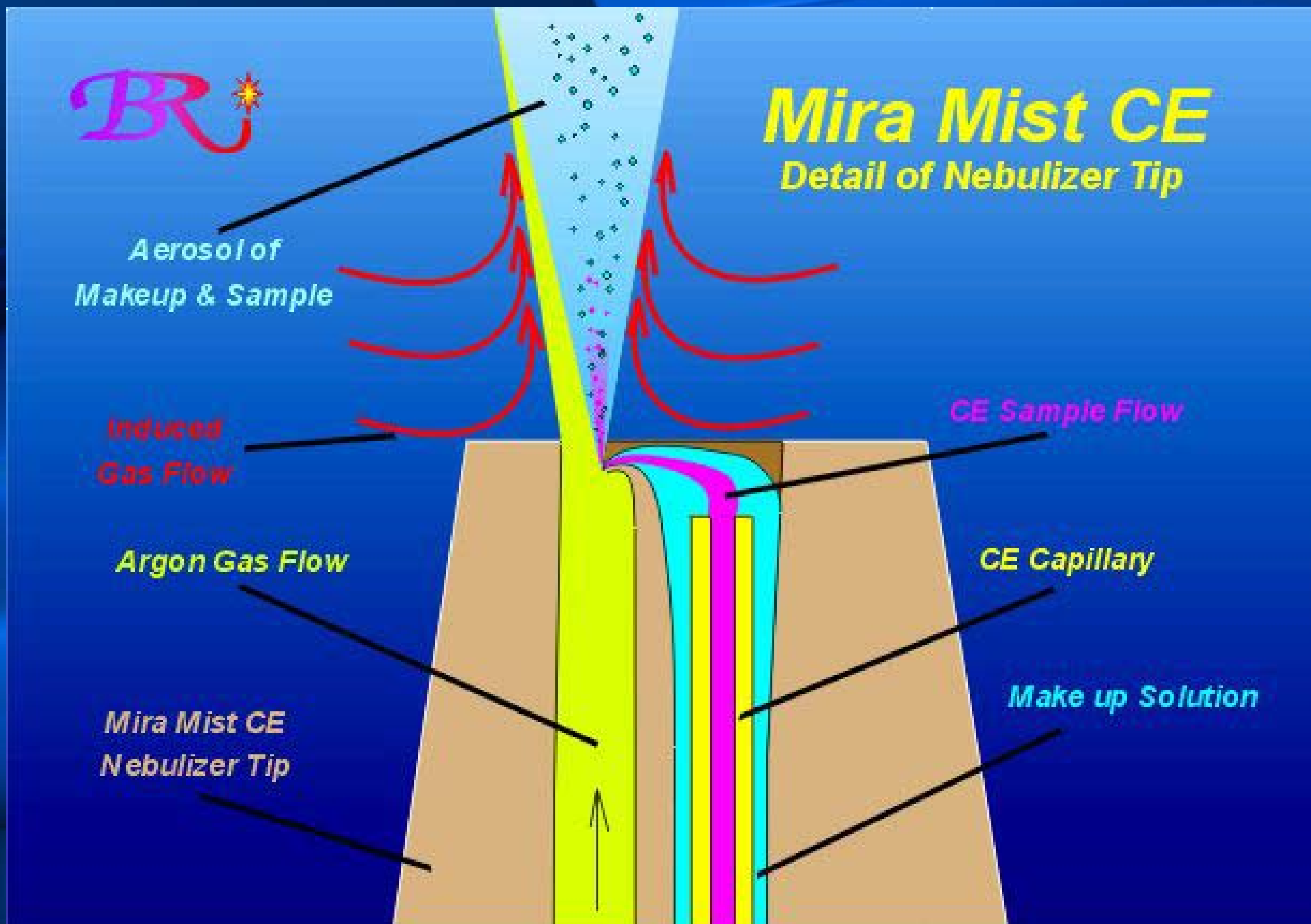
Principle of High Resolution Magnetic Sector ICP-MS



