Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) With or Without Laser Ablation (LA):

For a Better Understanding of Museum Collections

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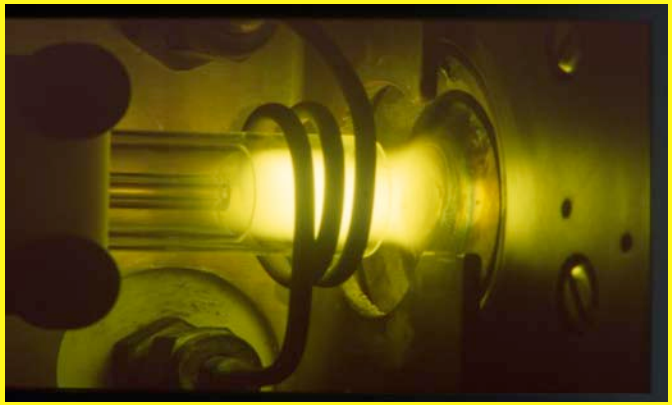
Smithsonian Center
for Materials Research and Education

Inductively Coupled Plasma – Mass Spectrometry With or Without Laser Ablation

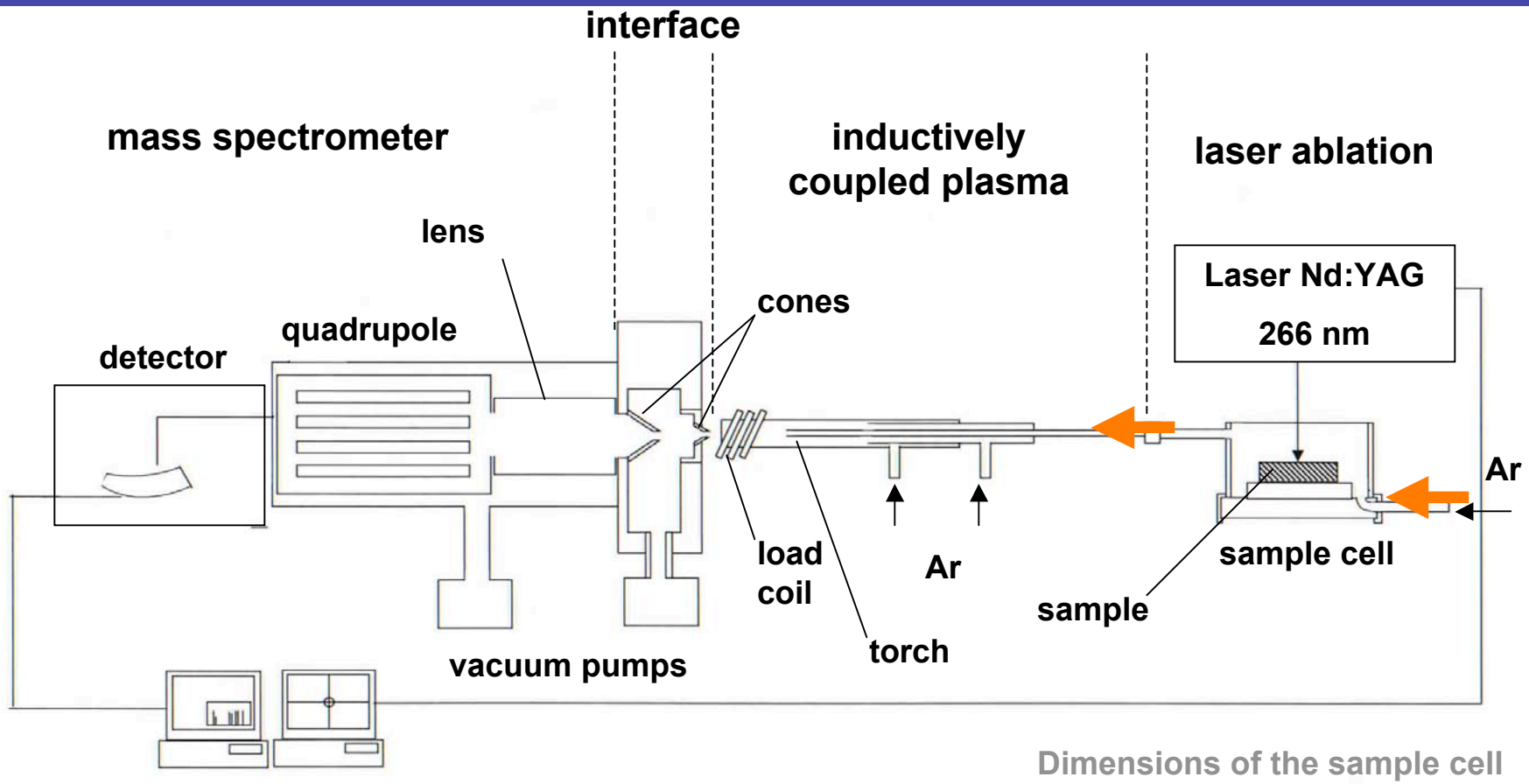
_ Multi-elemental analytical method

_ Very low limits of detection:
- in the range of ppm or below for solid sample
- in the range of ppb or below for solution sample

