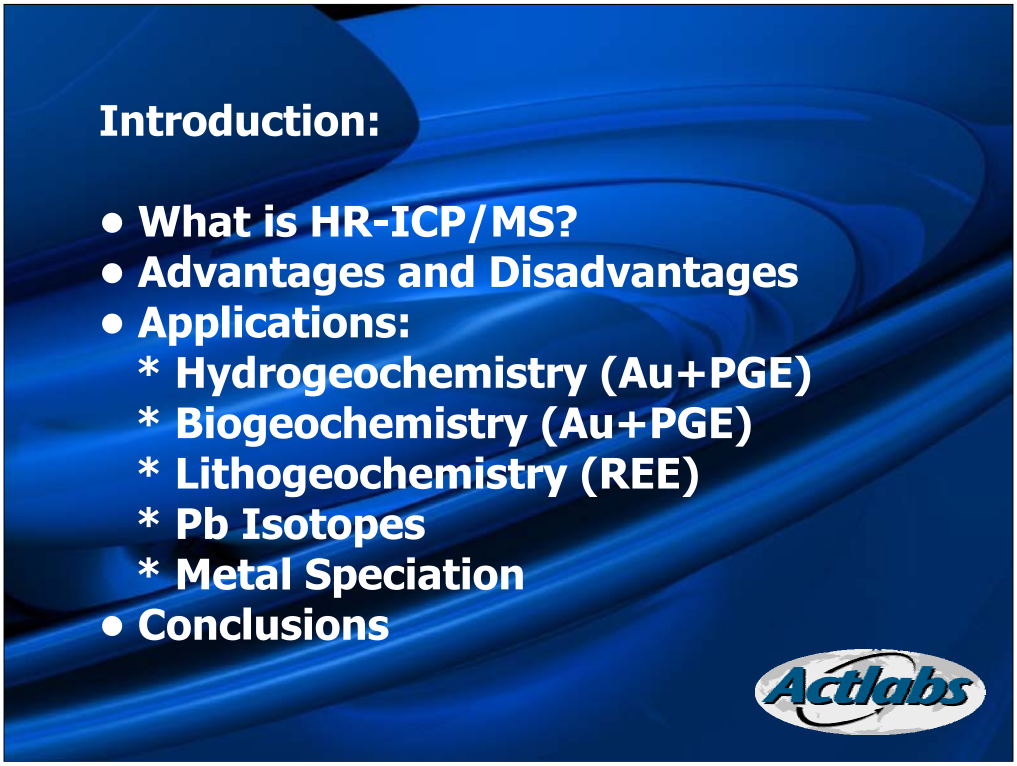
Implications for Exploration With The Use of High Resolution ICP-MS Technology

Eric L. Hoffman, Yakov Kapusta and M. Dzierzgowska

Actlabs

The toxicity of trace metals in the environment is an area of increasing concern. Toxicity of the trace metals is highly dependent on the molecular species to which they are chemically bound. For example Arsenic 5 is very toxic (check) whereas Arsenic 3 and the organoforms of arsenic are much less toxic.

Some of the species of interest for Arsenic is shown in Figure 2 .



Introduction:

- What is HR-ICP/MS?
- Advantages and Disadvantages
- Applications:
  - * Hydrogeochemistry (Au+PGE)
  - * Biogeochemistry (Au+PGE)
  - * Lithogeochemistry (REE)
  - * Pb Isotopes
  - * Metal Speciation
- Conclusions

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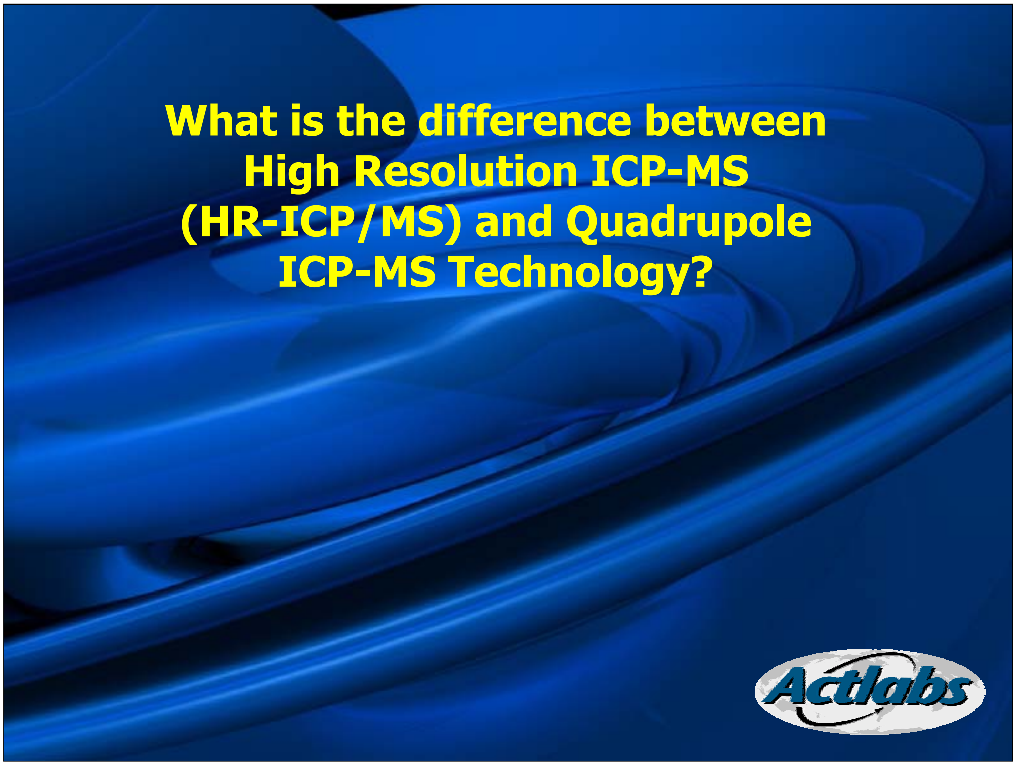
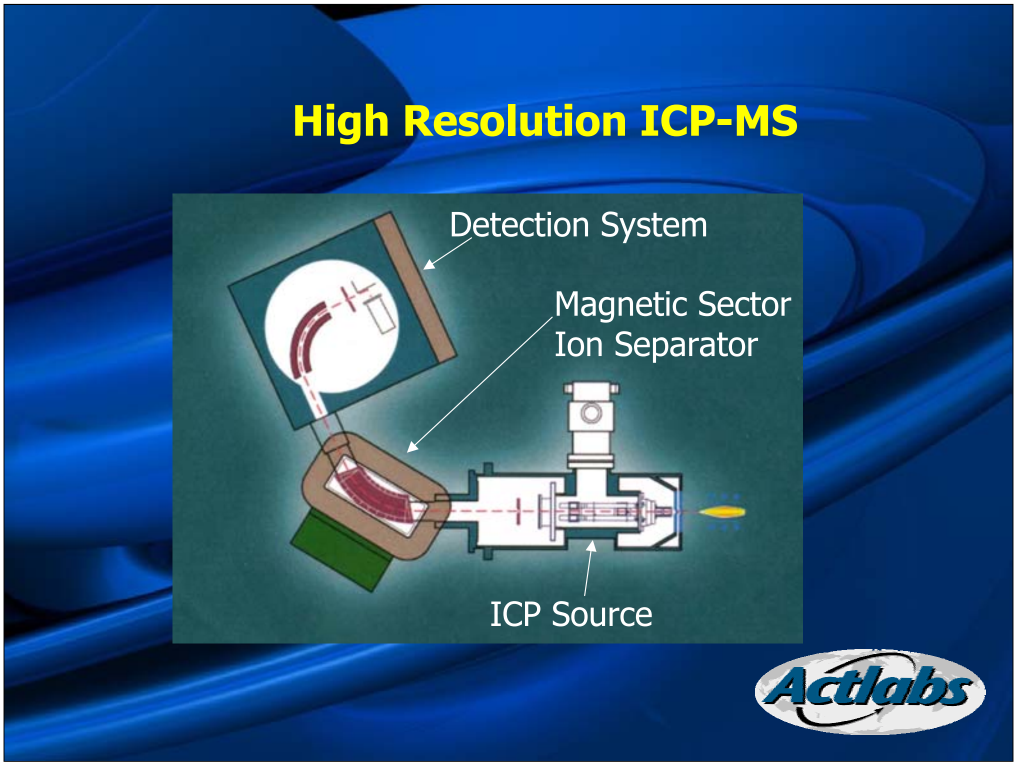


What is the difference between High Resolution ICP-MS (HR-ICP/MS) and Quadrupole ICP-MS Technology?



High Resolution ICP-MS

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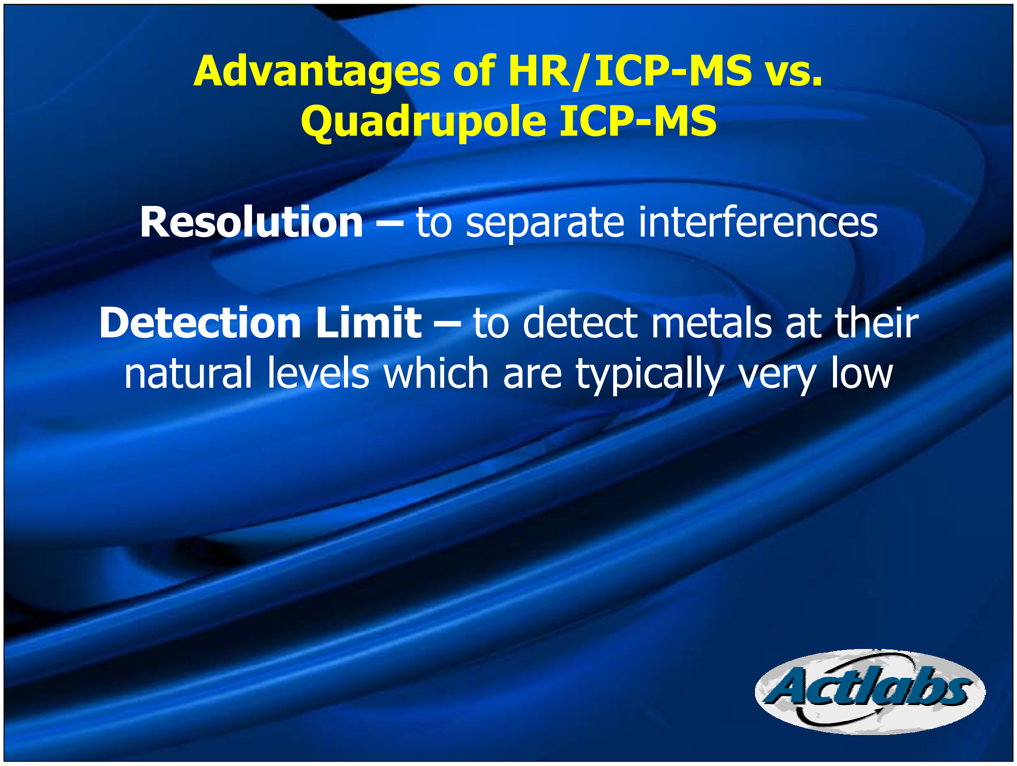


Advantages of HR/ICP-MS vs. Quadrupole ICP-MS

Resolution – to separate interferences

Detection Limit – to detect metals at their natural levels which are typically very low

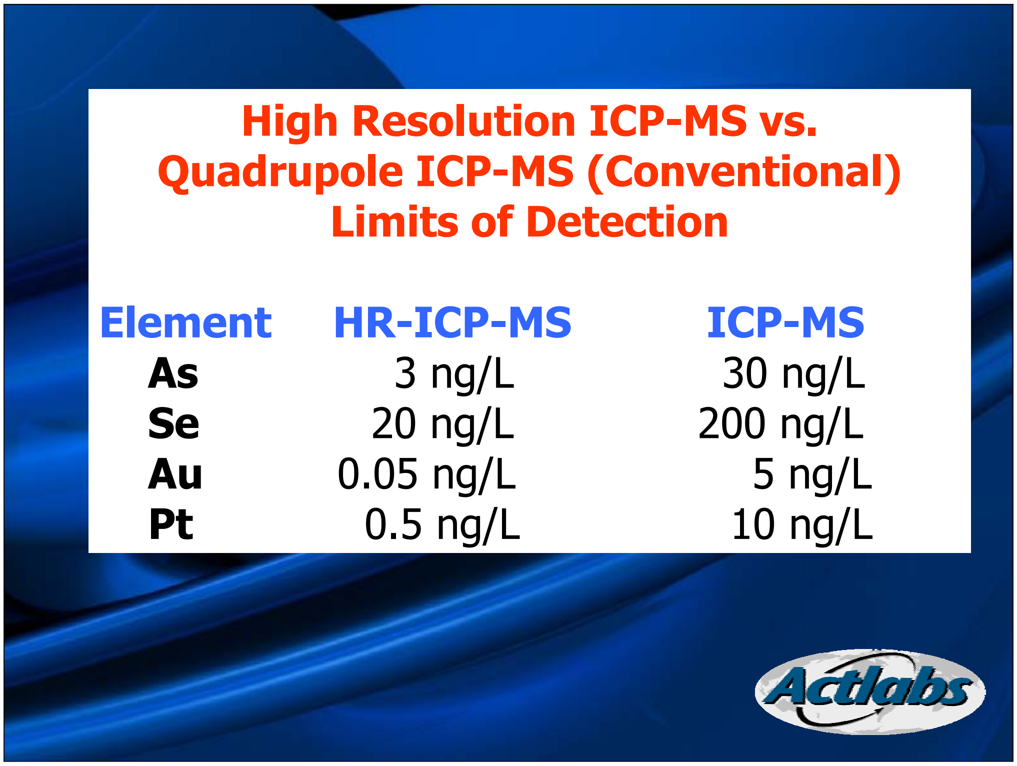
The first category is simple redox states: the species is a well-defined cation or anion. The second class is organometallic compounds. There is another group for some metals which includes metal complexes: the metal of concern form a coordination bond binding to a ligand.

Monitoring elemental species requires analytical technology with sufficient selectivity and

sensitivity to resolve and quantitate the individual species at ultra trace levels, since an individual toxic species may constitute only a small fraction of an element’s total concentration in a sample.

Modern HIGH PRESSURE LIQUID CHROMATOGRAPHY (HPLC) techniques are fairly versatile owing to the diversity of separation technologies available (multiple columns).

The separation mechanism complementary to HPLC is the capillary electrophoresis technique.



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

The combination of CE with HR-ICP-MS promises to be a very powerful tool for metal speciation. To produce commercial speciation data we require online analysis of CE coupled with the HR-ICP/MS. Use of conventional ICP/MS does not have the required detection limits.