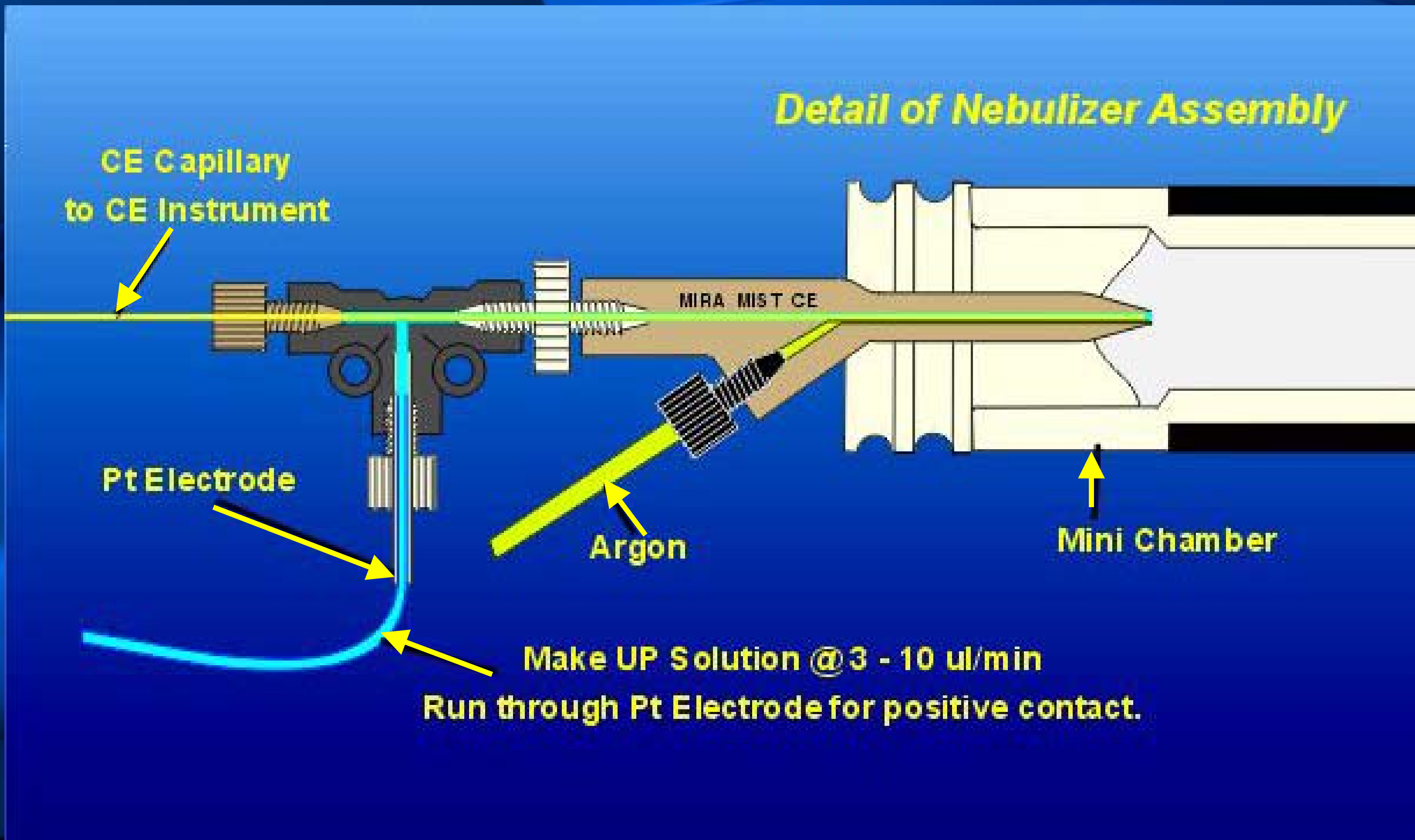
Coupling CE to HR/ICP-MS



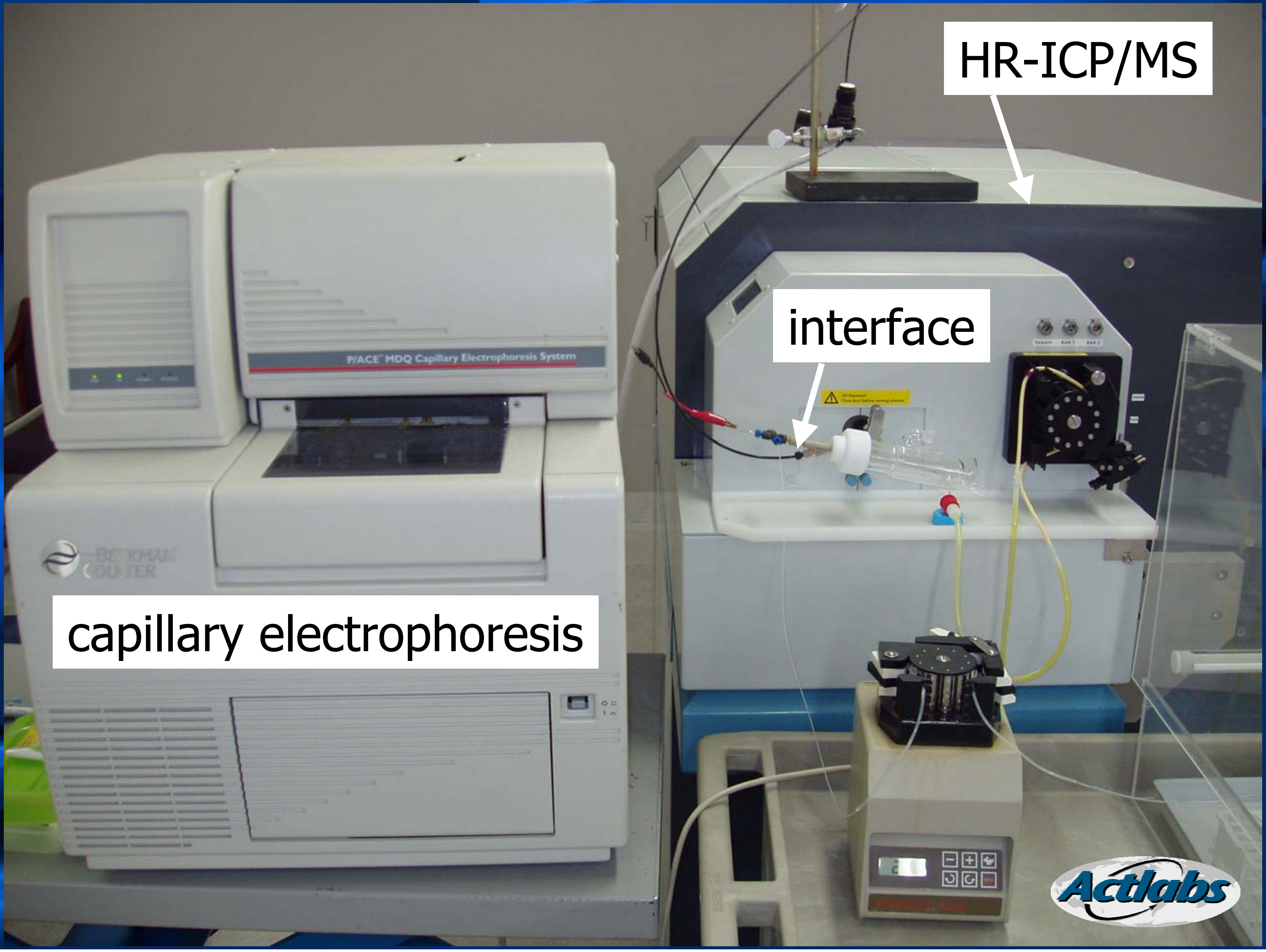