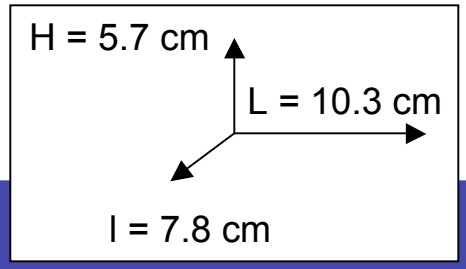


Inductively Coupled Plasma

LA-ICP-MS

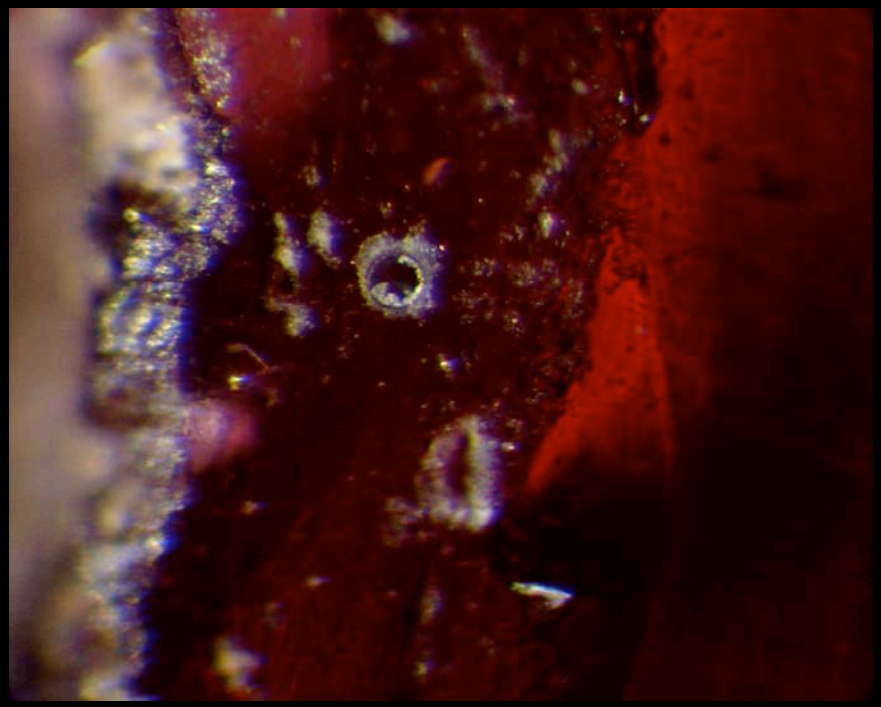


Dimensions of the sample cell



Laser Ablation on glass

Glass bead after analysis

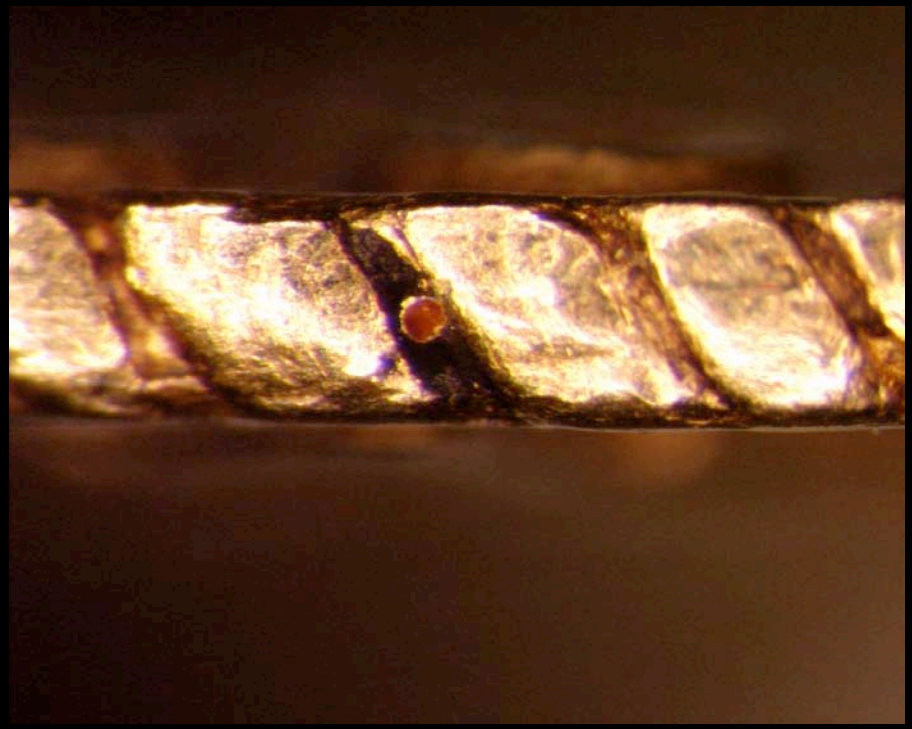


100 micron ablation crater pit

The damage on the glass bead is quasi-invisible to the naked-eye.

Laser Ablation on gold

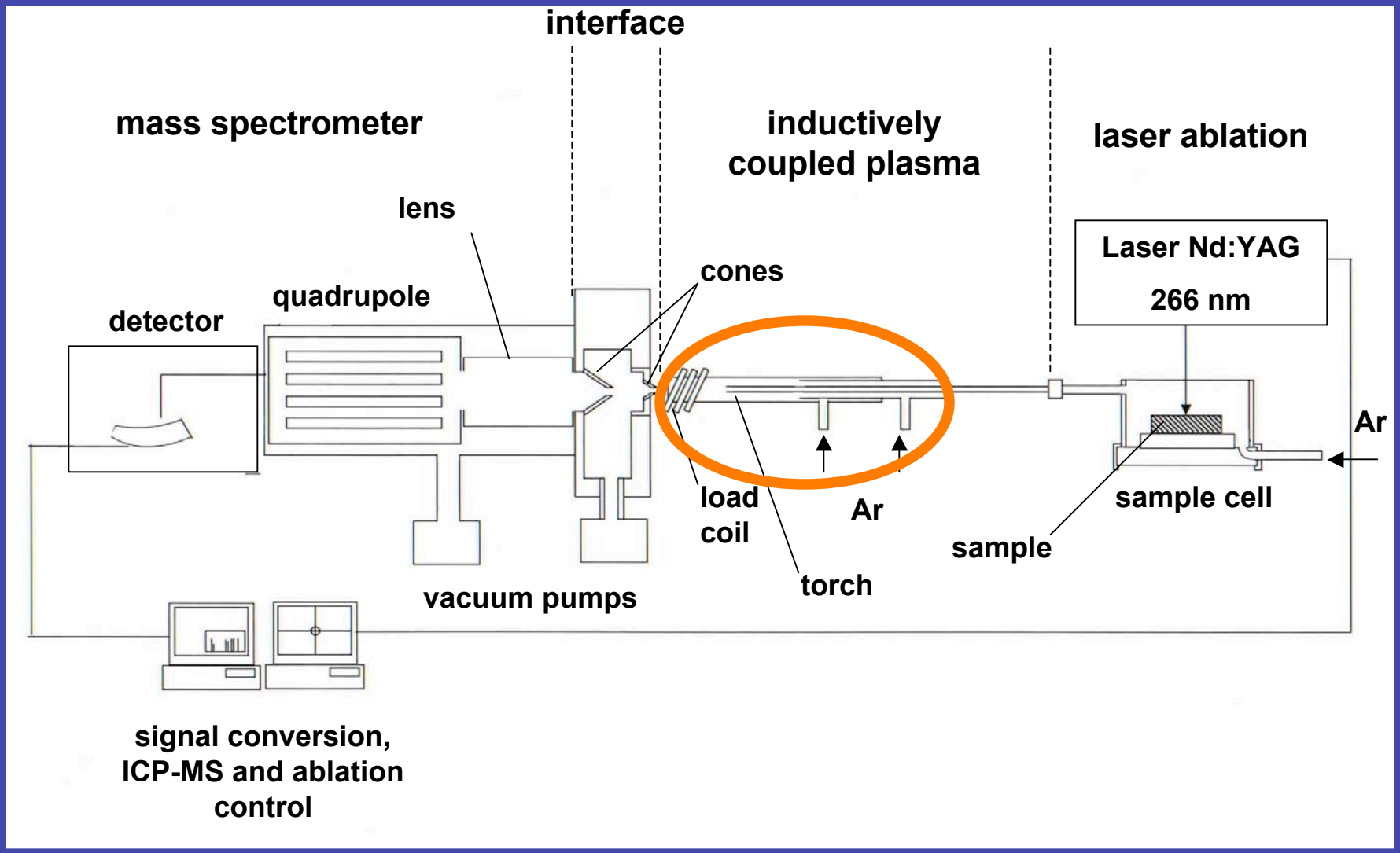
Gold coin after analysis



100 micron ablation crater pit

The damage on the gold coin is quasi-invisible to the naked-eye.