Resolution Improvements:

Resolves Many Interferences Using
Quadrupole ICP-MS

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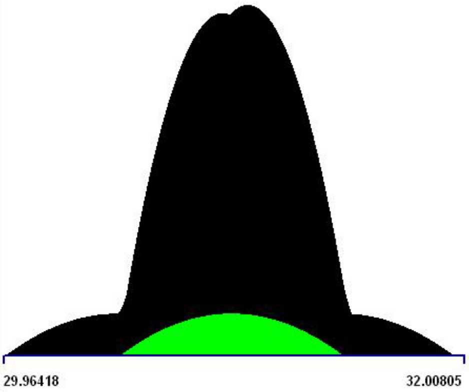
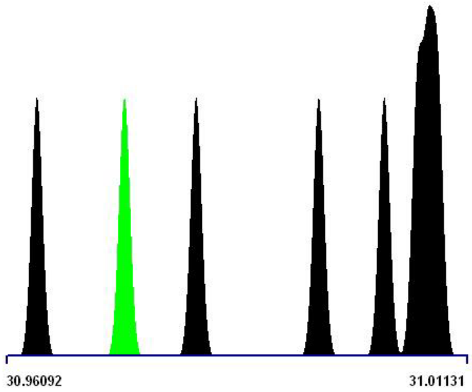
Nominal Mass	Accurate Mass	Abundance [%]
31	30.97376	100.00

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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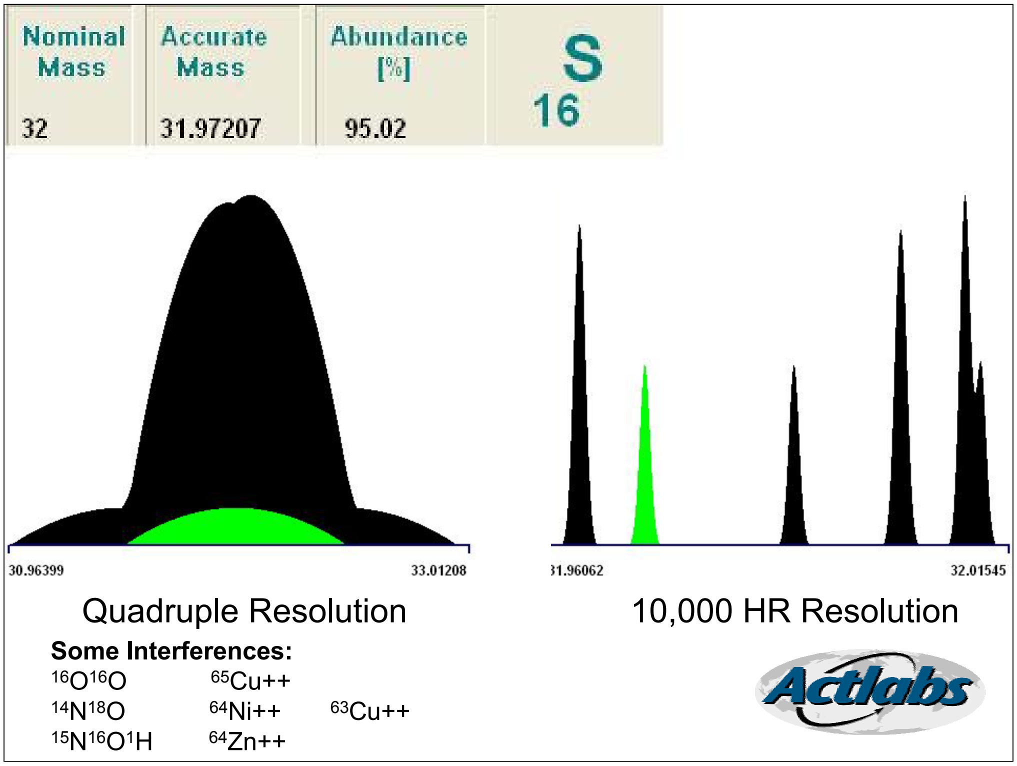


Nominal Mass	Accurate Mass	Abundance [%]	S 16
32	31.97207	95.02	

Quadruple Resolution

10,000 HR Resolution

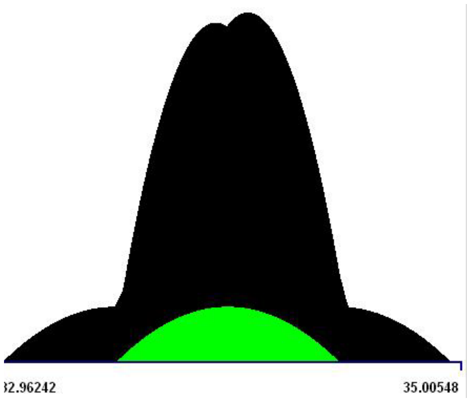
Some Interferences:

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

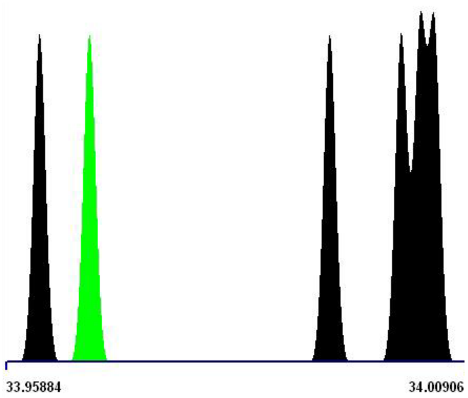
$^{14}N^{18}O$ $^{64}Ni^{++}$ $^{63}Cu^{++}$

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

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



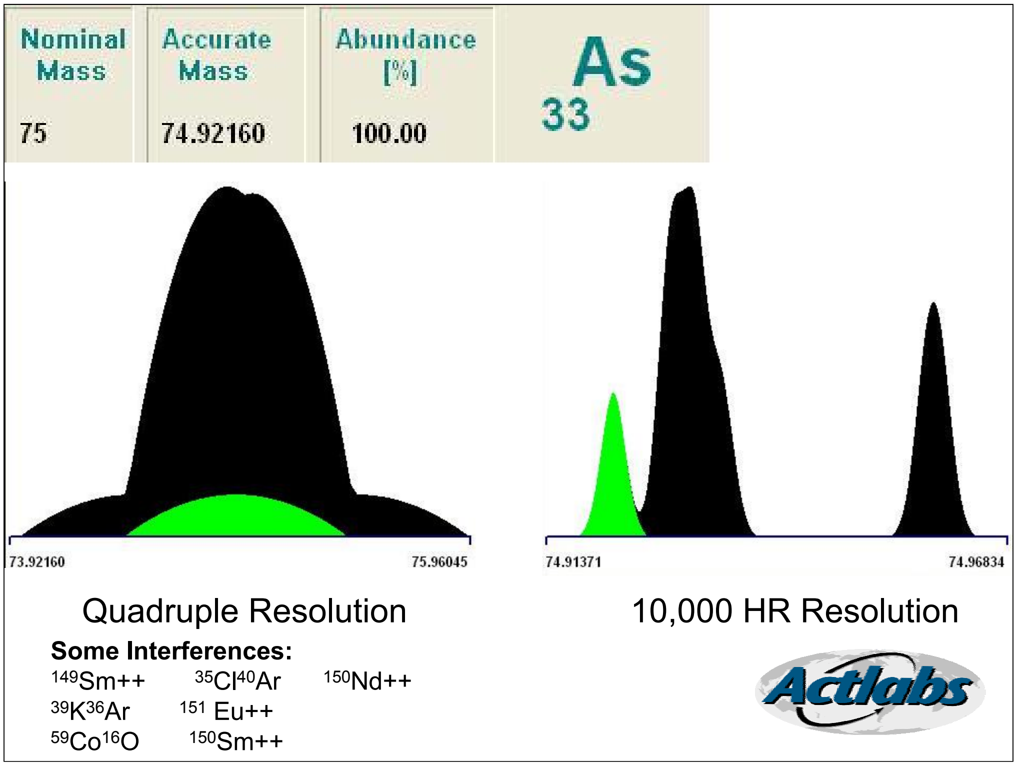
Quadruple Resolution



10,000 HR Resolution

Some Interferences:

^{67}Zn++ ^{16}O^{16}O^{1}H^{1}H
^{68}Zn++ ^{69}Ga++
^{18}O^{16}O



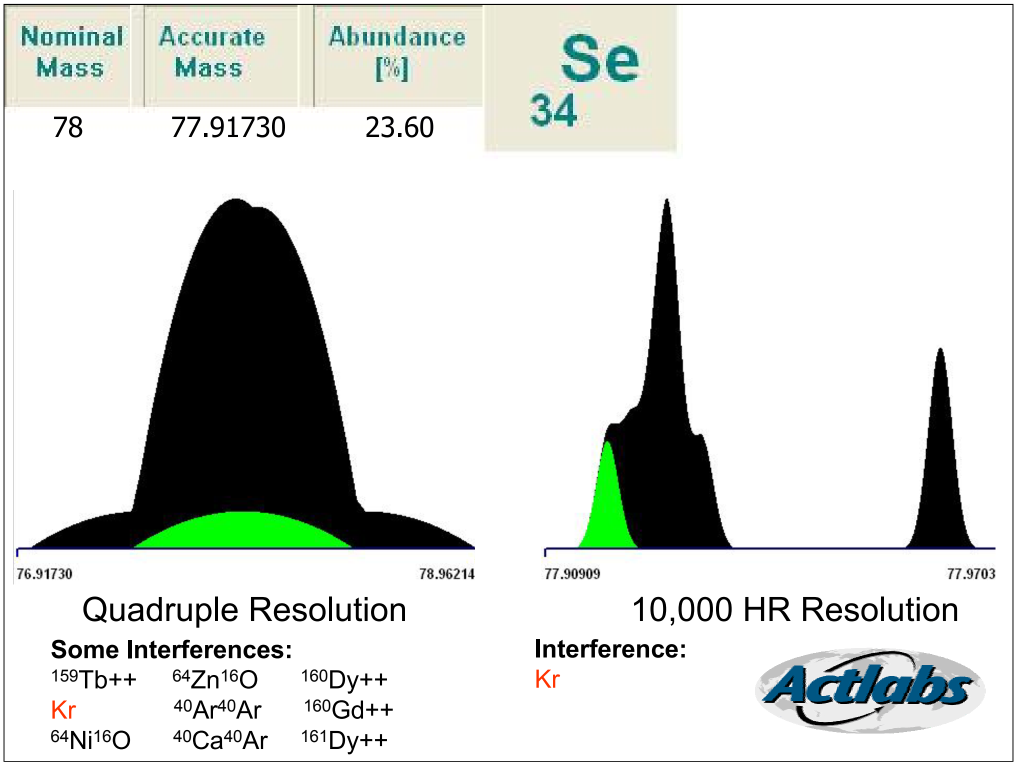
Nominal Mass	Accurate Mass	Abundance [%]	As
75	74.92160	100.00	33

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++



Nominal Mass	Accurate Mass	Abundance [%]
78	77.91730	23.60

Se
34

Quadruple Resolution

Some Interferences:

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

10,000 HR Resolution

Interference:
Kr

Actlabs

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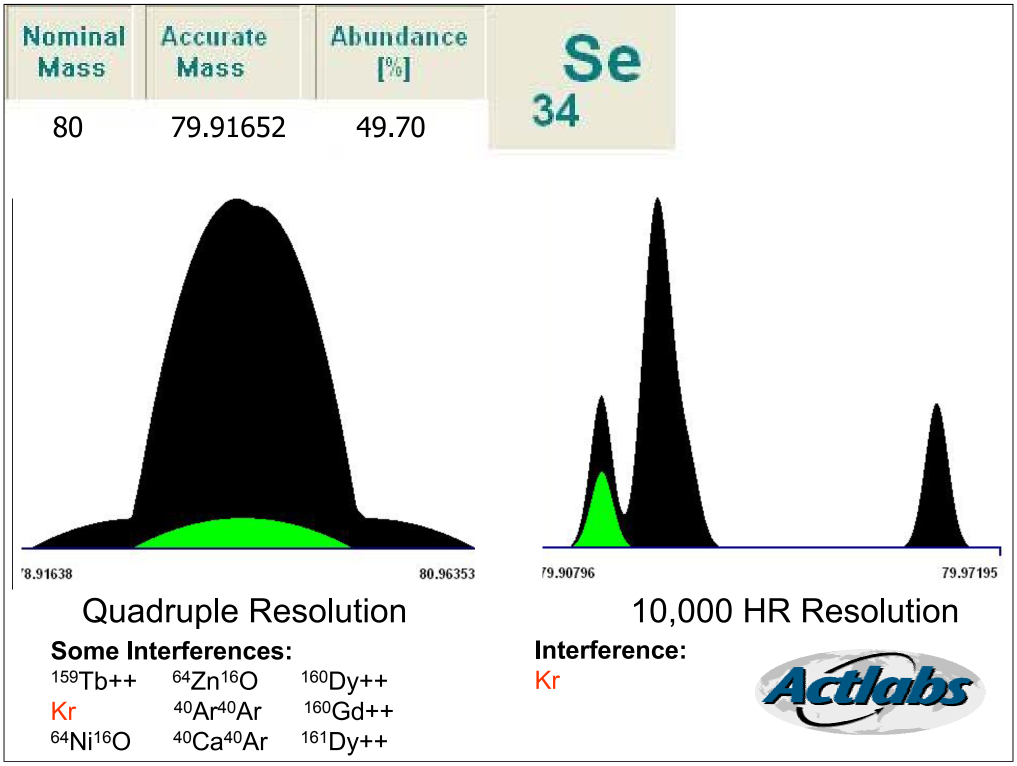

Nominal Mass	Accurate Mass	Abundance [%]
80	79.91652	49.70

Se
34

Quadruple Resolution

Some Interferences:

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

10,000 HR Resolution

Interference:

Kr

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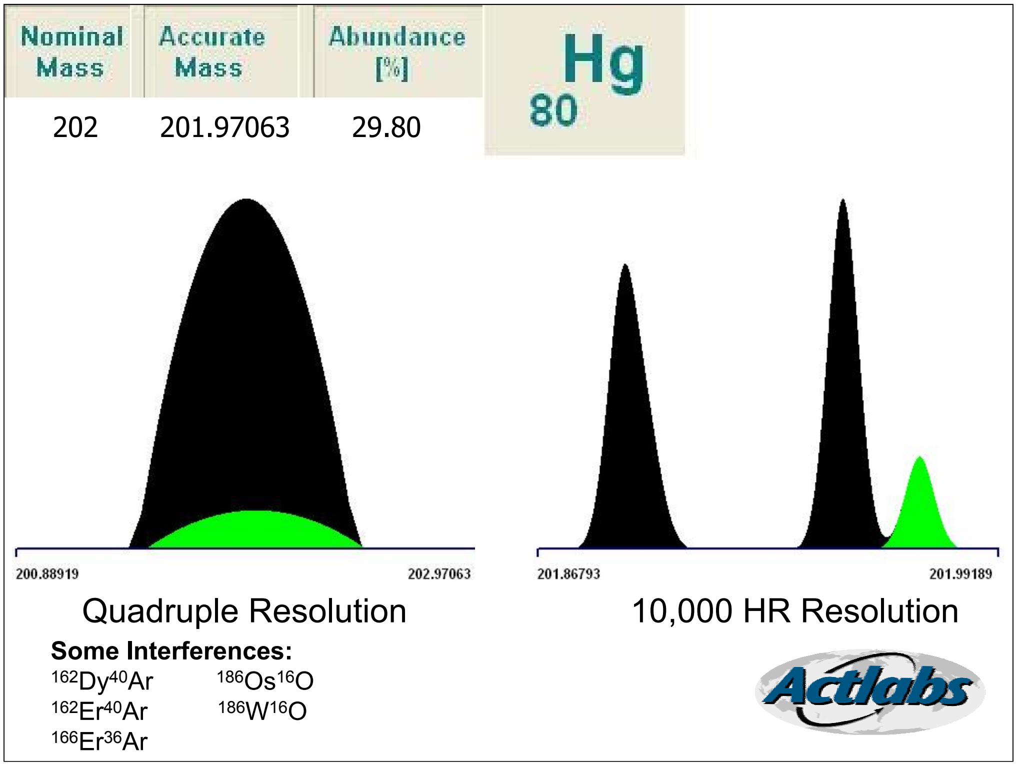

Nominal Mass	Accurate Mass	Abundance [%]
202	201.97063	29.80

Quadruple Resolution

10,000 HR Resolution

Some Interferences:

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

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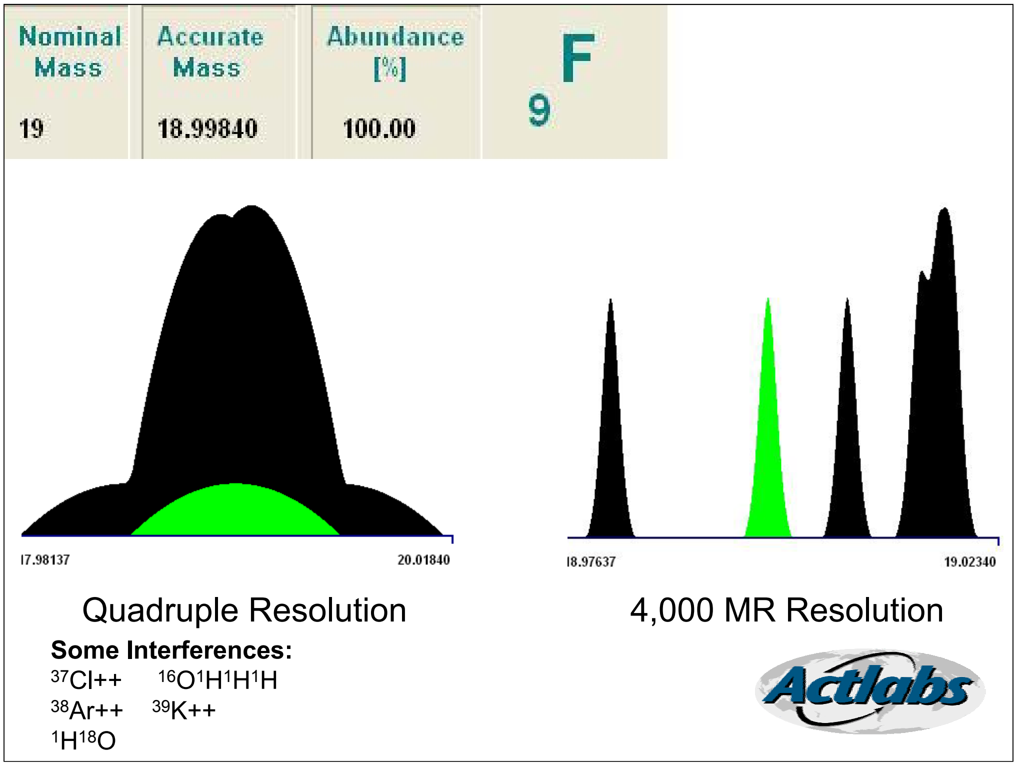
New Elements Can Be Done By HR-ICP/MS

- Fluorine

Speciation can be done on various sample media.