Principle of MIRA Mist CE Nebuliser



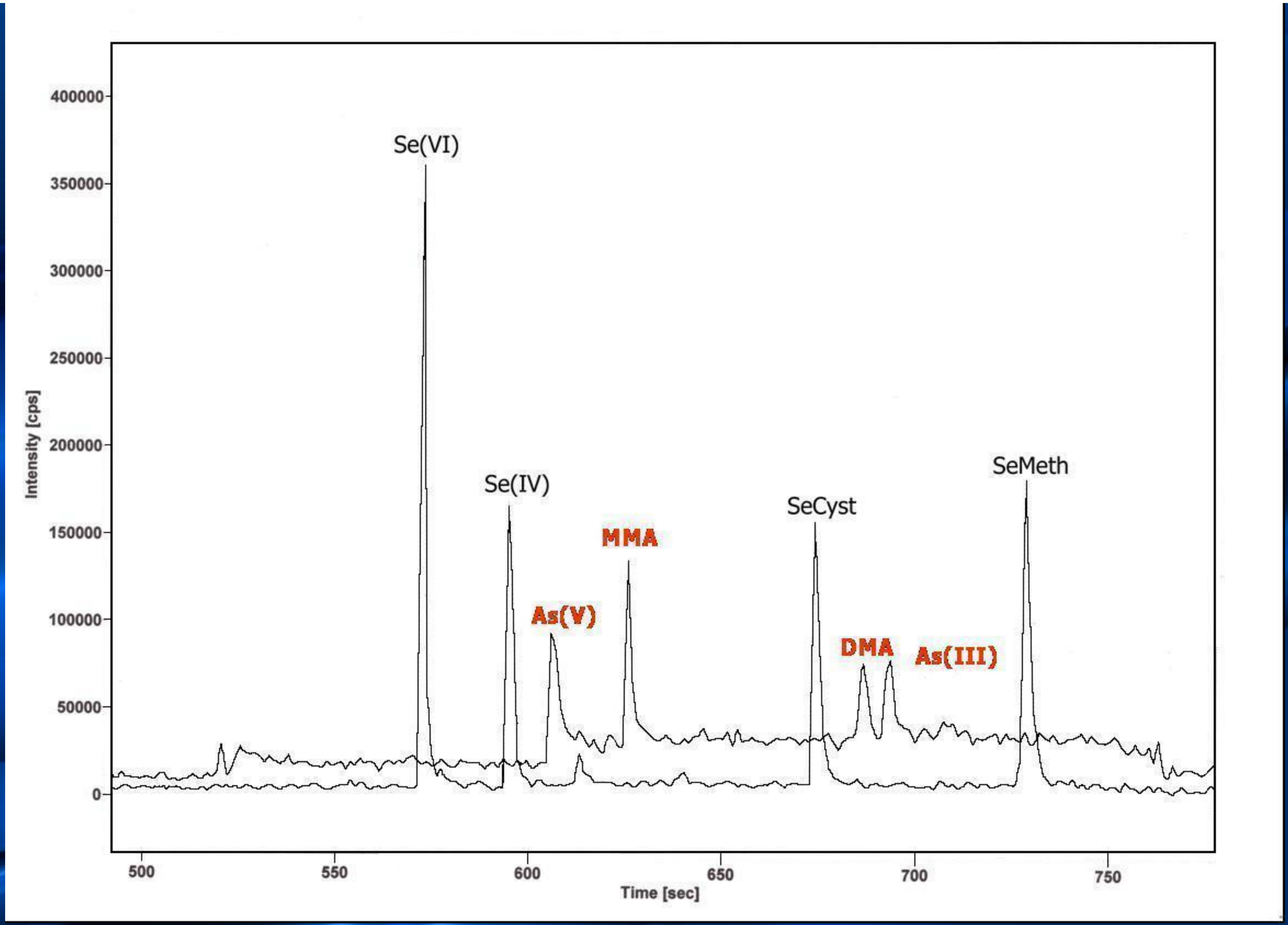
CE-HR/ICP-MS Interface



Capillary Electrophoresis and Interface



CE-HR/ICP-MS is a multi-element speciation technique



Pore Water Squeezing Apparatus
(courtesy of Dr. Dave Blowes, Waterloo)