LA-ICP-MS

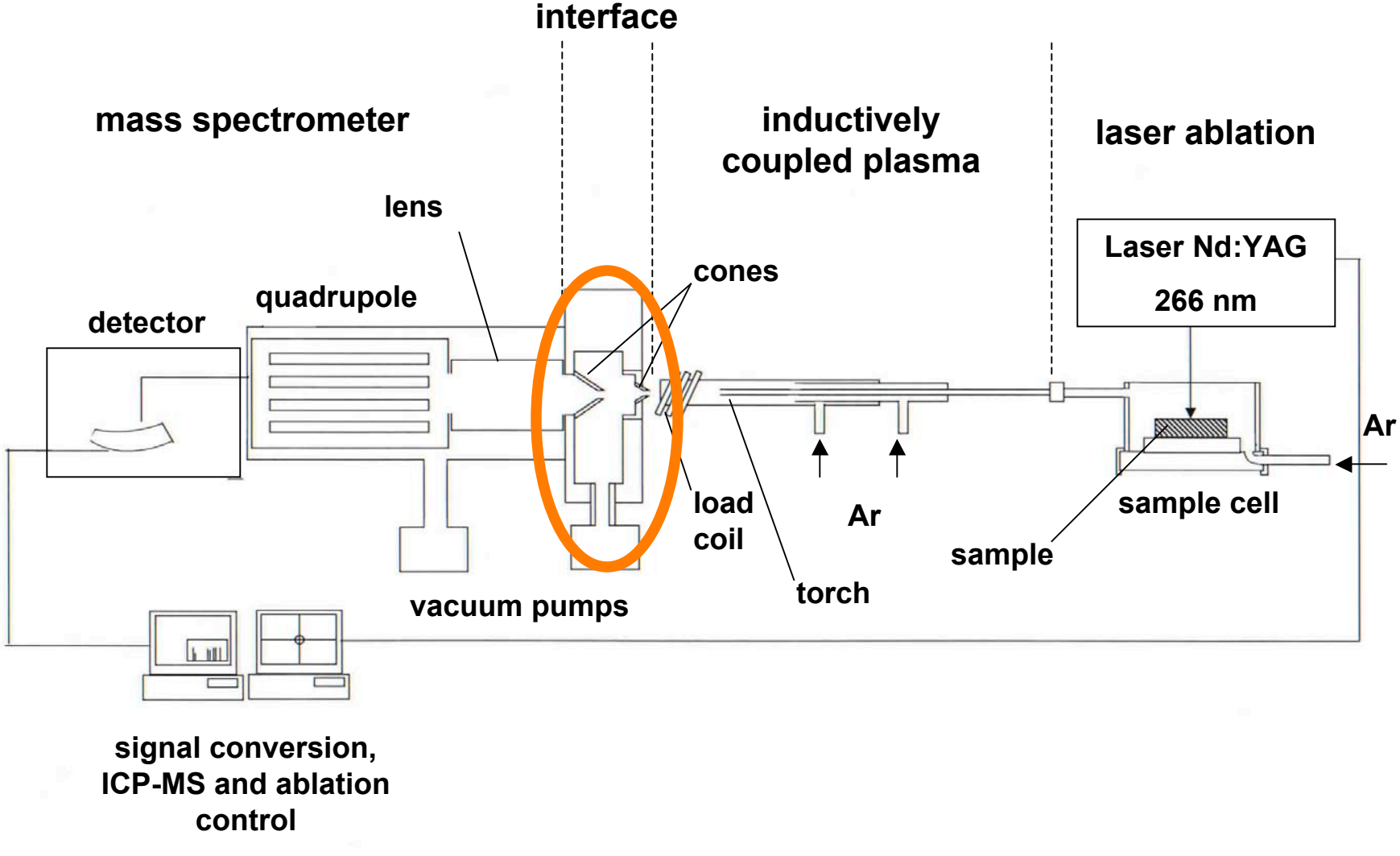

interface
mass spectrometer
inductively coupled plasma
laser ablation
lens
cones
Laser Nd:YAG
266 nm
quadrupole
detector
Ar
load coil
Ar
sample cell
sample
torch
vacuum pumps
signal conversion, ICP-MS and ablation control

Elements measurable with LA-ICP-MS or ICP-MS

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw	

Elements not measurable

LA-ICP-MS


interface
mass spectrometer
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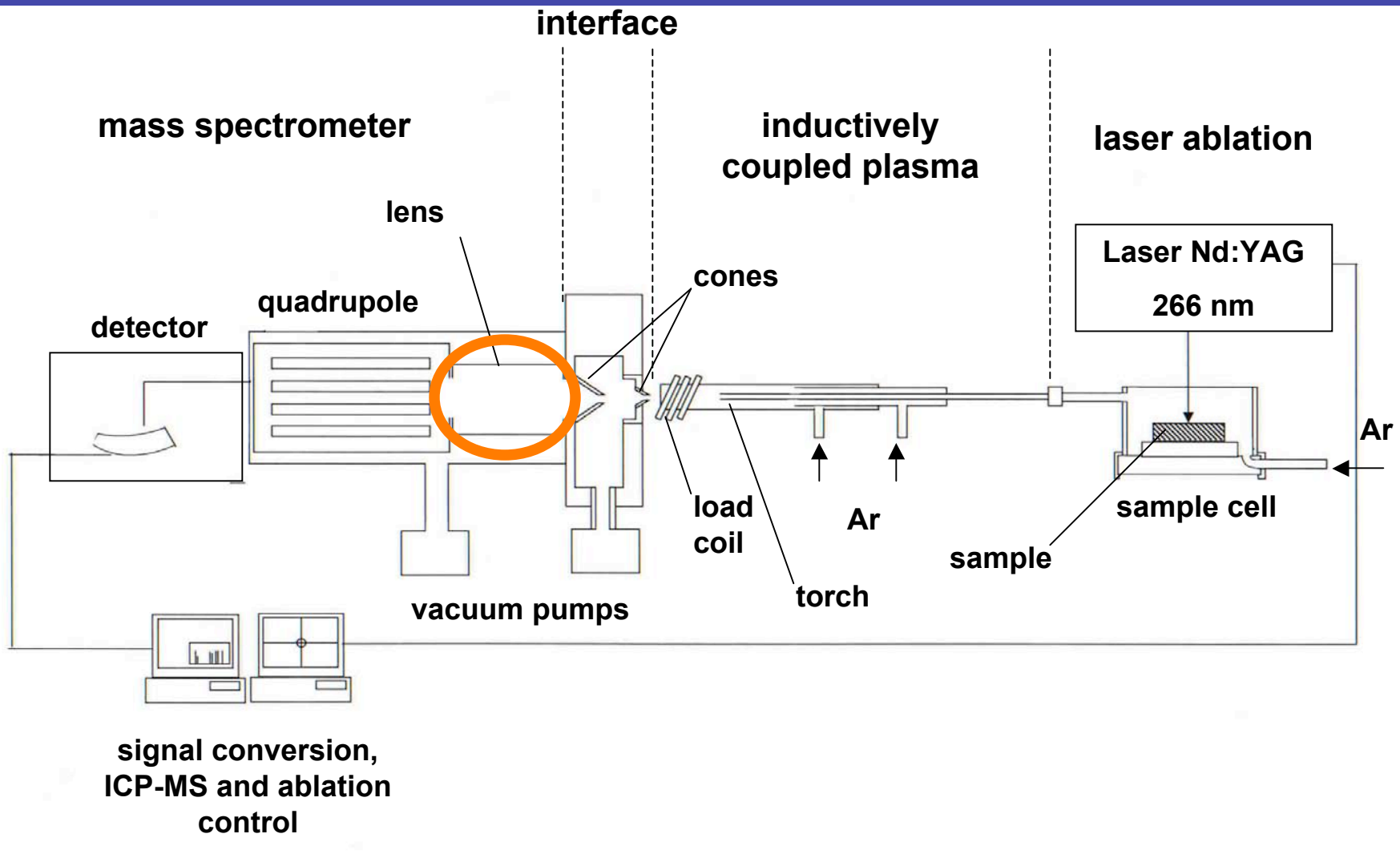
laser ablation
lens
cones
Laser Nd:YAG
266 nm
quadrupole
detector
Ar
load coil
Ar
sample cell
sample
torch
vacuum pumps
signal conversion, ICP-MS and ablation control