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

Quadruple Resolution

4,000 MR Resolution

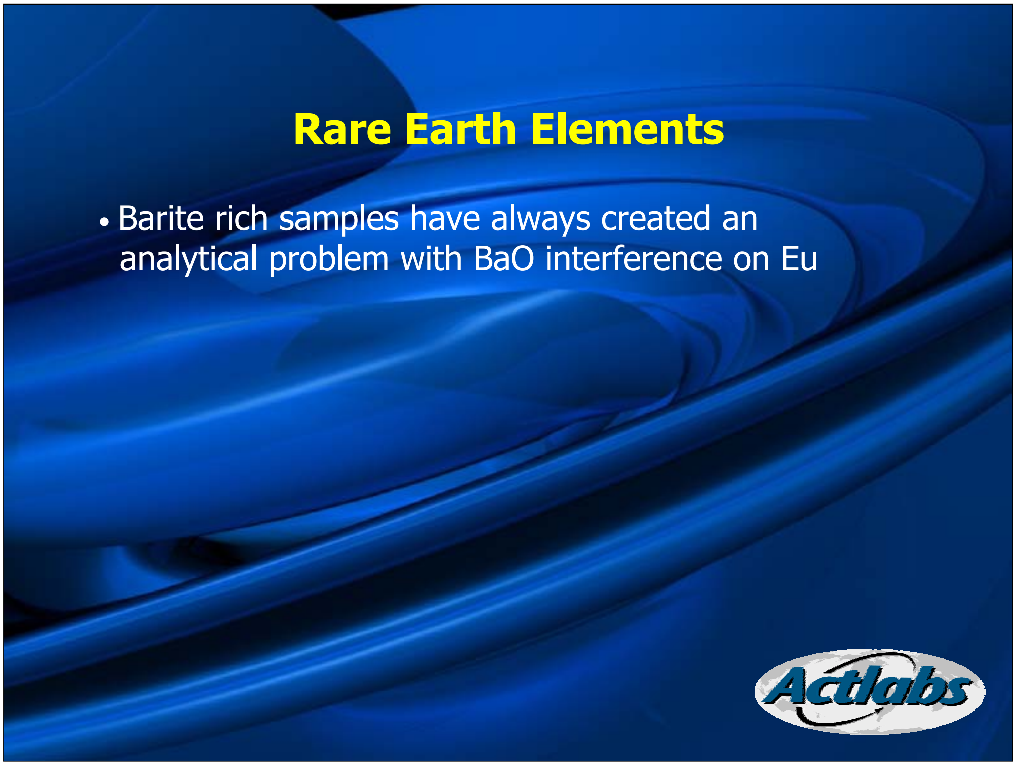
Some Interferences:

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

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

^{1}H^{18}O

Speciation can be done on various sample media.



Rare Earth Elements

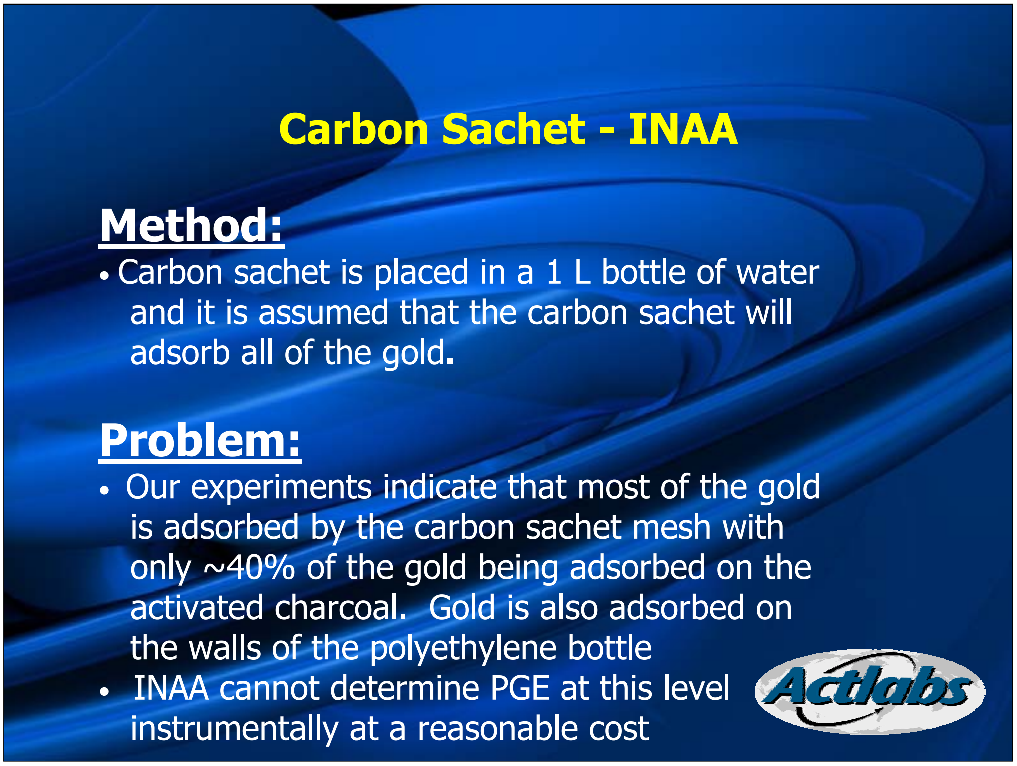
- Barite rich samples have always created an analytical problem with BaO interference on Eu

Speciation can be done on various sample media.

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

Speciation can be done on various sample media.



Carbon Sachet - INAA

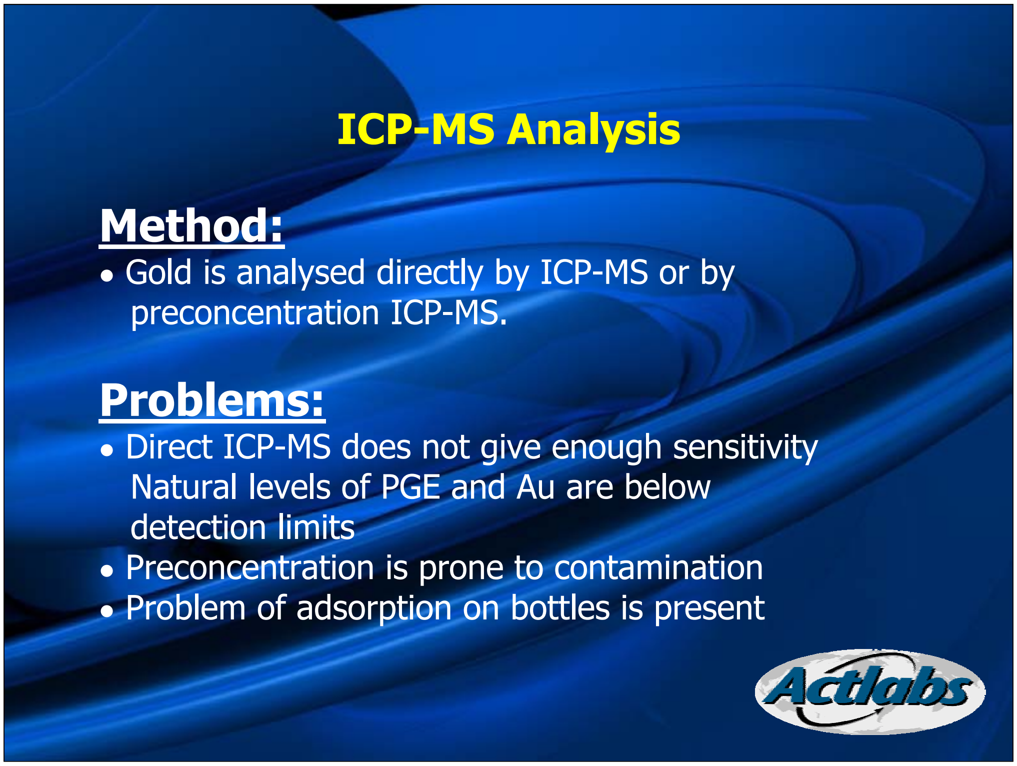
Method:

- 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

Speciation can be done on various sample media.



ICP-MS Analysis

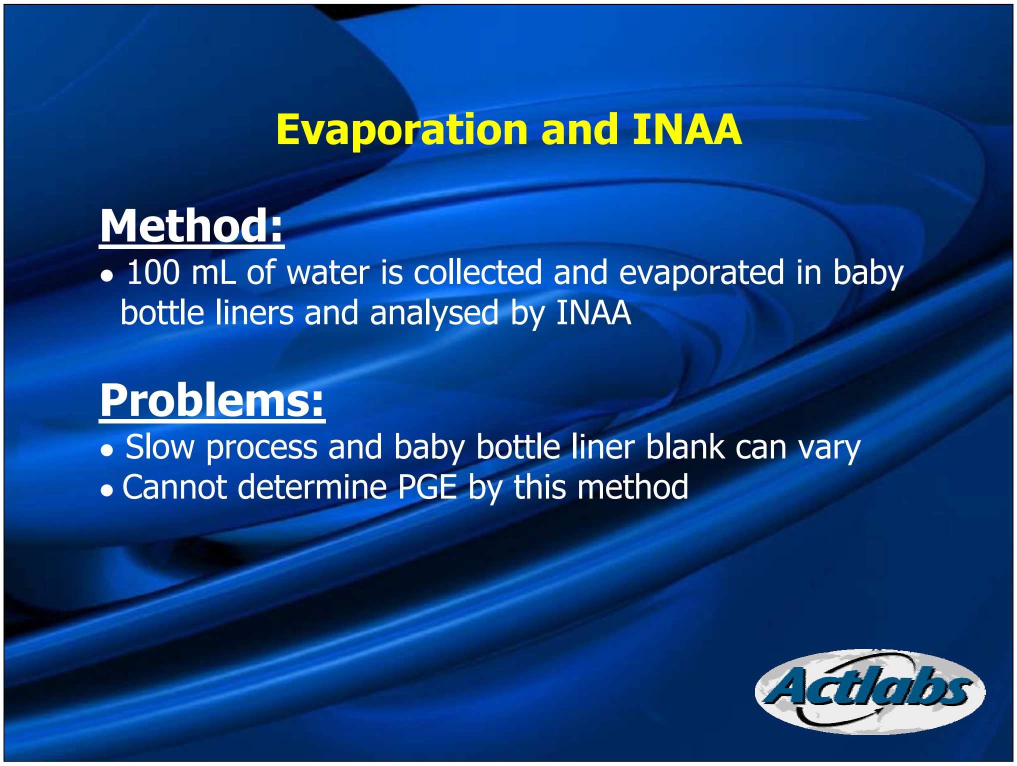
Method:

- 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

Speciation can be done on various sample media.



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

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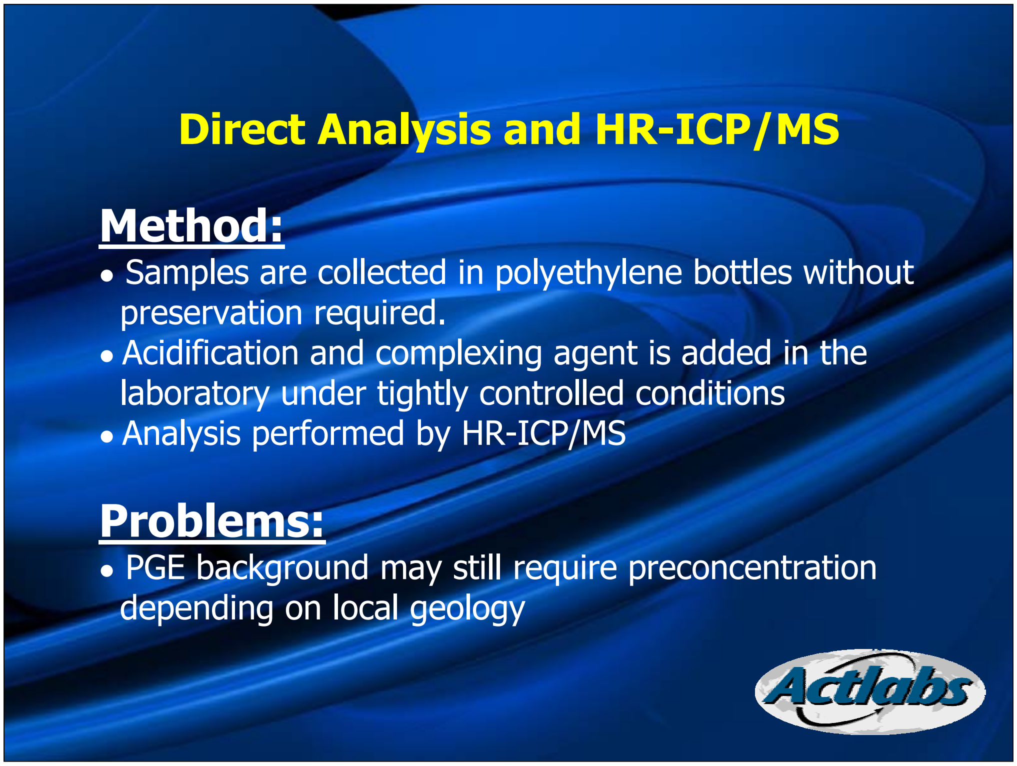
Speciation can be done on various sample media.



Direct Analysis and HR-ICP/MS

Method:

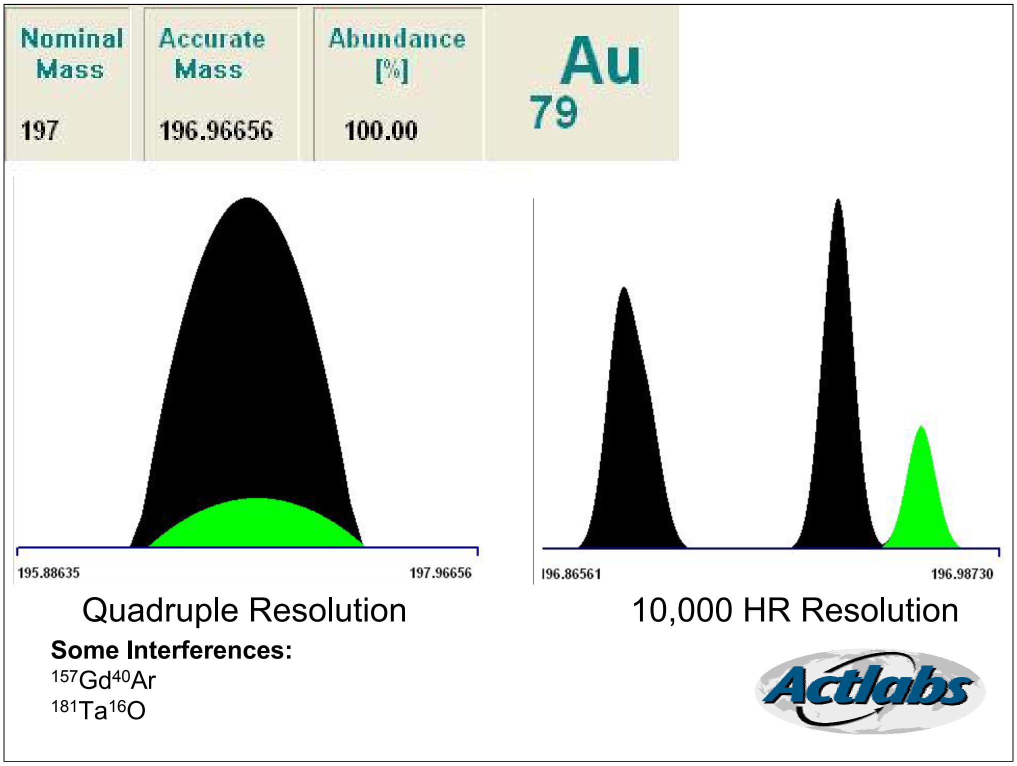
- Samples are collected in polyethylene bottles without preservation required.
- Acidification and complexing agent is added in the laboratory under tightly controlled conditions
- Analysis performed by HR-ICP/MS

Problems:

- PGE background may still require preconcentration depending on local geology

Actlabs

Speciation can be done on various sample media.