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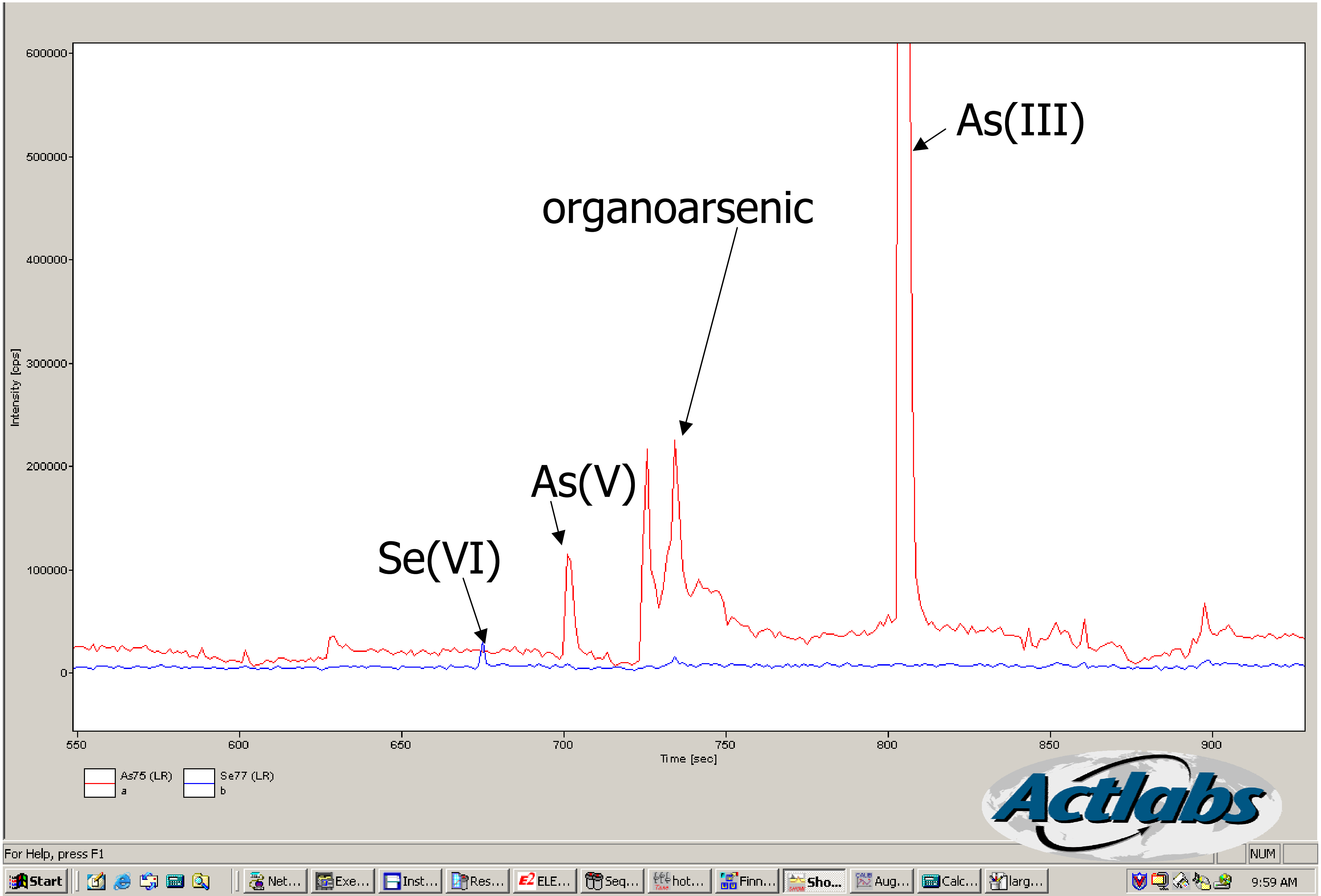