LA-ICP-MS


interface
mass spectrometer
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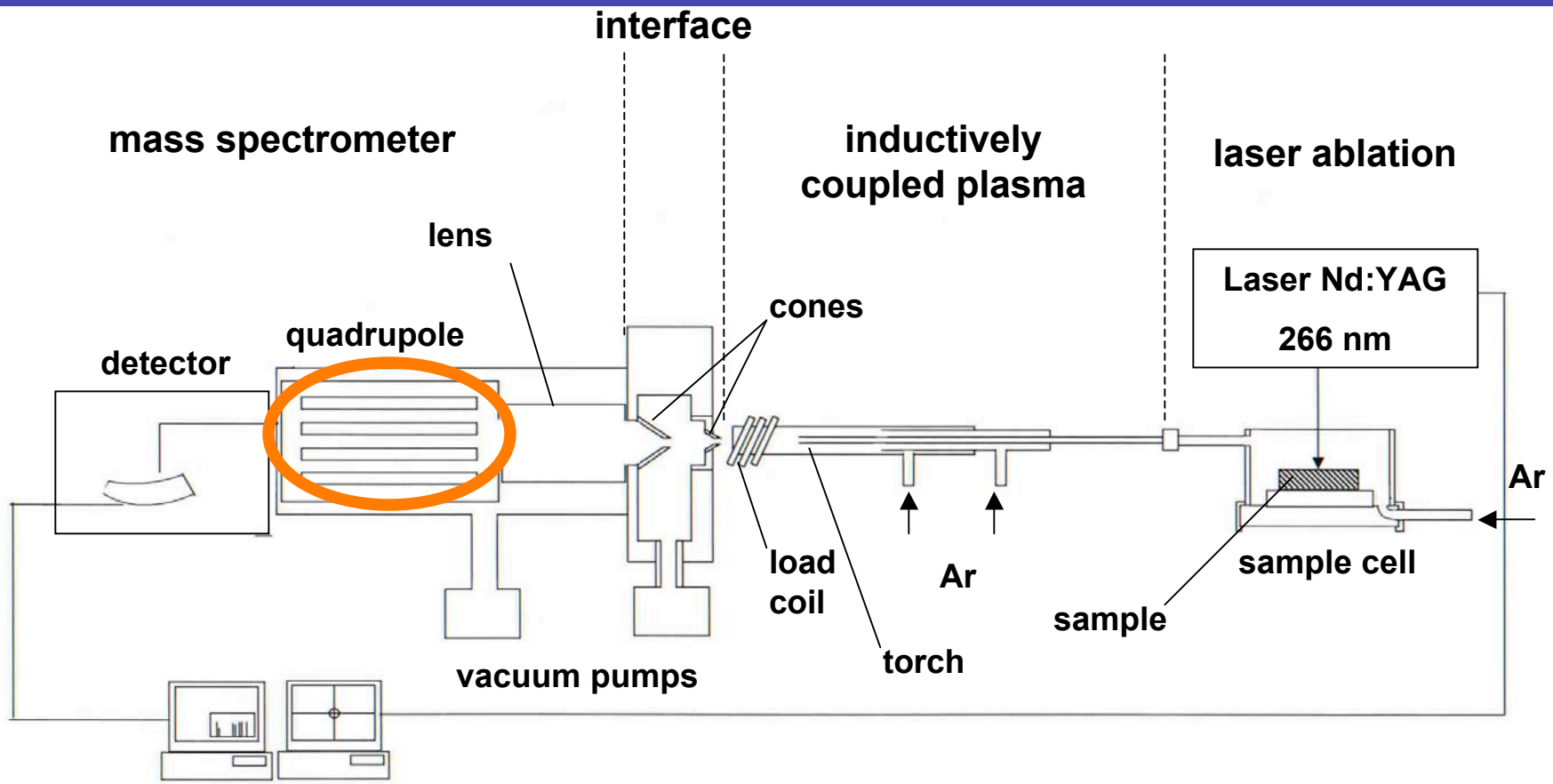
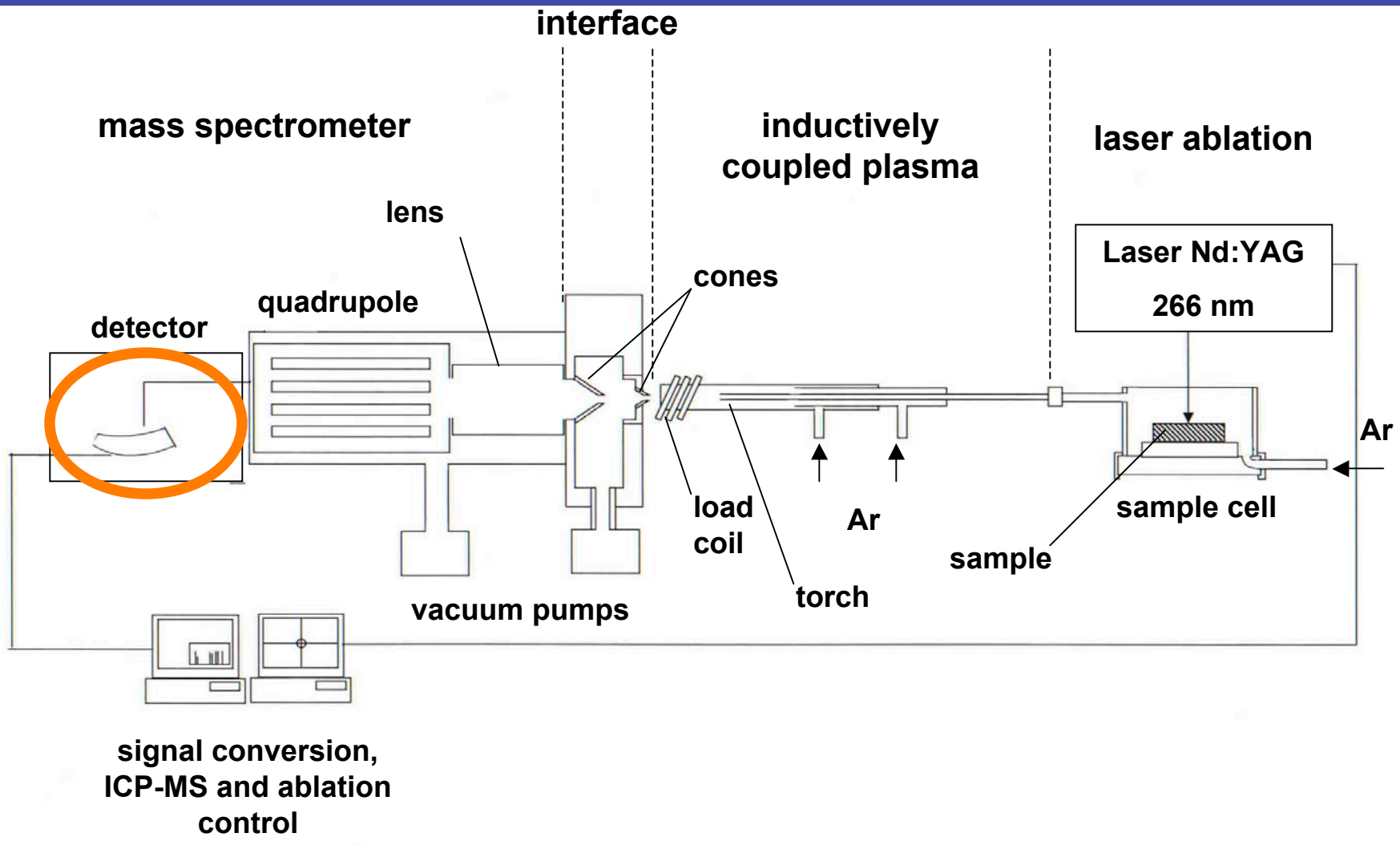
laser ablation
lens
cones
Laser Nd:YAG
266 nm
quadrupole
detector
Ar
load coil
Ar
sample cell
sample
torch
vacuum pumps
signal conversion, ICP-MS and ablation control