Nominal Mass	Accurate Mass	Abundance [%]
197	196.96656	100.00

Au
79

Quadruple Resolution

10,000 HR Resolution

Some Interferences:
$^{157}Gd^{40}Ar$
$^{181}Ta^{16}O$

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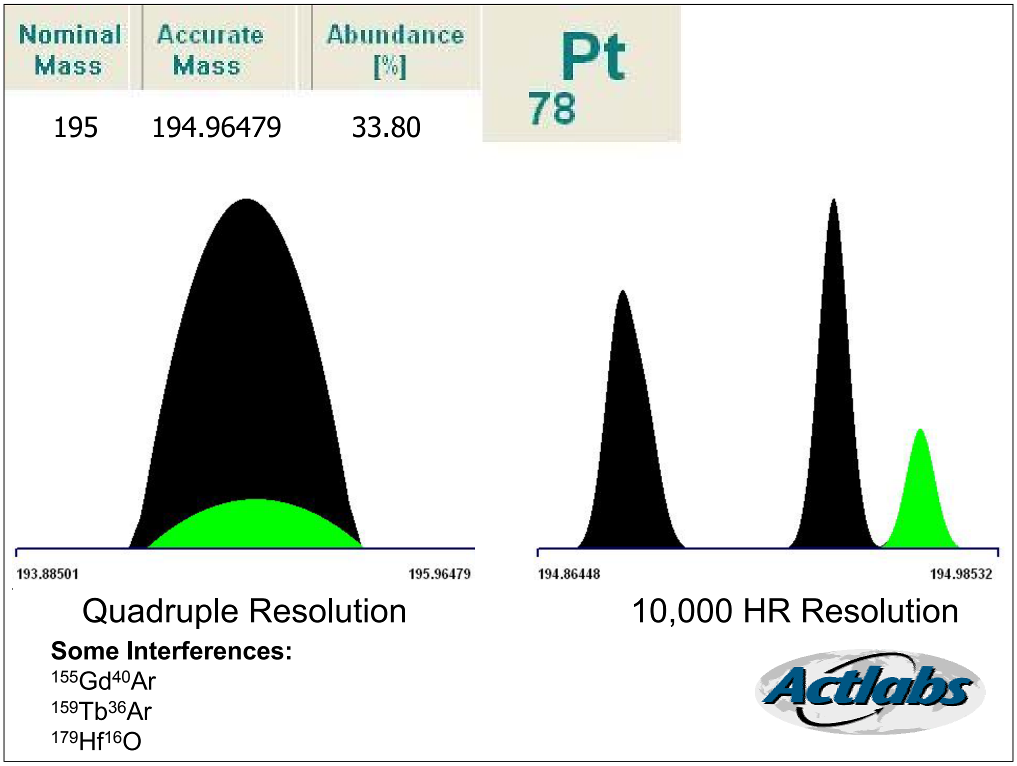

Nominal Mass	Accurate Mass	Abundance [%]
195	194.96479	33.80

Quadruple Resolution

10,000 HR Resolution

Some Interferences:

^{155}Gd^{40}Ar
^{159}Tb^{36}Ar
^{179}Hf^{16}O

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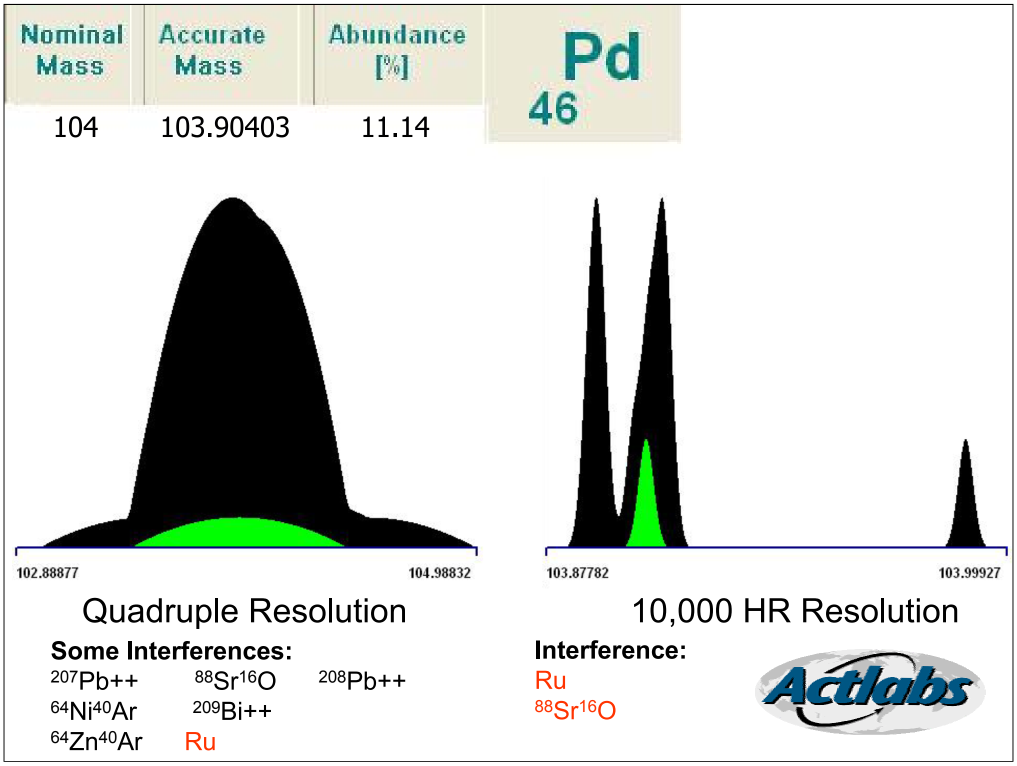

Nominal Mass	Accurate Mass	Abundance [%]
104	103.90403	11.14

Pd
46

Quadruple Resolution

10,000 HR Resolution

Some Interferences:

^{207}Pb++ ^{88}Sr^{16}O ^{208}Pb++
^{64}Ni^{40}Ar ^{209}Bi++
^{64}Zn^{40}Ar Ru

Interference:

Ru
^{88}Sr^{16}O

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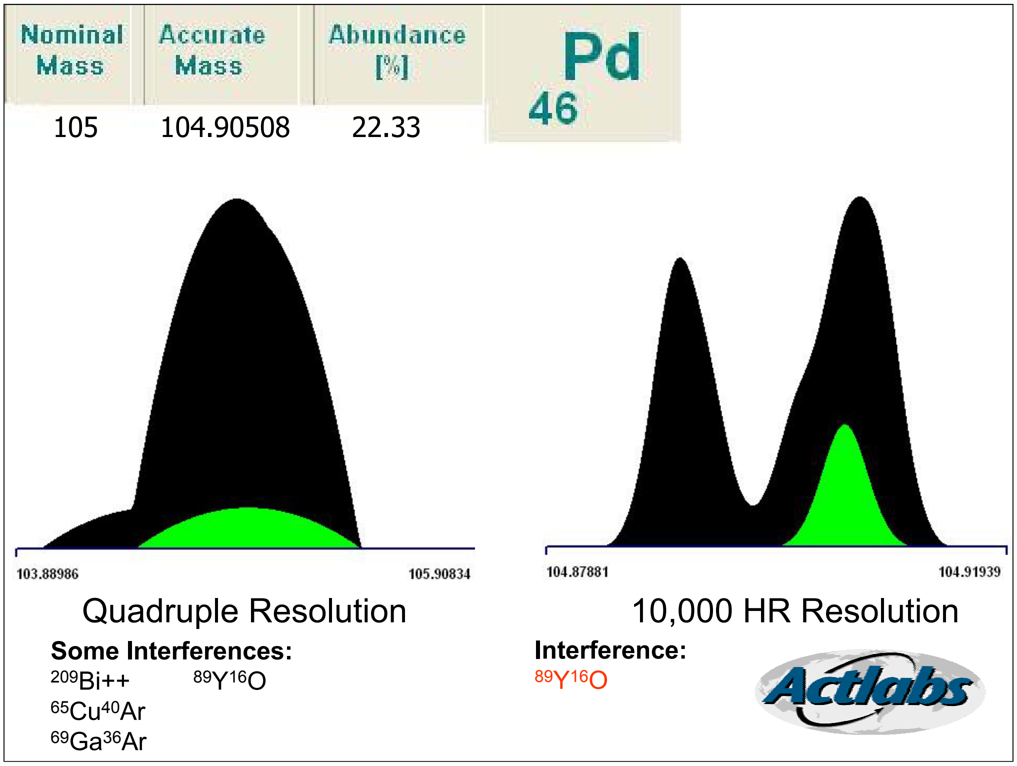


Nominal Mass	Accurate Mass	Abundance [%]	Pd 46
105	104.90508	22.33	

Quadruple Resolution

Some Interferences:

^{209}Bi++ ^{89}Y^{16}O

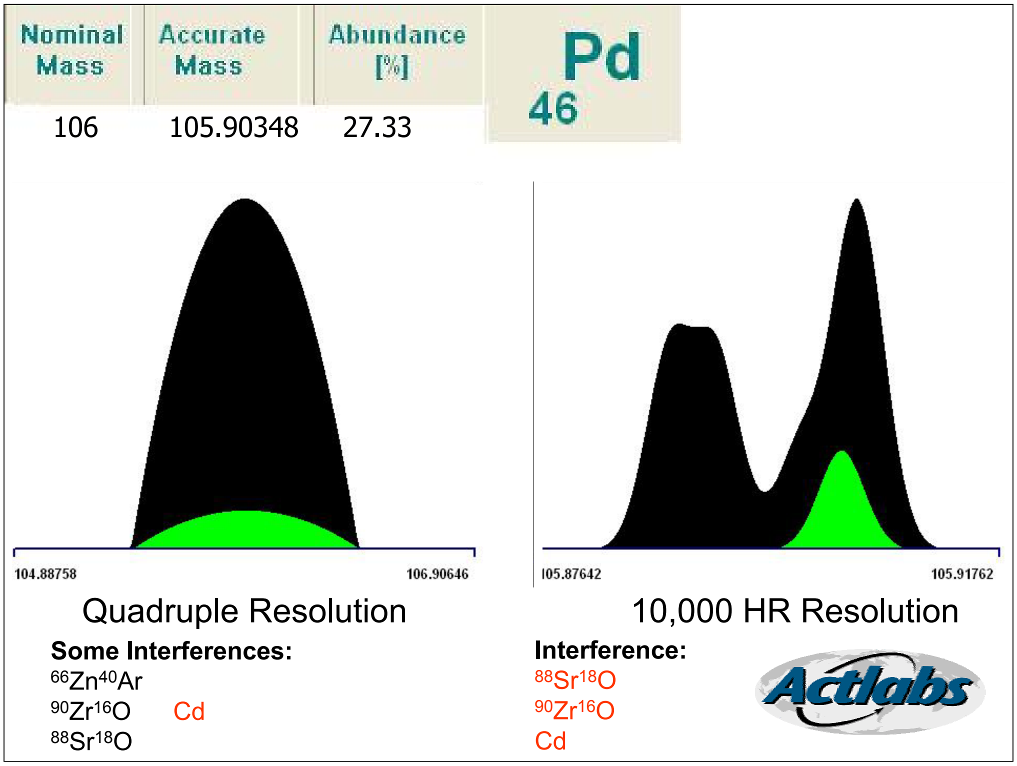
^{65}Cu^{40}Ar

^{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

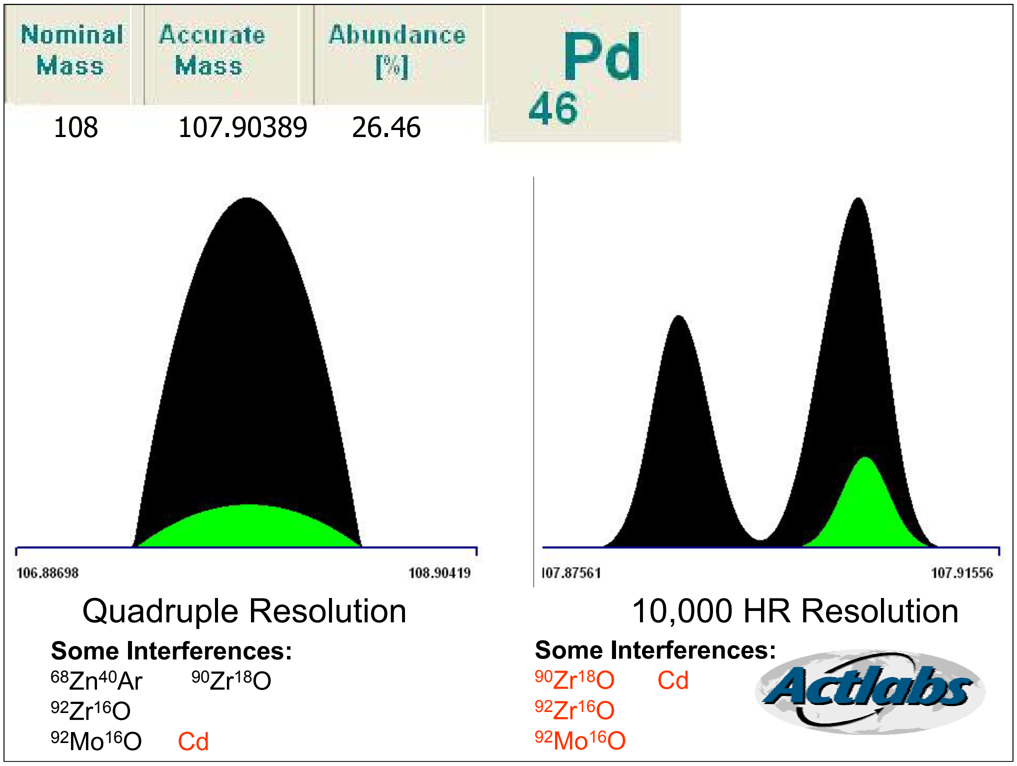
Some Interferences:

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

10,000 HR Resolution

Interference:

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



Nominal Mass	Accurate Mass	Abundance [%]
108	107.90389	26.46

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

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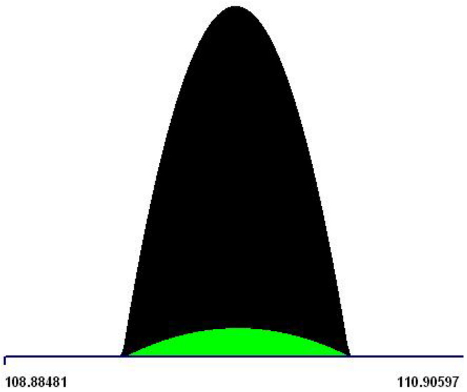
Nominal Mass	Accurate Mass	Abundance [%]
110	109.90517	11.72

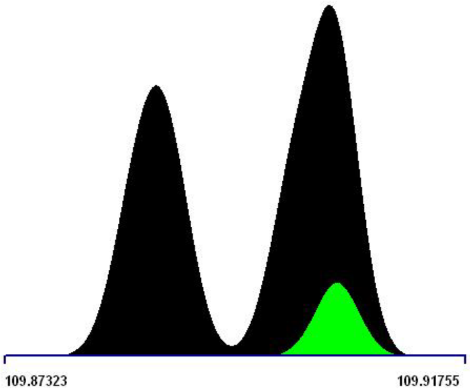
Pd
46



Quadruple Resolution

Some Interferences:

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

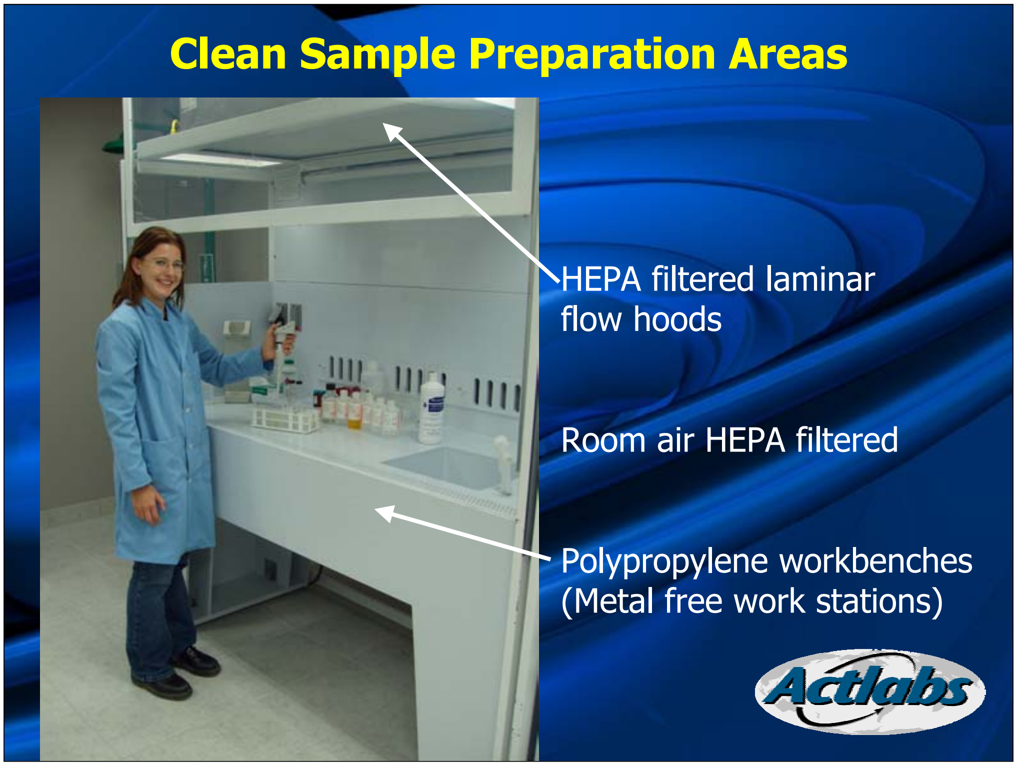


10,000 HR Resolution

Some Interferences:

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

Actlabs



Clean Sample Preparation Areas

HEPA filtered laminar flow hoods

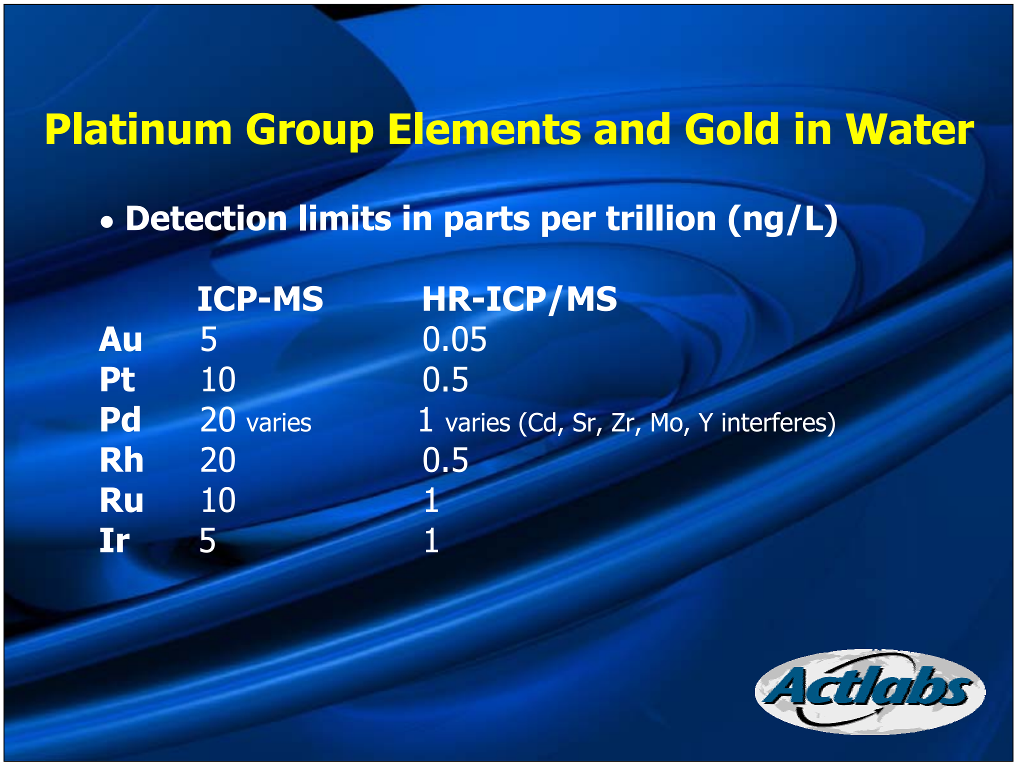
Room air HEPA filtered

Polypropylene workbenches (Metal free work stations)

How do we do it?