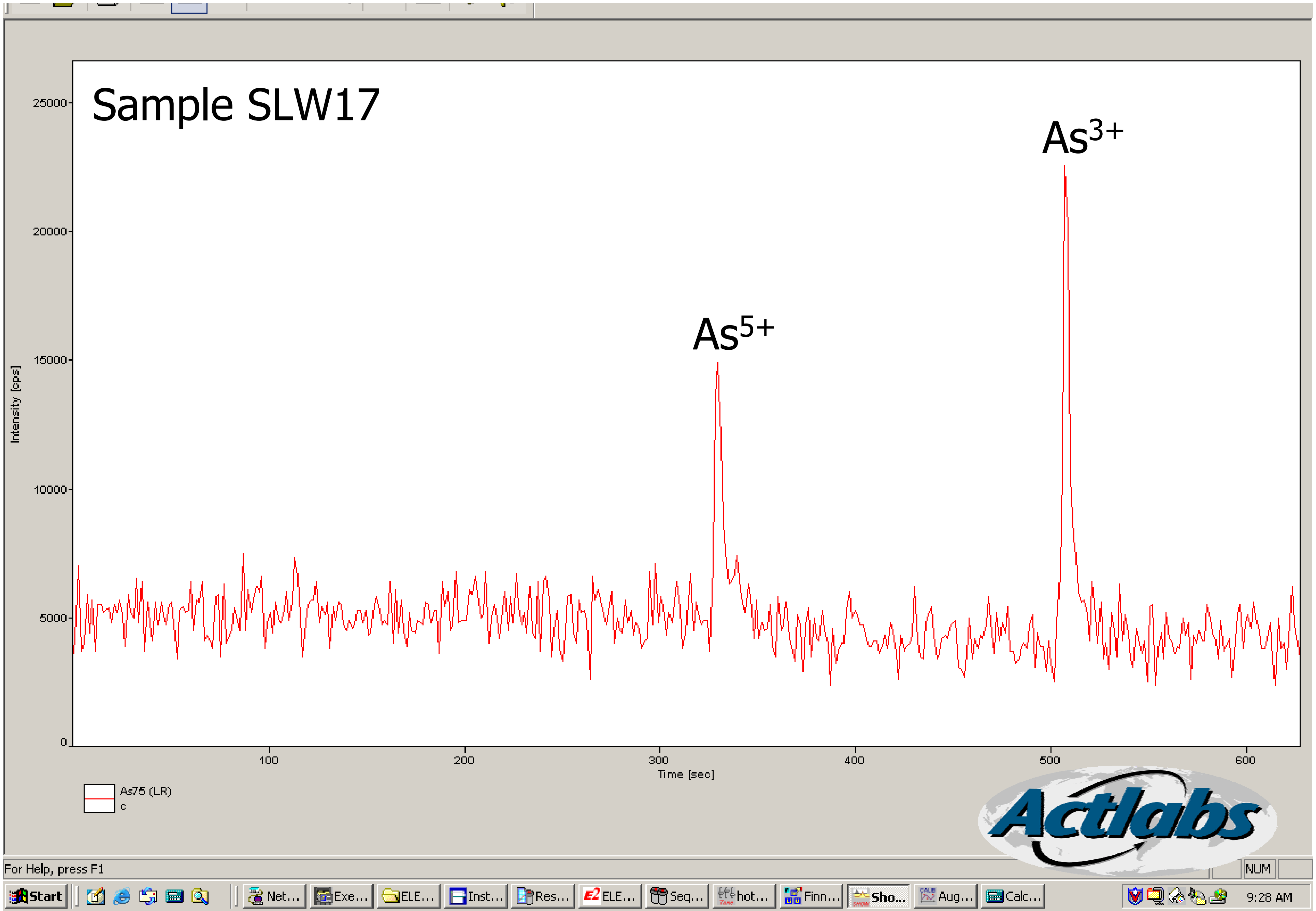
Pore water from mine tailings