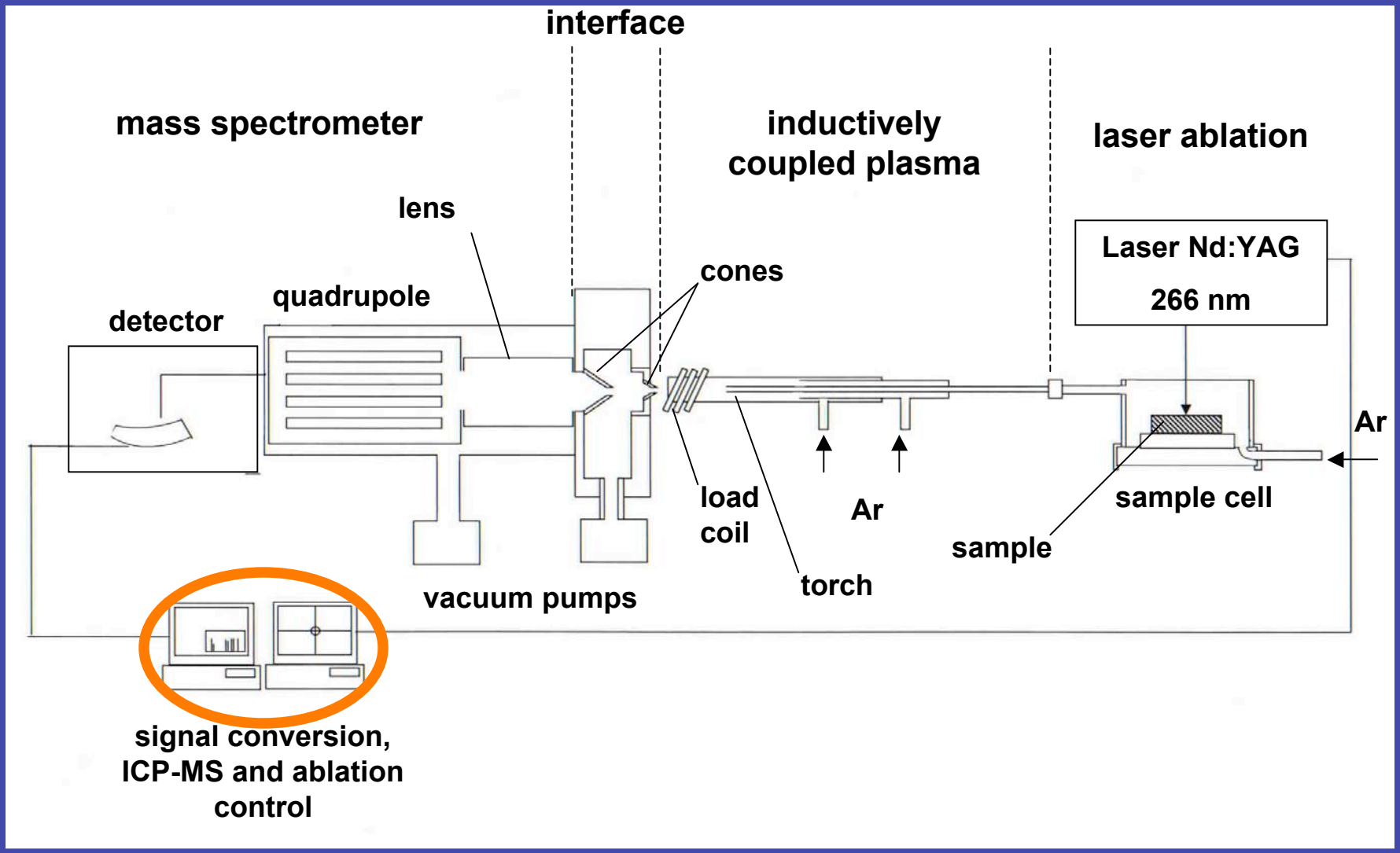
LA-ICP-MS


interface
mass spectrometer
inductively coupled plasma
laser ablation
lens
cones
Laser Nd:YAG
266 nm
quadrupole
detector
Ar
load coil
Ar
sample cell
sample
torch
vacuum pumps
signal conversion, ICP-MS and ablation control