HEPA Filtered Air in ICP-MS Laboratory

How do we do it?

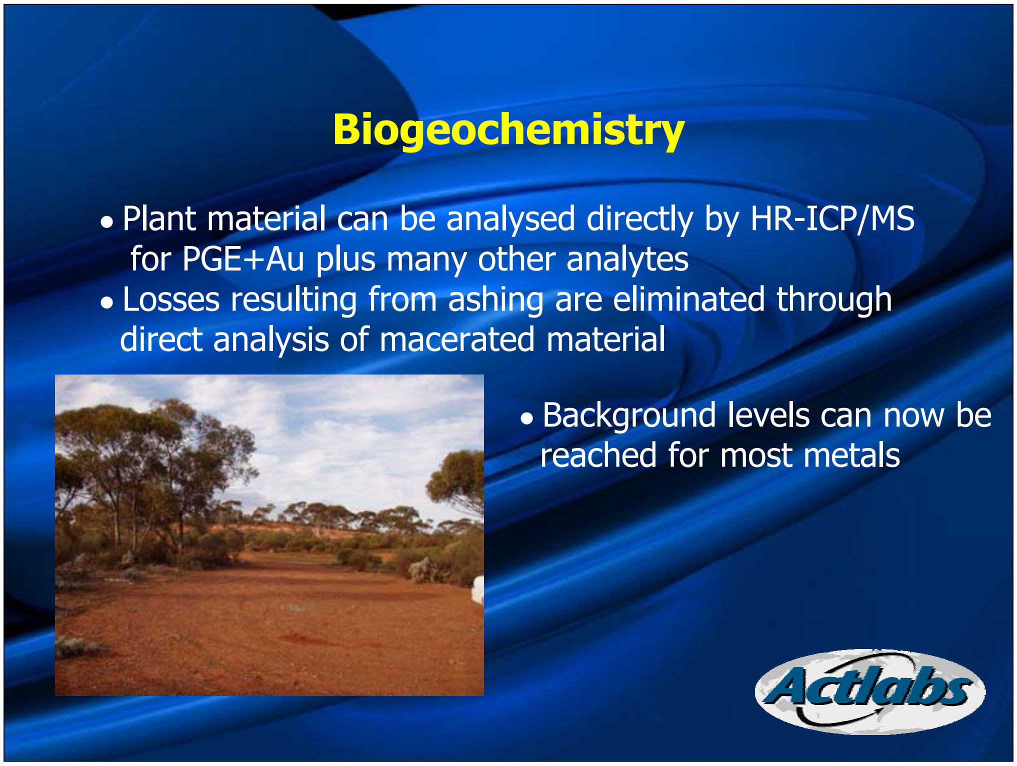


Platinum Group Elements and Gold in Water

- **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

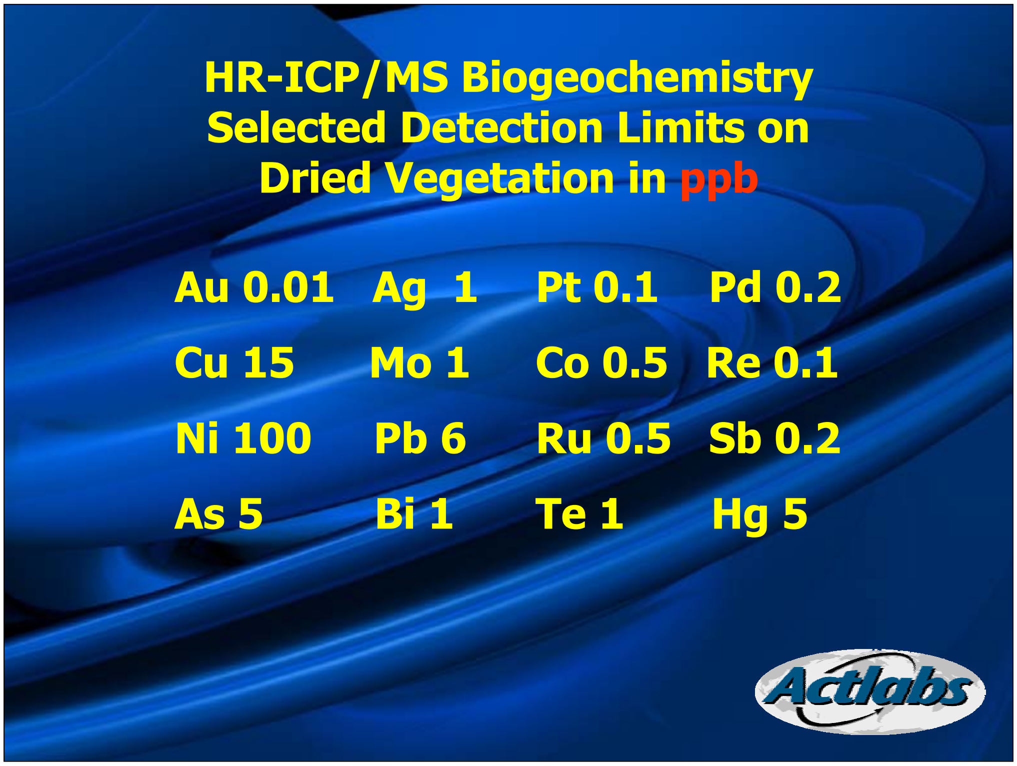
Speciation can be done on various sample media.



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

Speciation can be done on various sample media.



HR-ICP/MS Biogeochemistry Selected Detection Limits on Dried Vegetation in ppb

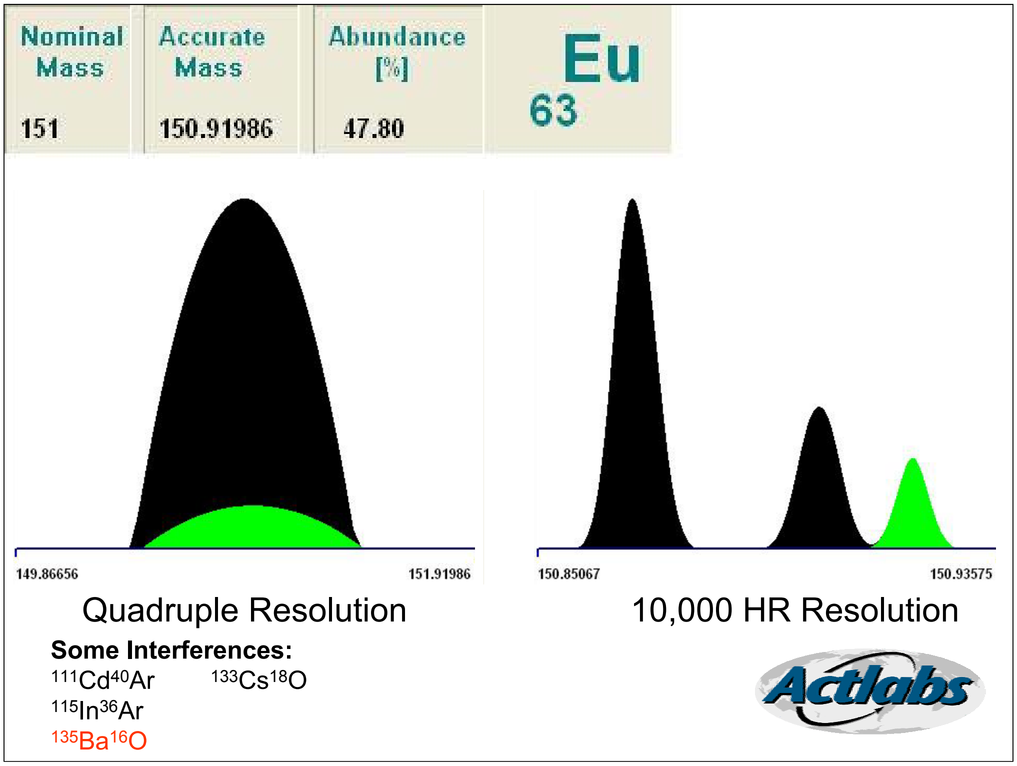
Au 0.01	Ag 1	Pt 0.1	Pd 0.2
Cu 15	Mo 1	Co 0.5	Re 0.1
Ni 100	Pb 6	Ru 0.5	Sb 0.2
As 5	Bi 1	Te 1	Hg 5

Speciation can be done on various sample media.

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

Speciation can be done on various sample media.



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

Quadruple Resolution

10,000 HR Resolution

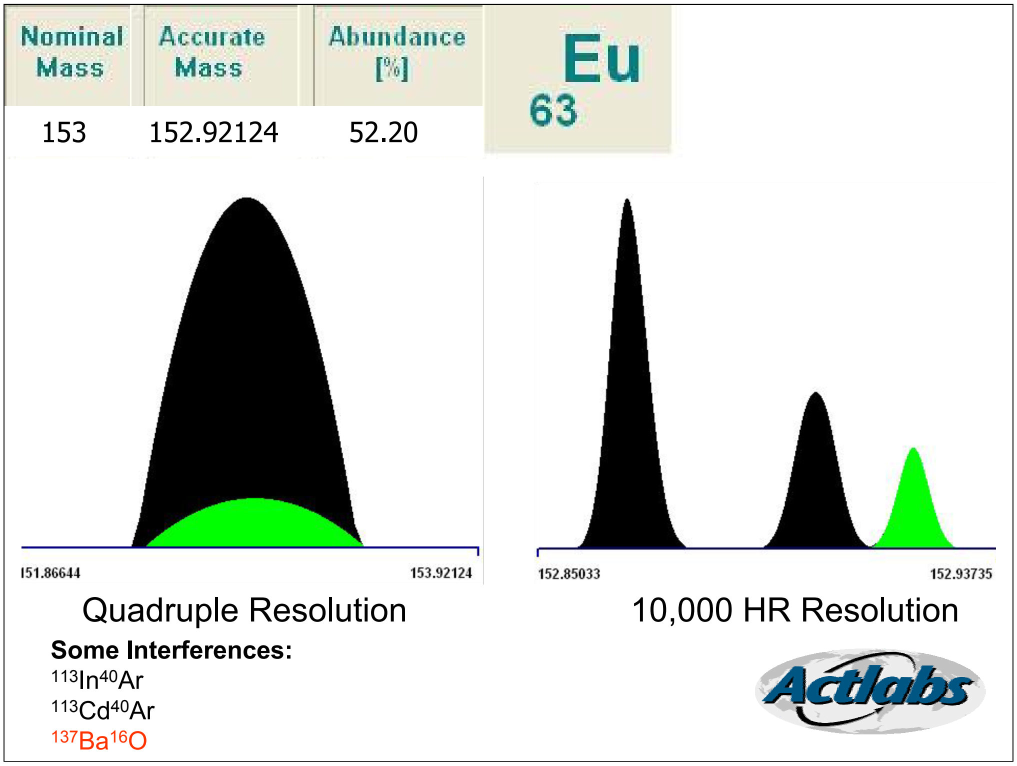
Some Interferences:

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

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

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

Speciation can be done on various sample media.



Nominal Mass	Accurate Mass	Abundance [%]
153	152.92124	52.20

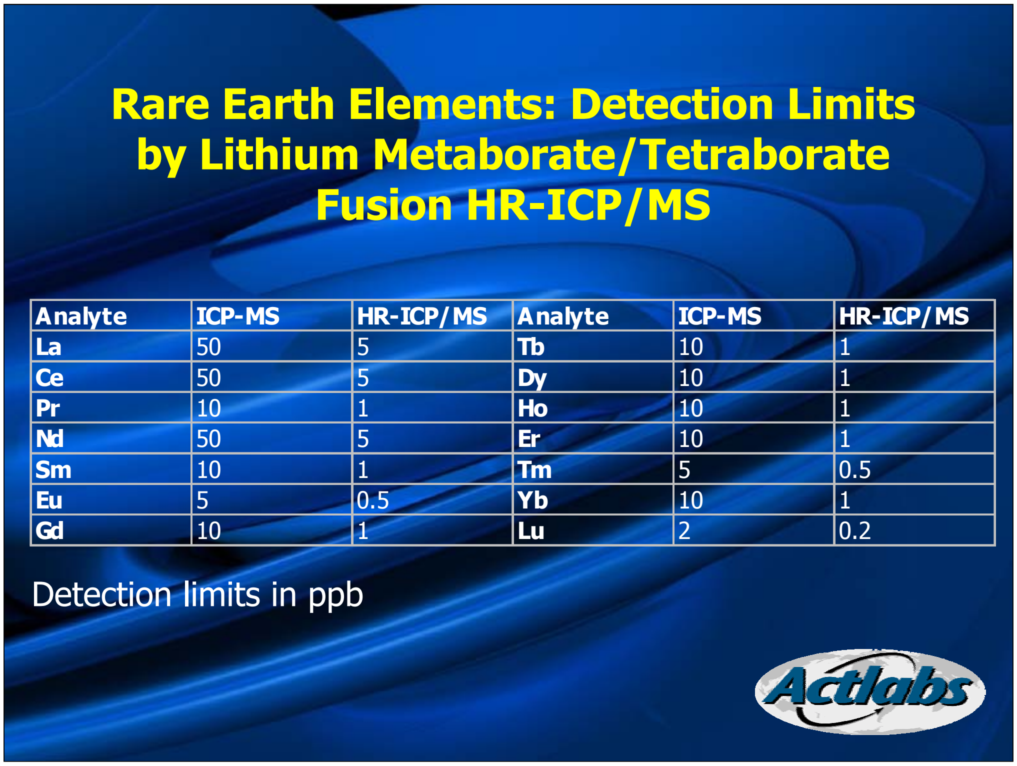
Eu
63

Quadruple Resolution

10,000 HR Resolution

Some Interferences:
$^{113}\mathrm{In}^{40}\mathrm{Ar}$
$^{113}\mathrm{Cd}^{40}\mathrm{Ar}$
$^{137}\mathrm{Ba}^{16}\mathrm{O}$

Speciation can be done on various sample media.

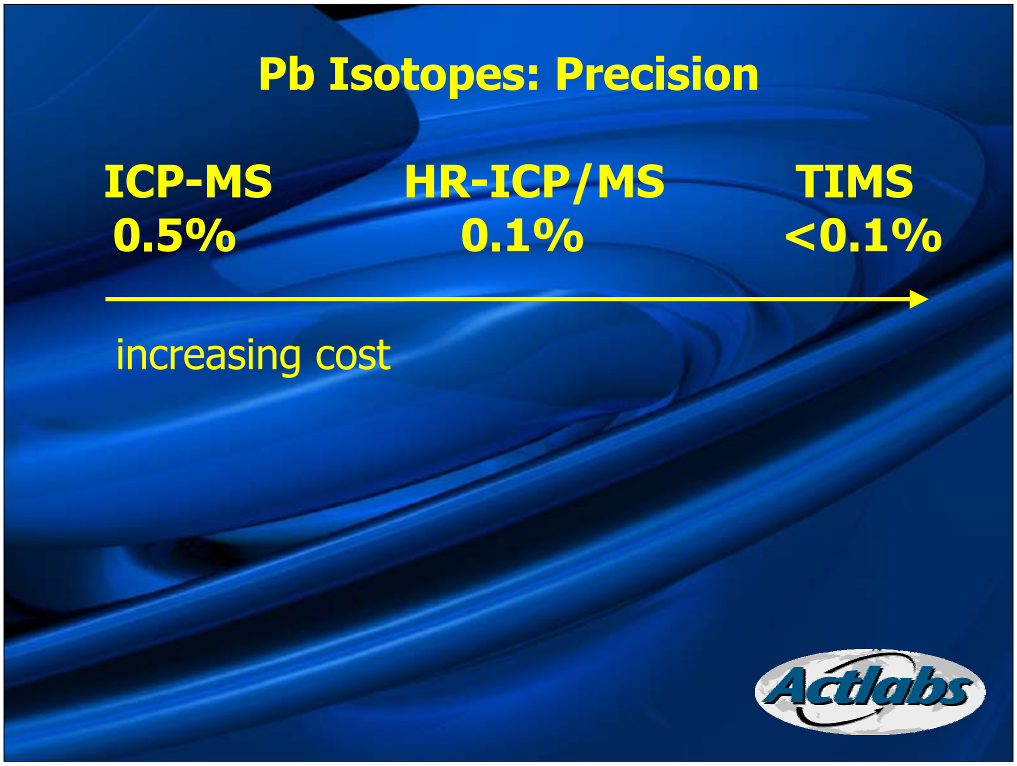


Rare Earth Elements: Detection Limits by Lithium Metaborate/Tetraborate Fusion HR-ICP/MS

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

Speciation can be done on various sample media.