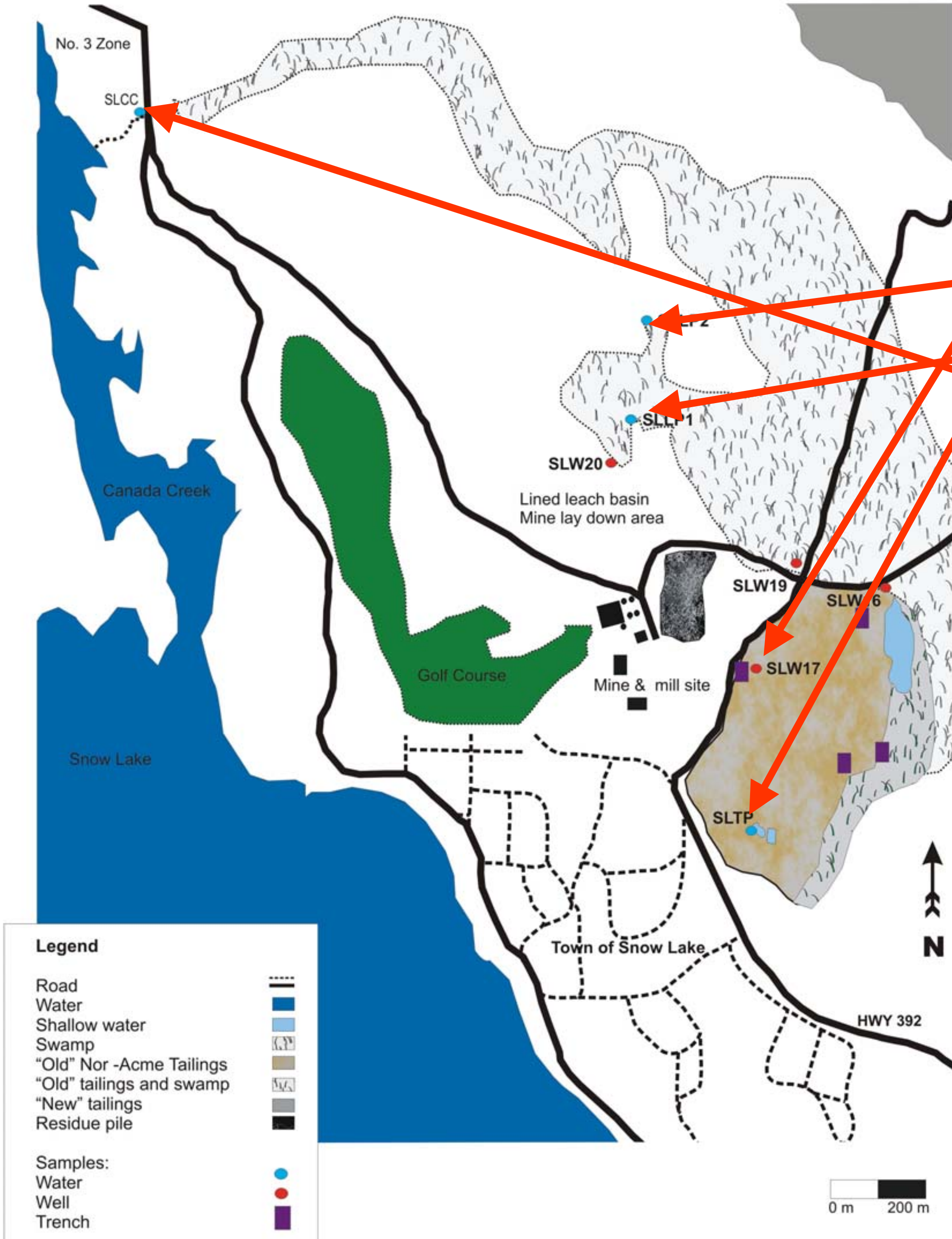
Water Well Sample Near Arsenopyrite Stockpile