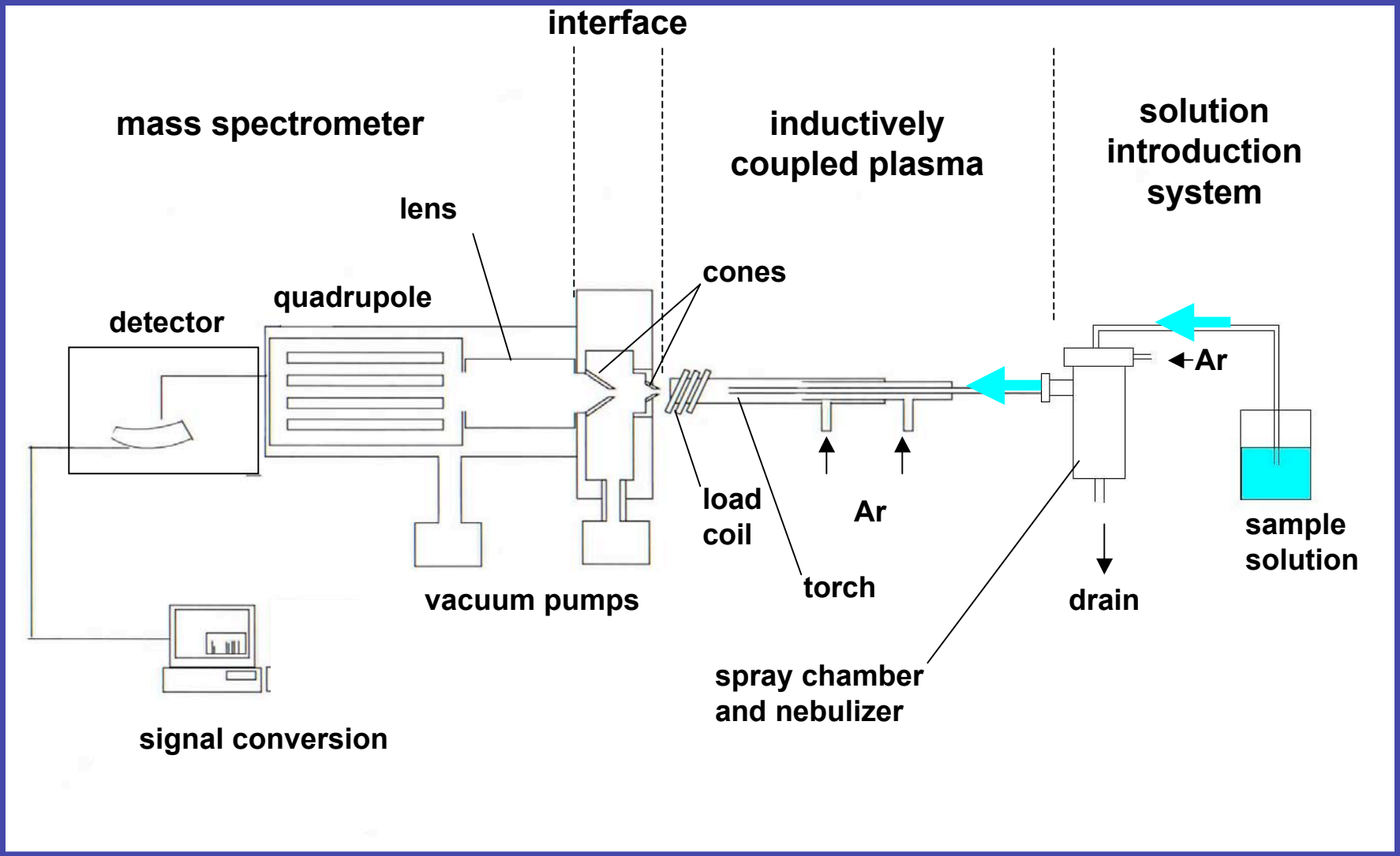
LA-ICP-MS


interface
mass spectrometer
inductively coupled plasma
laser ablation
lens
cones
Laser Nd:YAG
266 nm
quadrupole
detector
Ar
load coil
Ar
sample cell
sample
torch
vacuum pumps
signal conversion, ICP-MS and ablation control

LA-ICP-MS


interface
mass spectrometer
inductively coupled plasma
laser ablation
lens
cones
Laser Nd:YAG
266 nm
quadrupole
detector
Ar
load coil
Ar
sample cell
sample
torch
vacuum pumps
signal conversion, ICP-MS and ablation control

ICP-MS


interface
mass spectrometer
inductively coupled plasma
solution introduction system
lens
cones
quadrupole
detector
Ar
load coil
Ar
sample solution
torch
vacuum pumps
drain
spray chamber and nebulizer
signal conversion

Characterization of different materials with ICP-MS or LA-ICP-MS

_ Inorganic materials

_ Organic materials

Determination of the composition of inorganic materials using LA-ICP-MS

Siliceous materials

_ glass

_ glaze

Metals

_ gold alloy

_ copper alloy

GLASS

19th century European and Asian Glass Trade Beads from North America (Laurie Burgess, Repatriation Office, NMNH).

_ Characterization of the glass beads according to their provenance.

Early 1600 to 1830 Blue Glass Trade Beads from North America (Bill Billeck, Repatriation Office, NMNH).

_ Is there a variation of the composition according to the time period ?

GLASS

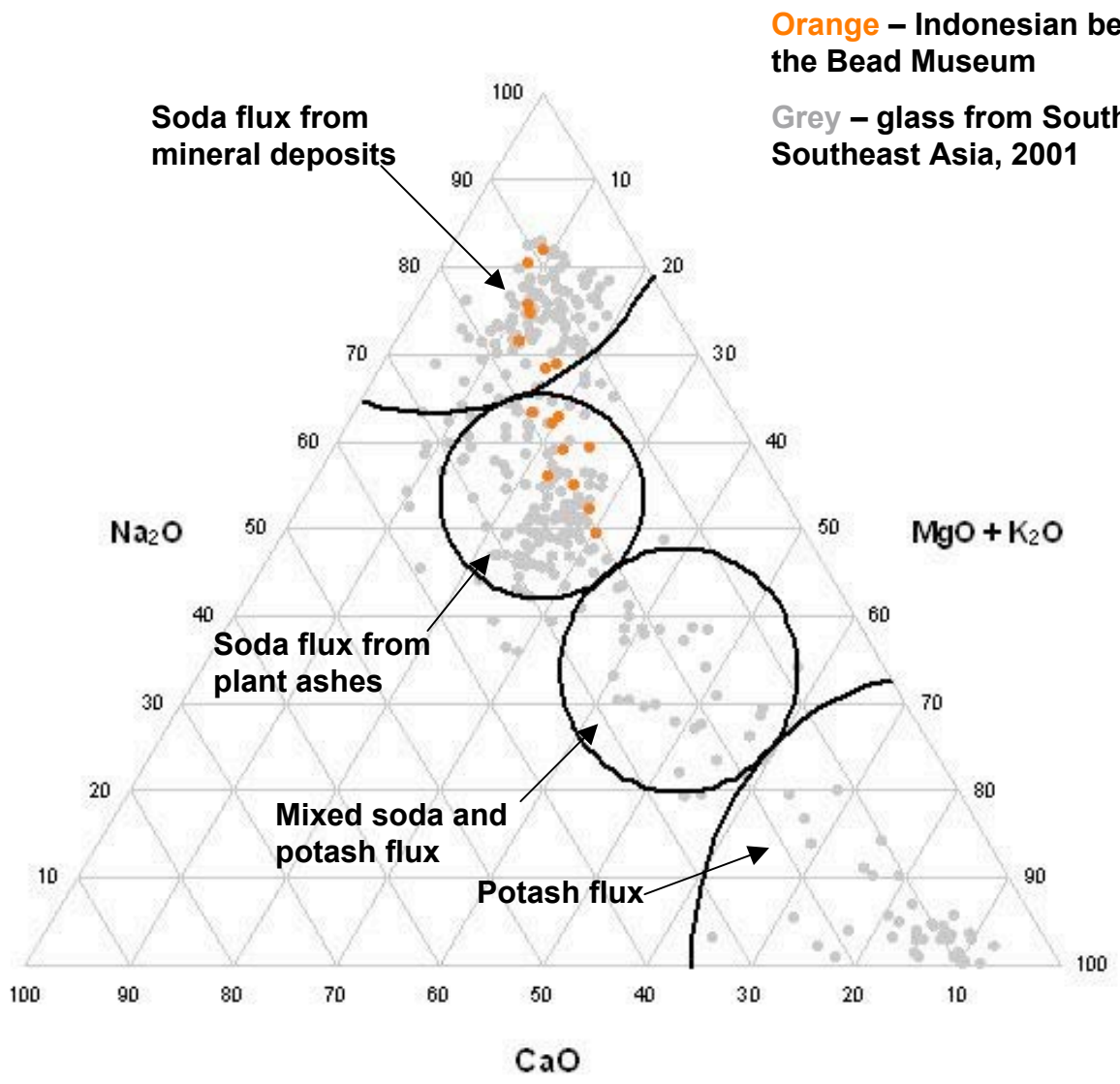
Ancient glass beads found in Indonesia (Bead Museum, Washington, DC).