Pb Isotopes: Precision

ICP-MS	HR-ICP/MS	TIMS
0.5%	0.1%	<0.1%

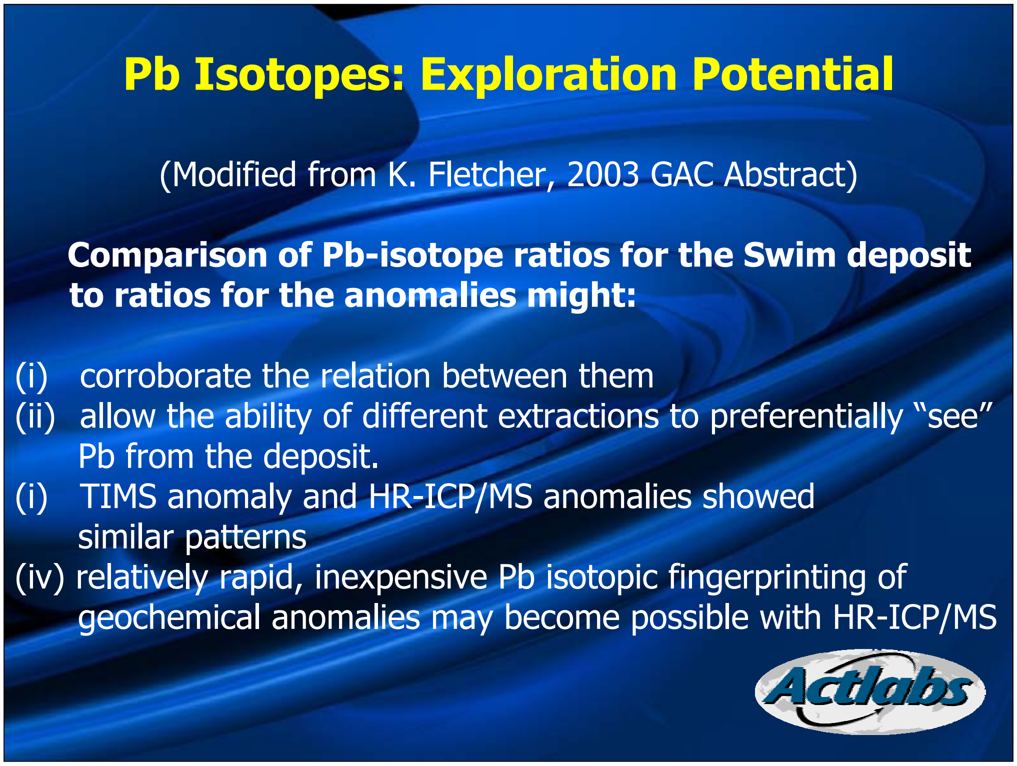
→ increasing cost

The first category is simple redox states: the species is a well-defined cation or anion. The second class is organometallic compounds. There is another group for some metals which includes metal complexes: the metal of concern form a coordination bond binding to a ligand.

Monitoring elemental species requires analytical technology with sufficient selectivity and sensitivity to resolve and quantitate the individual species at ultra trace levels, since an individual toxic species may constitute only a small fraction of an element's total concentration in a sample.

Modern HIGH PRESSURE LIQUID CHROMATOGRAPHY (HPLC) techniques are fairly versatile owing to the diversity of separation technologies available (multiple columns).

The separation mechanism complementary to HPLC is the capillary electrophoresis technique.



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

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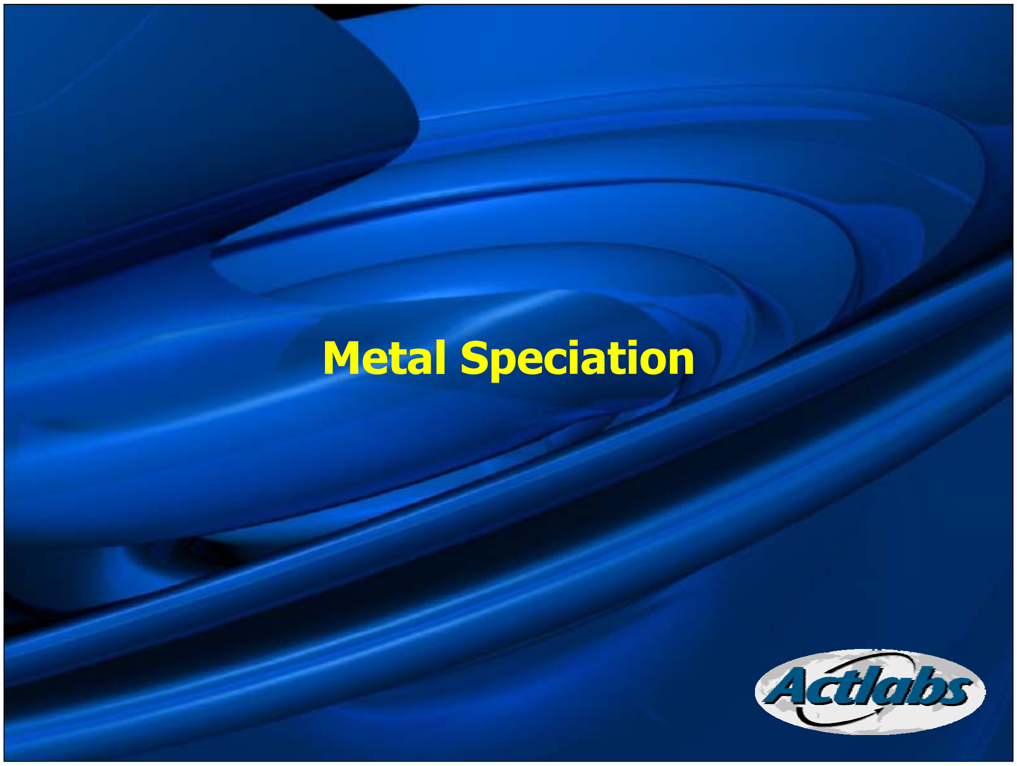

Metal Speciation

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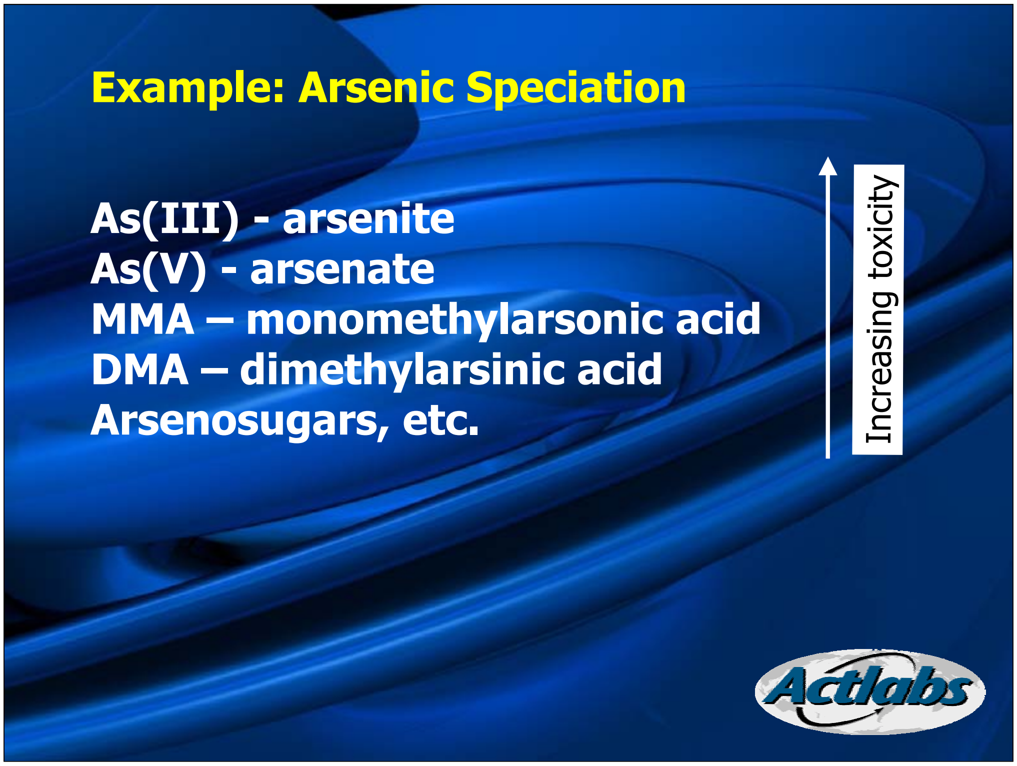

Example: Arsenic Speciation

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

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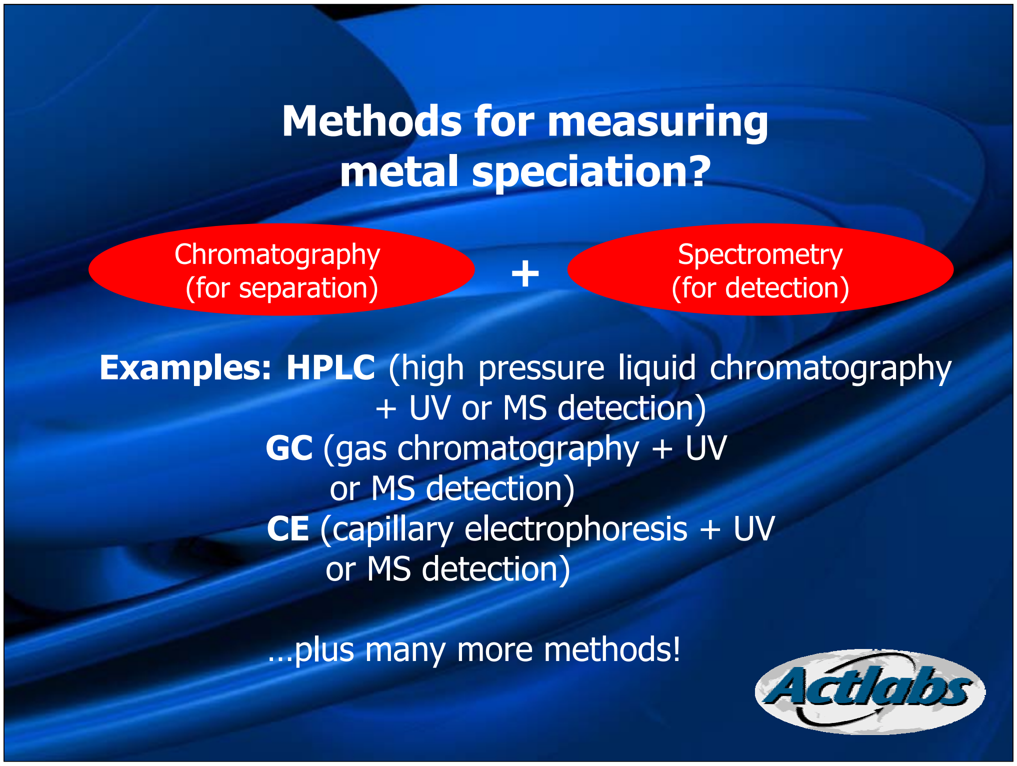

Methods for measuring metal speciation?

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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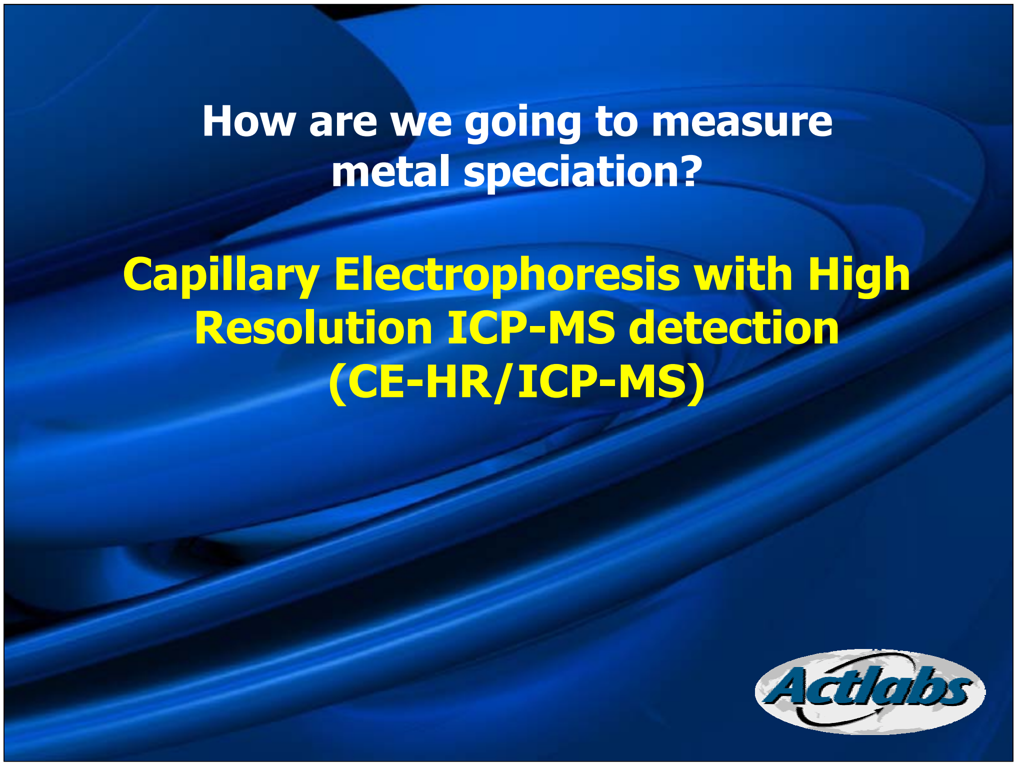

How are we going to measure metal speciation?

Capillary Electrophoresis with High Resolution ICP-MS detection (CE-HR/ICP-MS)

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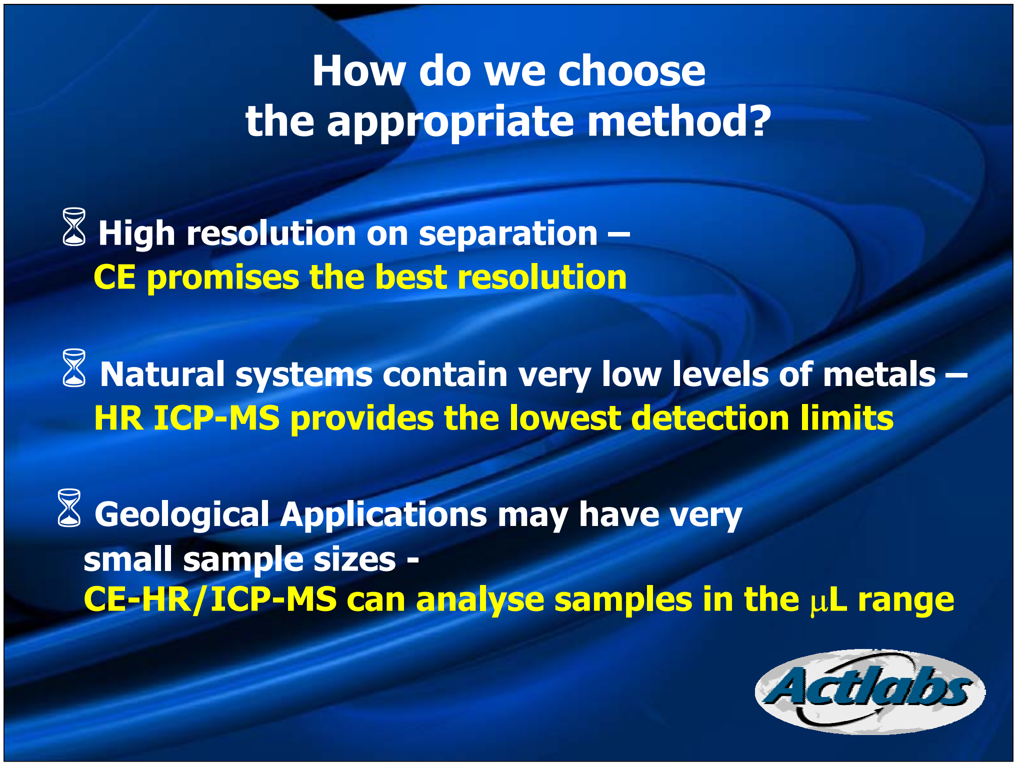

How do we choose the appropriate method?

- 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?