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?

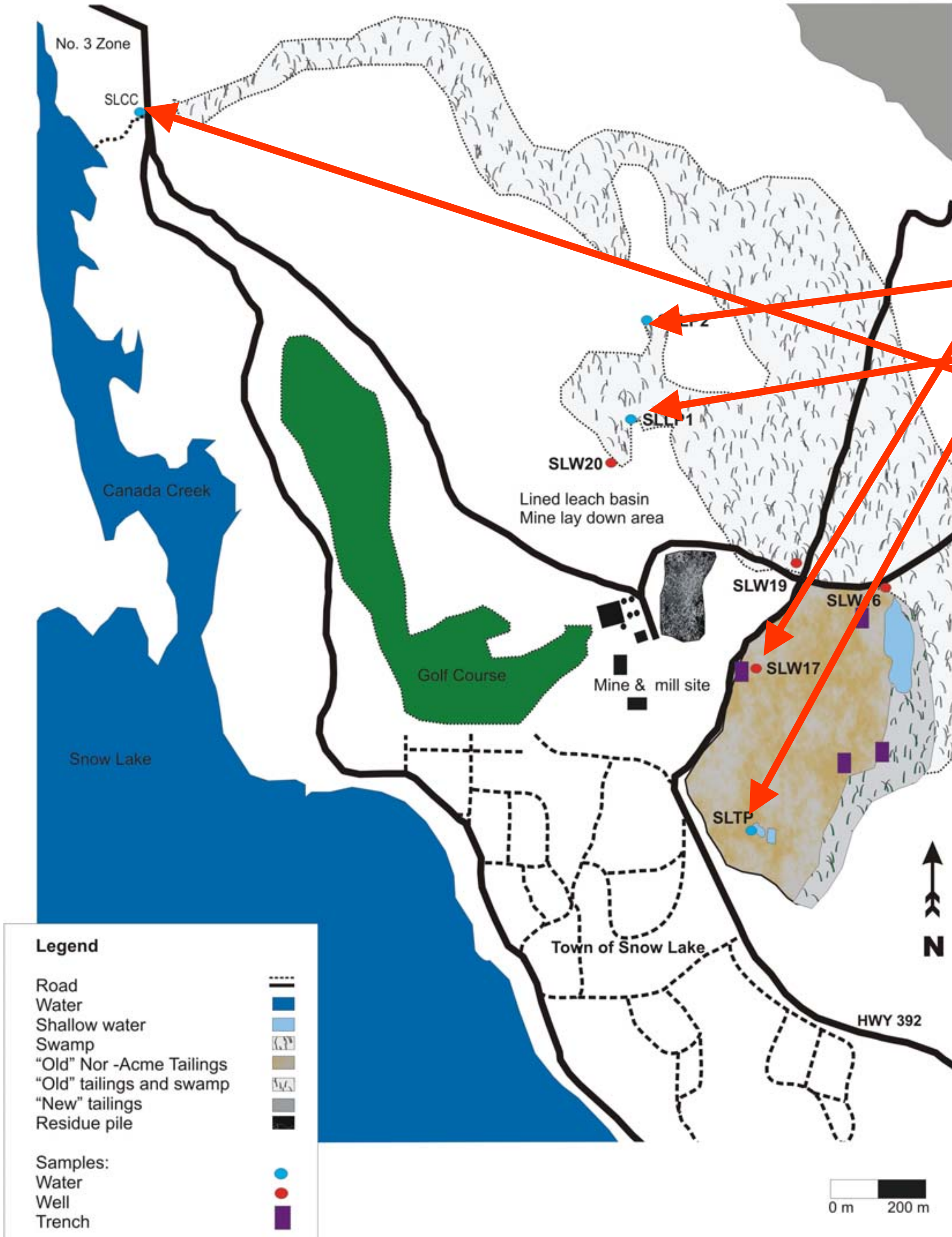
Linda Bloom in 3D Geochemistry CAMIRO Project is proposing to test this hypothesis



	As^{3+}	As^{5+}
SLW17	0.6	0.2
SLTP	<0.1	2.6
SLLP2	<0.1	0.6
SLLP1	<0.1	0.3
SLCC	<0.1	<0.1

Gold Mine in Canada

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



	Fe^{2+}	Fe^{3+}
SLW17	47	11
SLTP	<0.2	1.2
SLLP2	1.2	<0.2
SLLP1	0.3	<0.2
SLCC	0.5	0.3

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

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