_ What is the provenance of the glass used to manufactured Indonesian beads ?

From Ingredients to Composition

Silica source	Flux	Coloring or opacifying agents
_ Sand _ Quartz pebbles or crushed siliceous stones	_ Plant ashes _ Alkaline mineral deposit _ Lead	_ Oxides _ Metallic salts
Si, Al, Fe, Ti, Ca, K, Mg, trace elements, rare earth, …	Na, K, Pb, Ca, Mg, Cl, P, trace elements,…	Transition elements, Sb, Sn, Pb, Ca, trace elements

$MgO + K_2O – Na_2O – CaO$ Ternary diagram for the Different Fluxes Identified among Glass from South and Southeast Asia

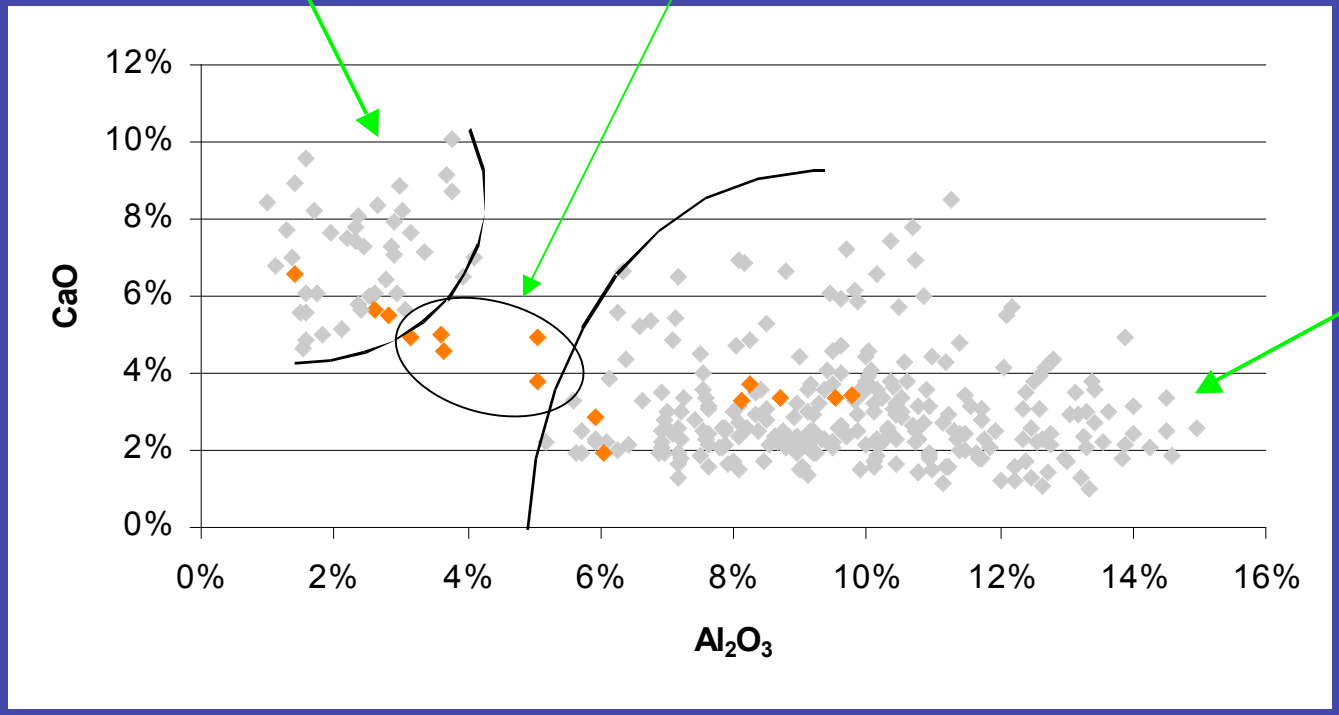


Al_2O_3 – CaO Graph for Glass from South and Southeast Asia

High calcium glass with soda flux from plant ashes

Intermediate composition

Orange – Indonesian beads from the Bead Museum
Grey – glass from South and Southeast Asia, 2001



High alumina glass with soda flux taken from mineral deposits

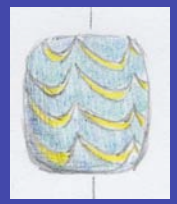
Al_2O_3 – CaO Graph for Glass from South and Southeast Asia