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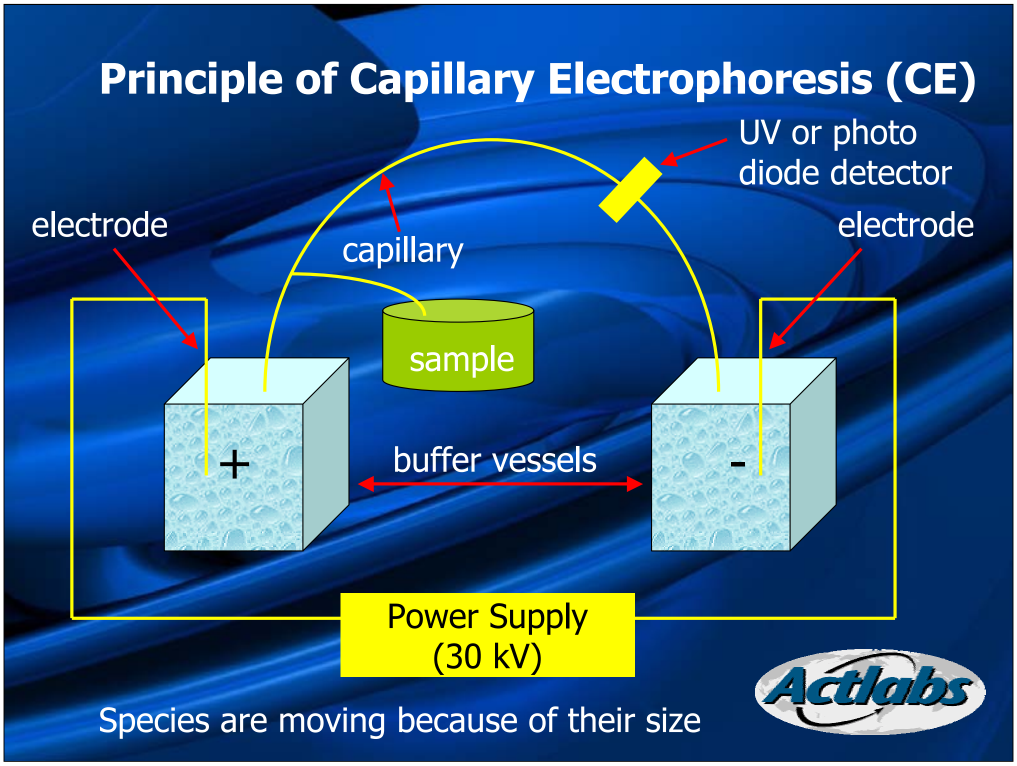


Principle of Capillary Electrophoresis (CE)

UV or photo
diode detector

electrode

electrode

capillary

sample

+

-

buffer vessels

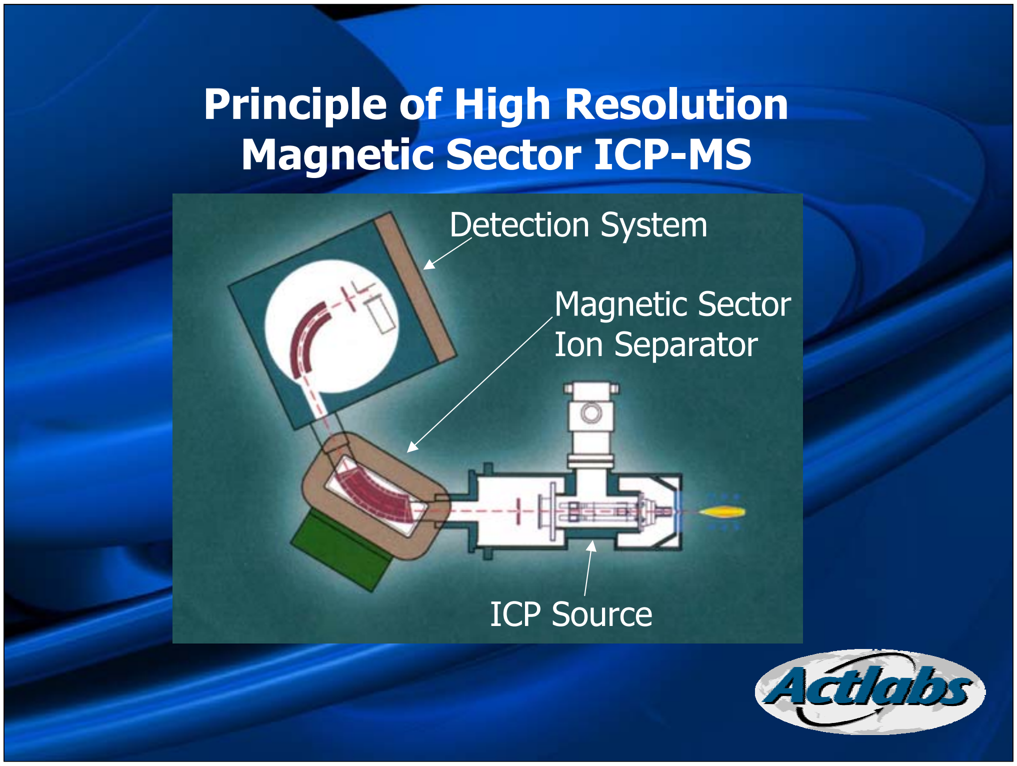
Power Supply
(30 kV)

Species are moving because of their size

Actlabs

The high-resolution potential of capillary electrophoresis makes the CE technique valuable for separation of metal species, both organic and inorganic.

Capillary-zone electrophoresis has a widely demonstrated potential for the separation of As and other species like Se. This includes not only the inorganic species but also organometallic species and species like metallothioneins which are very important biologically. Applications to real samples however have been rare because the UV detection used was often not capable of either detecting the analyte in a real sample or of confirming its identity. The major problem in the application of capillary electrophoresis-based coupling to real-world samples is the small sampling volume which may be available sometimes only a few microliters. This small volume requires a very sensitive detection system to match the naturally occruing analyte concentration levels.



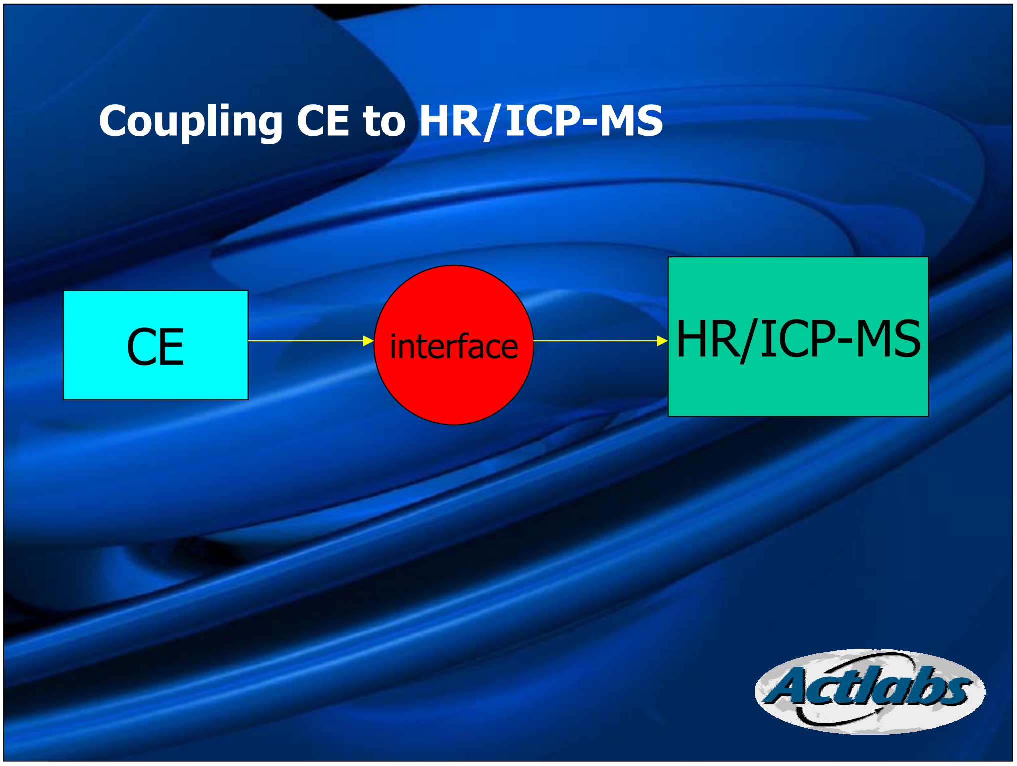
Principle of High Resolution Magnetic Sector ICP-MS

Detection System

Magnetic Sector Ion Separator

ICP Source

HIGH RESOLUTION ICP/MS (HR- ICP-MS) is an element-specific multi-element detector,**(figure 4 diagram of Element)** providing extremely low detection limits. The sensitivity is 10 to 100 times better than conventional ICP/MS which uses a quadrupole detector whereas the high resolution machine uses a magnetic sector detector.

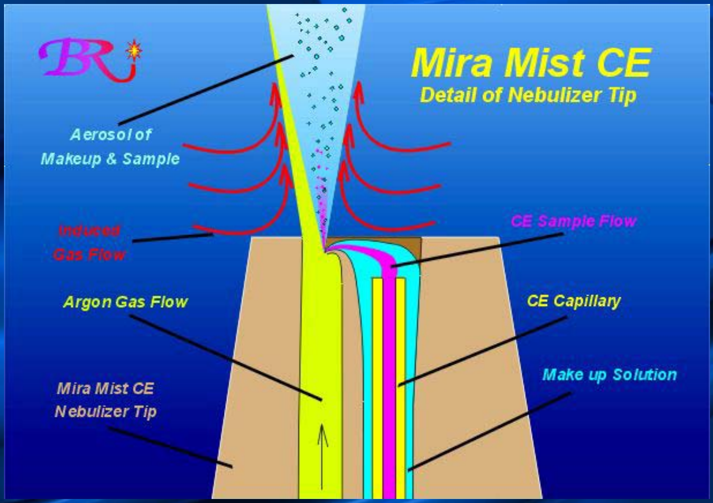


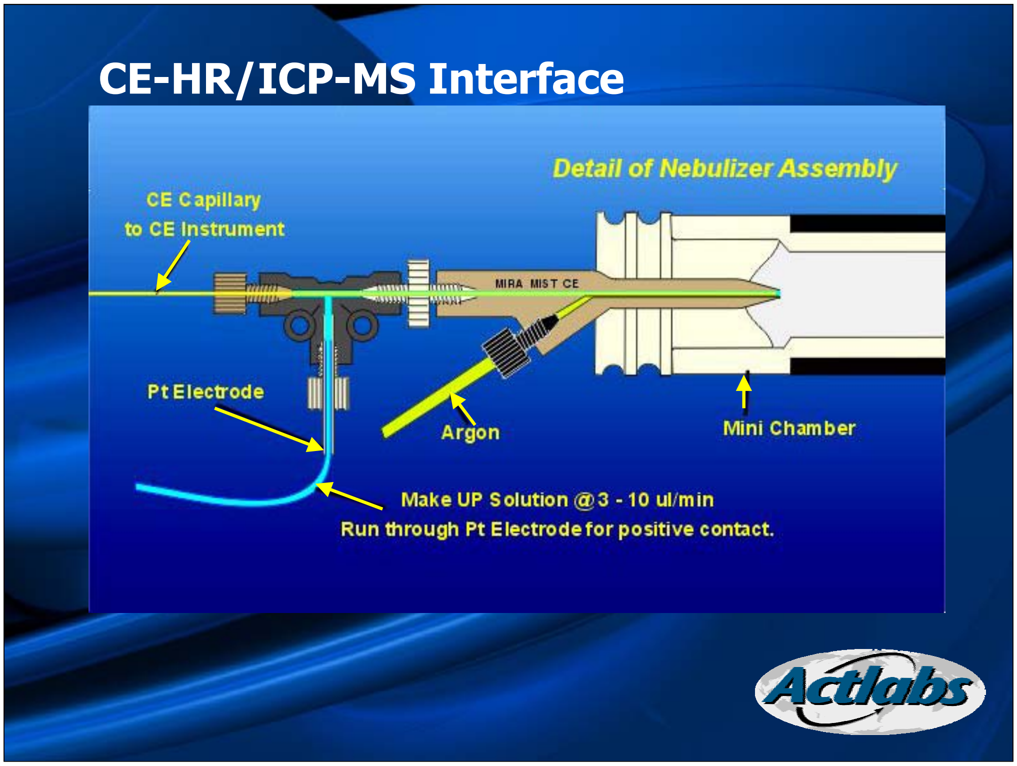
Coupling CE to HR/ICP-MS

CE → interface → HR/ICP-MS

How do we do it?

Principle of MIRA Mist CE Nebuliser





CE-HR/ICP-MS Interface

Detail of Nebulizer Assembly

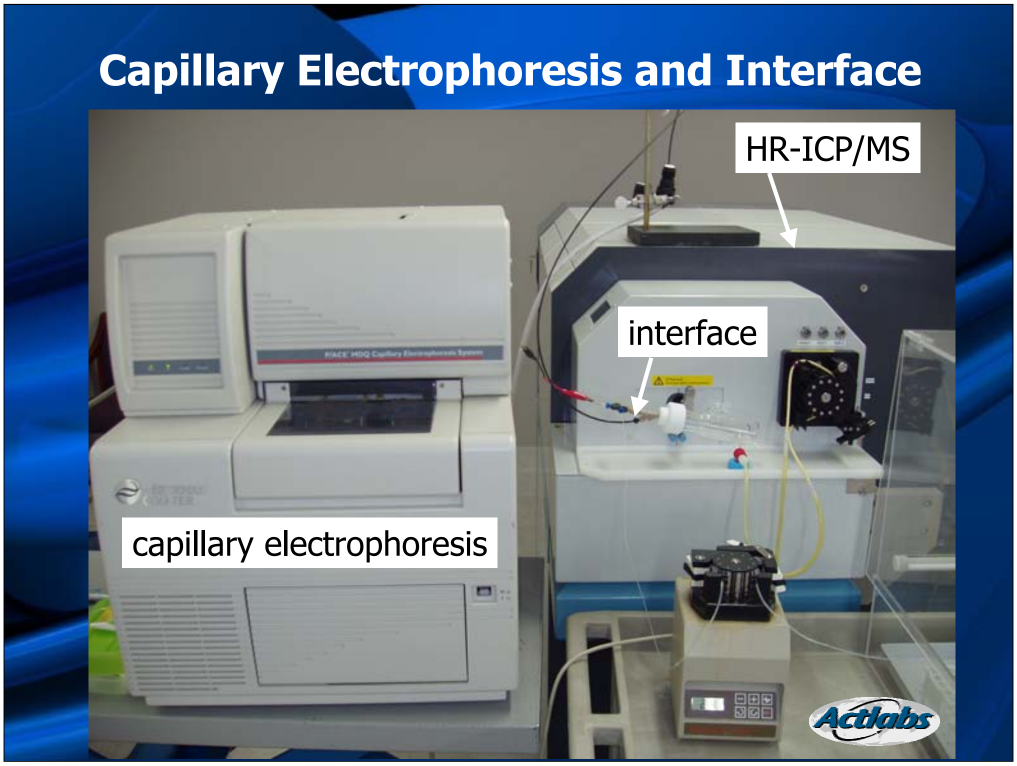
CE Capillary
to CE Instrument

Pt Electrode

Argon

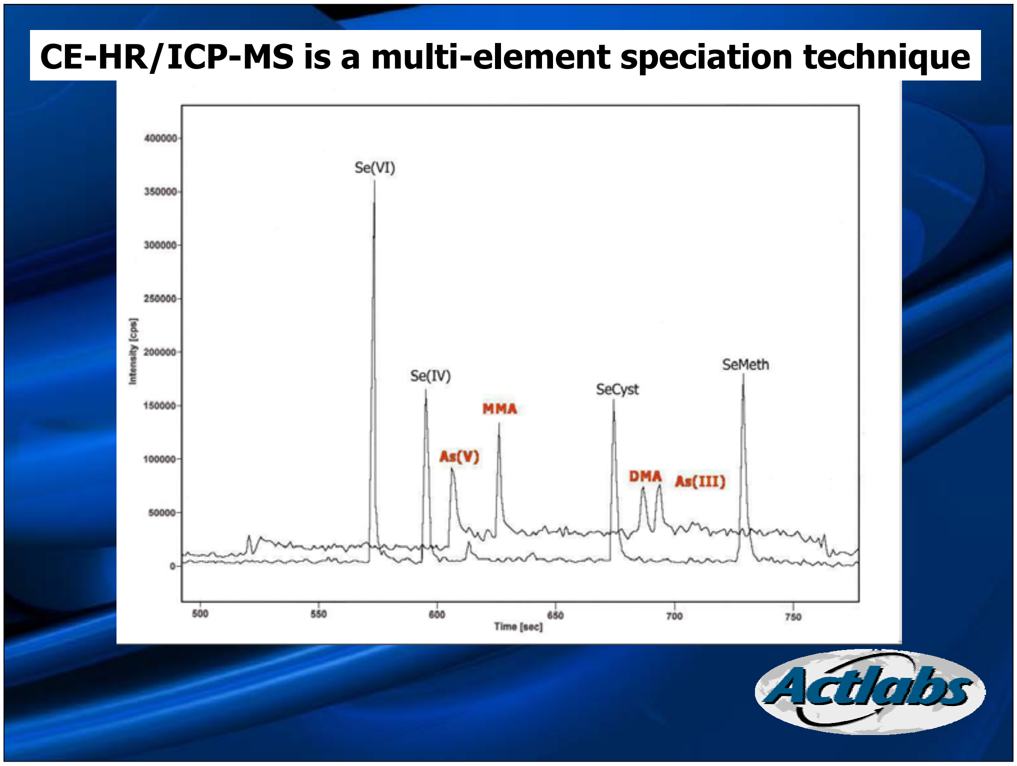
Mini Chamber

Make UP Solution @3 - 10 ul/min
Run through Pt Electrode for positive contact.



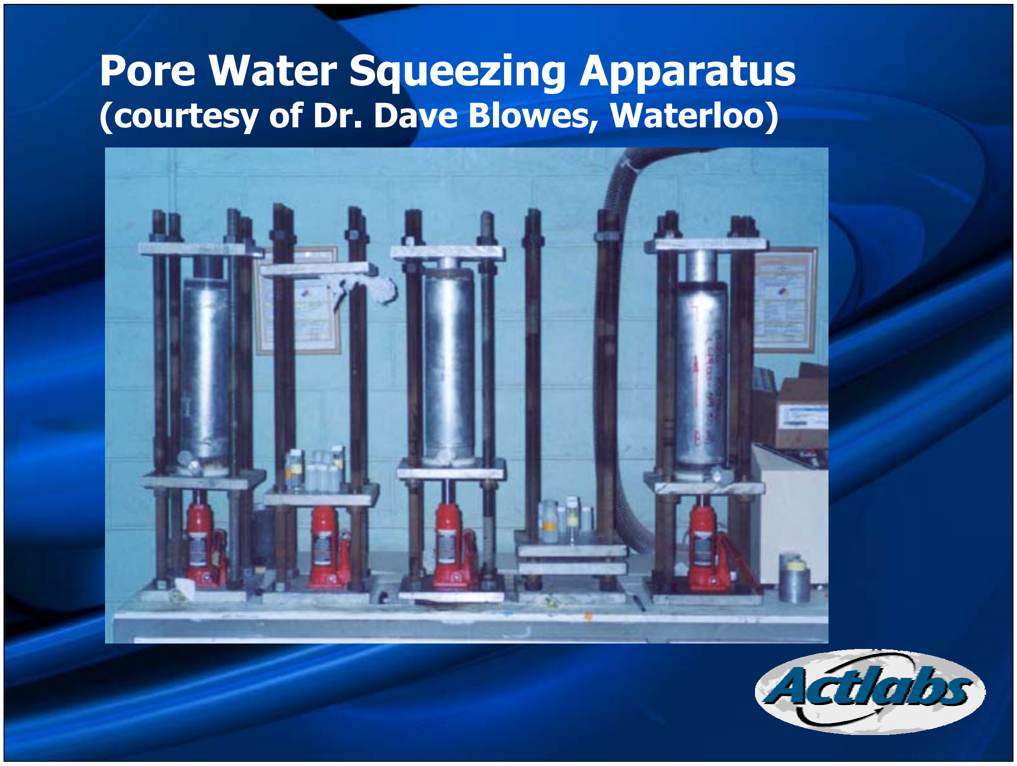
Capillary Electrophoresis and Interface

How do we do it?



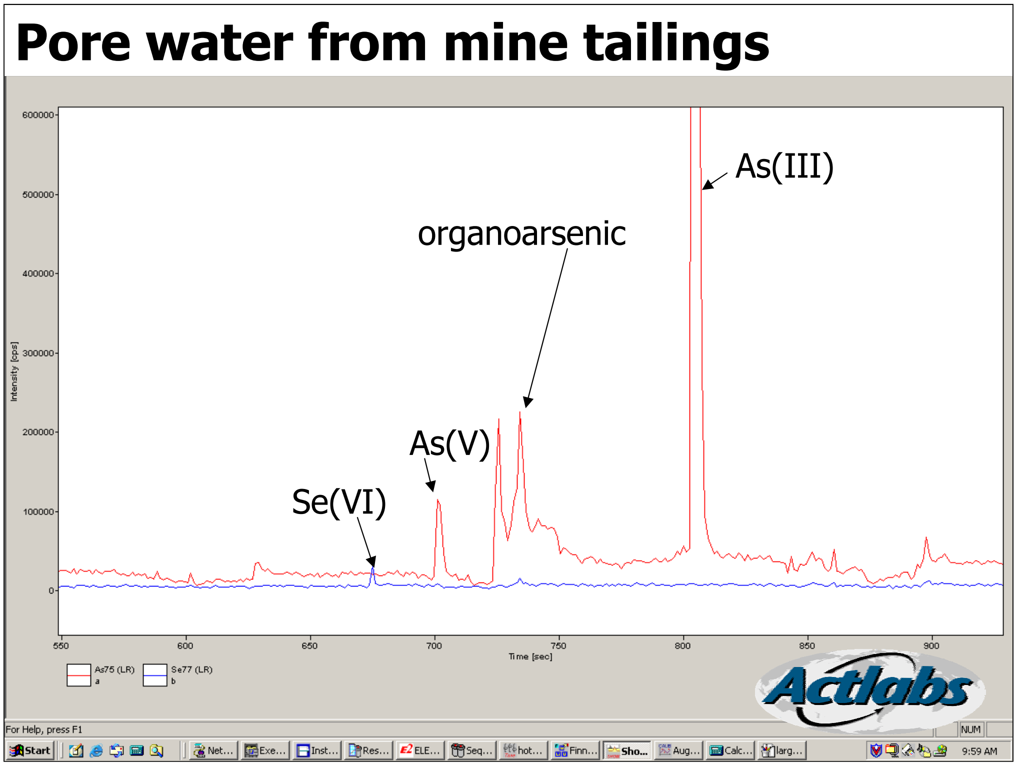
CE-HR/ICP-MS is a multi-element speciation technique

The next 3 slides show As speciation, Se speciation and then the multi-element capabilities by recording both together.



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

The amount of pore fluid varied from 2-15mls however a very significant number of tests including Ph, Eh, alkalinity, trace metals by ICP/OES and ICP/MS as well as speciation for As and Fe required that our methodology use only a minimum of sample.



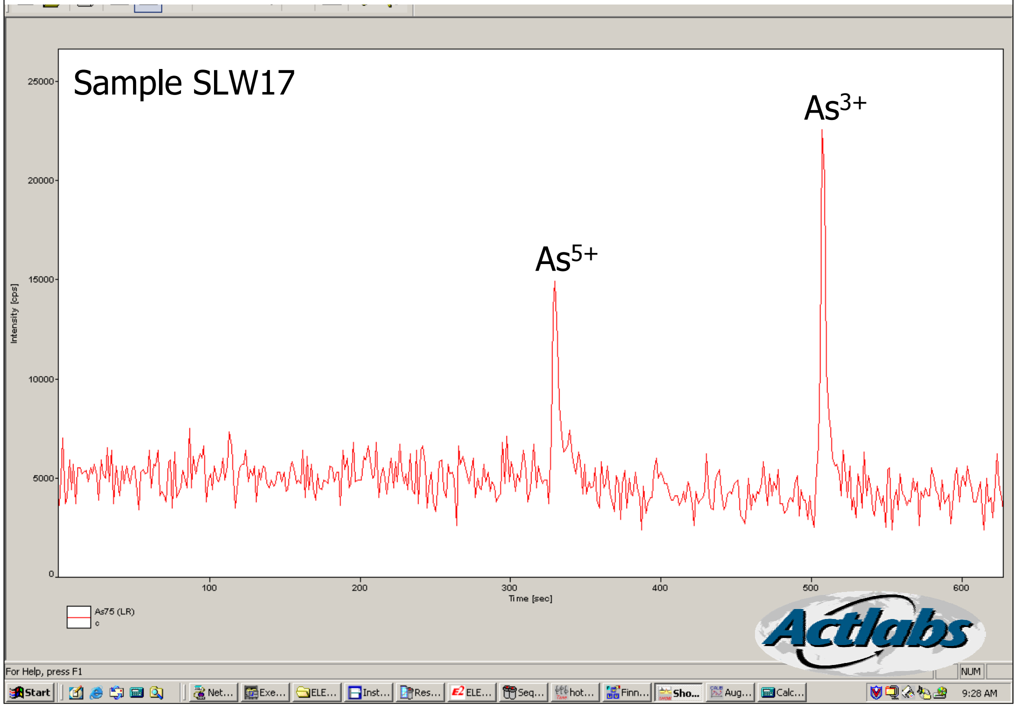
Pore water from mine tailings

This chromatogram shows the As species separated from pore water extracted indicating that most As was As 3+ although As 5 was also identified as well as 2 of the organoarsenic species.

We have also applied this technology to the analysis of stream waters for routine environmental monitoring and are applying the technology up the food chain to biological species.

This technology also promises to have application in mineral exploration where we might expect various species to be present in the vicinity of orebodies that are not generally available in unmineralized areas.

Water Well Sample Near Arsenopyrite Stockpile



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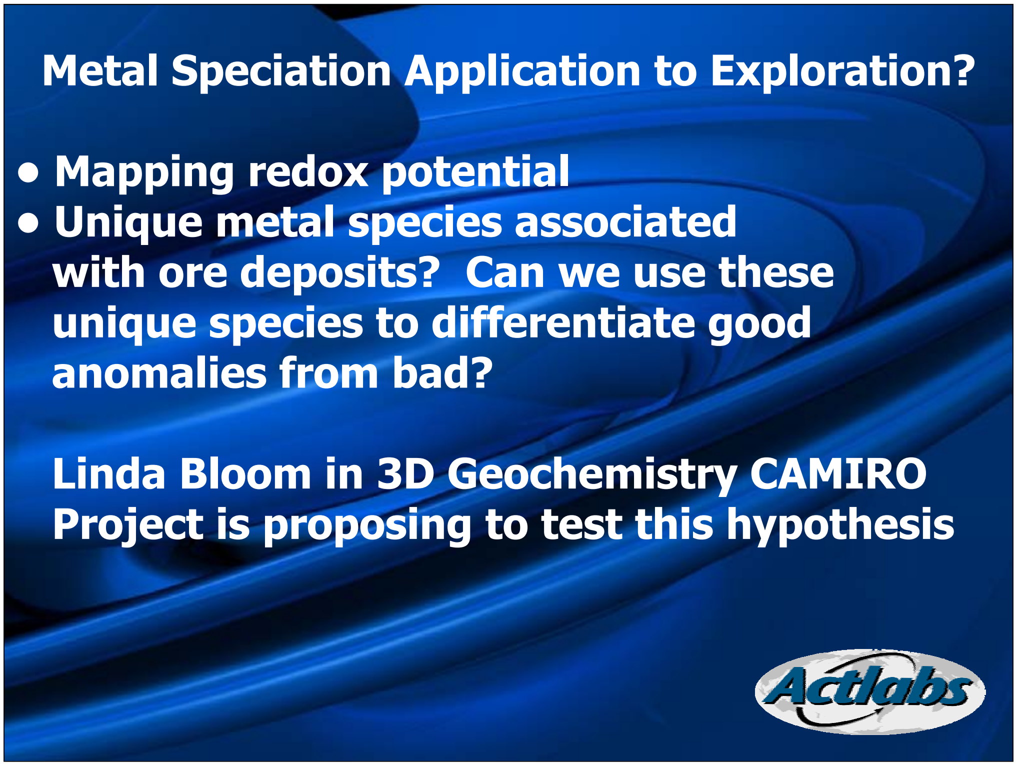

Metal Speciation Application to Exploration?

- 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

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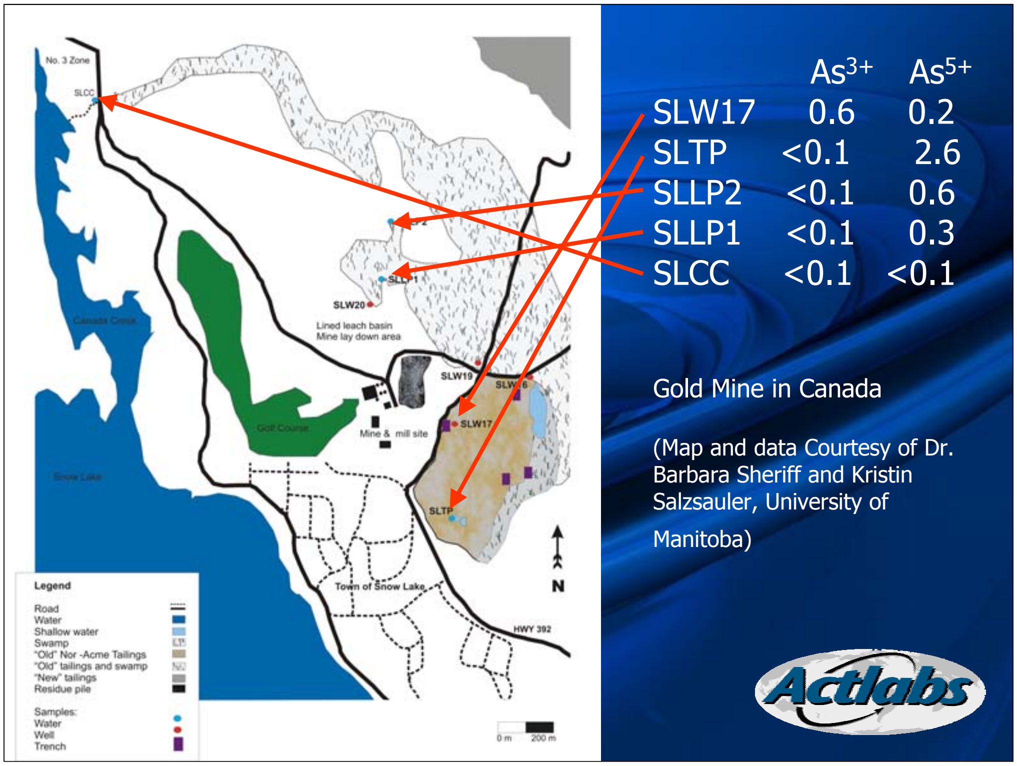

	As^{3+}	As^{5+}
SLW17	0.6	0.2
SLTP	<0.1	2.6
SLLP2	<0.1	0.6
SLLP1	<0.1	0.3
SLCC	<0.1	<0.1

Gold Mine in Canada

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

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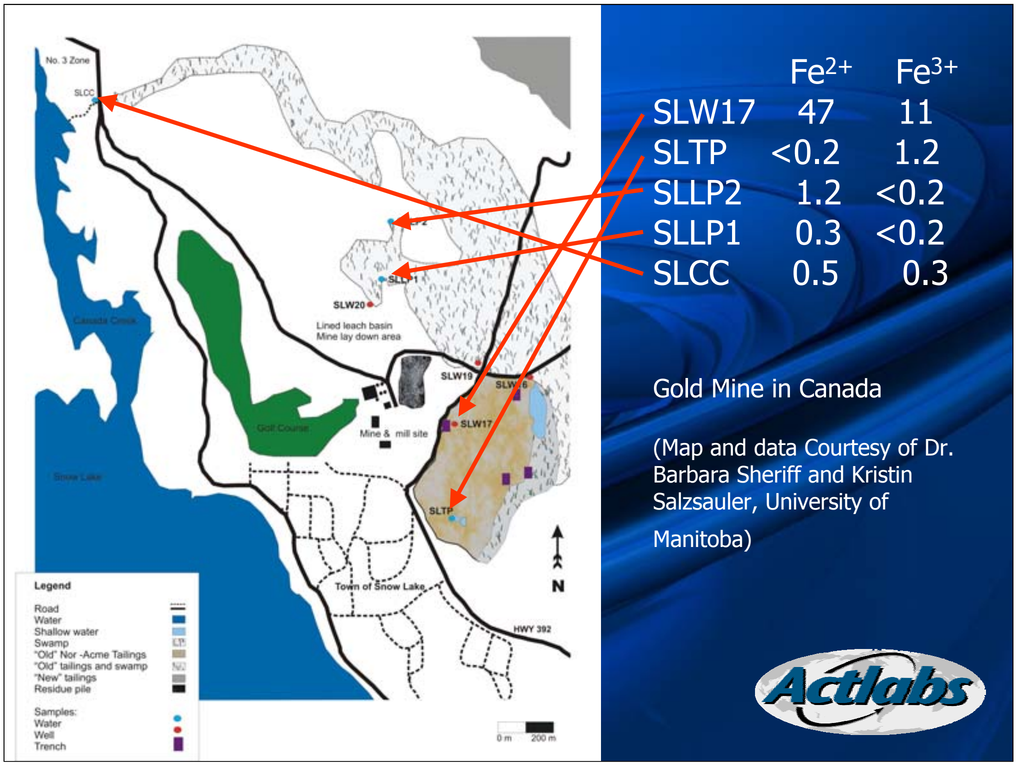

	Fe^{2+}	Fe^{3+}
SLW17	47	11
SLTP	<0.2	1.2
SLLP2	1.2	<0.2
SLLP1	0.3	<0.2
SLCC	0.5	0.3

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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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