High calcium glass with soda flux from plant ashes

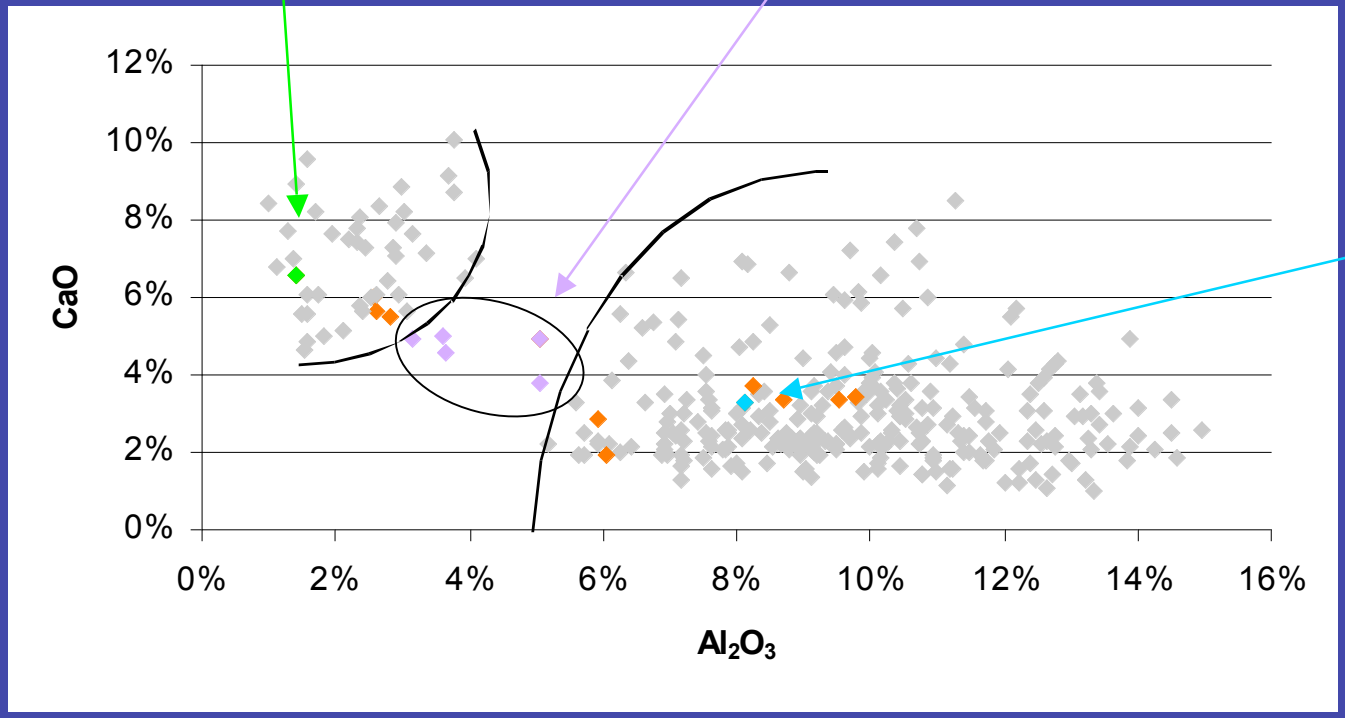
921

C

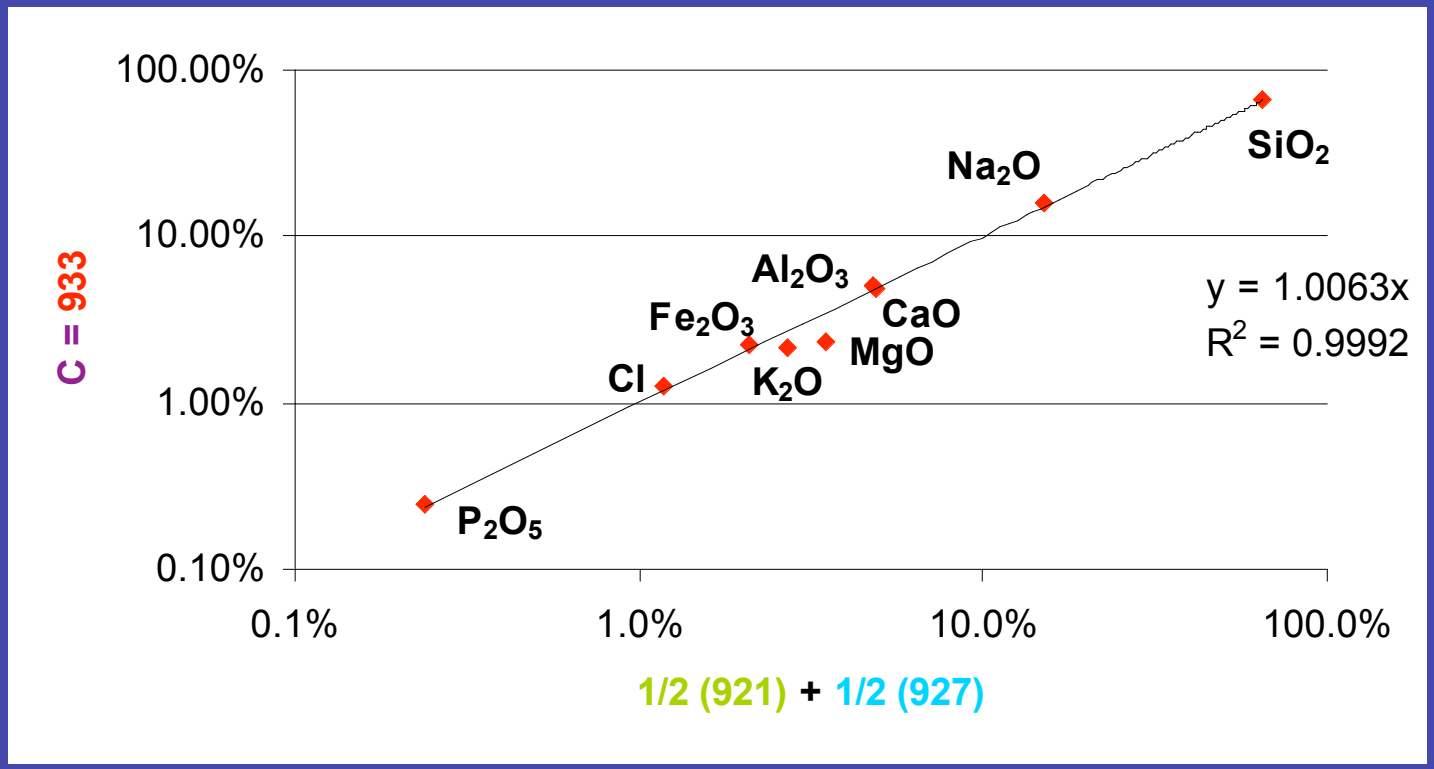
High alumina glass with soda flux taken from mineral deposits



927 brownish core



Comparison between the composition of C and a Composition Calculated as if 921 and 927 were Mixed in Equal Proportion



The Three Different Types of Glass

Imported glass
(Middle-East)

921db
931db
931w
920g

C = Mixed glass

914a_db
914a_w
933b
933y
933r

Imported glass
(South Asia)

927tb
927yi
927ye
914b_w
914b_b
928_b

High calcium glass with soda flux from plant ashes

High alumina glass with soda flux taken from mineral deposits

High calcium glass with soda flux from plant ashes

From Middle-East

→ Mixed glass ←

High alumina glass with soda flux taken from mineral deposits

From South Asia

↓

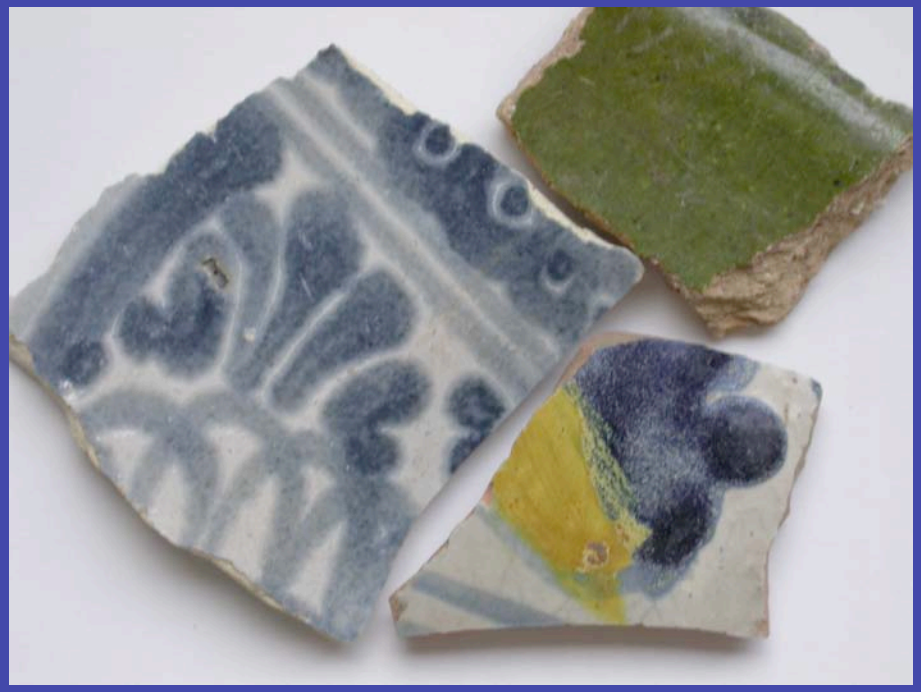
Indonesia

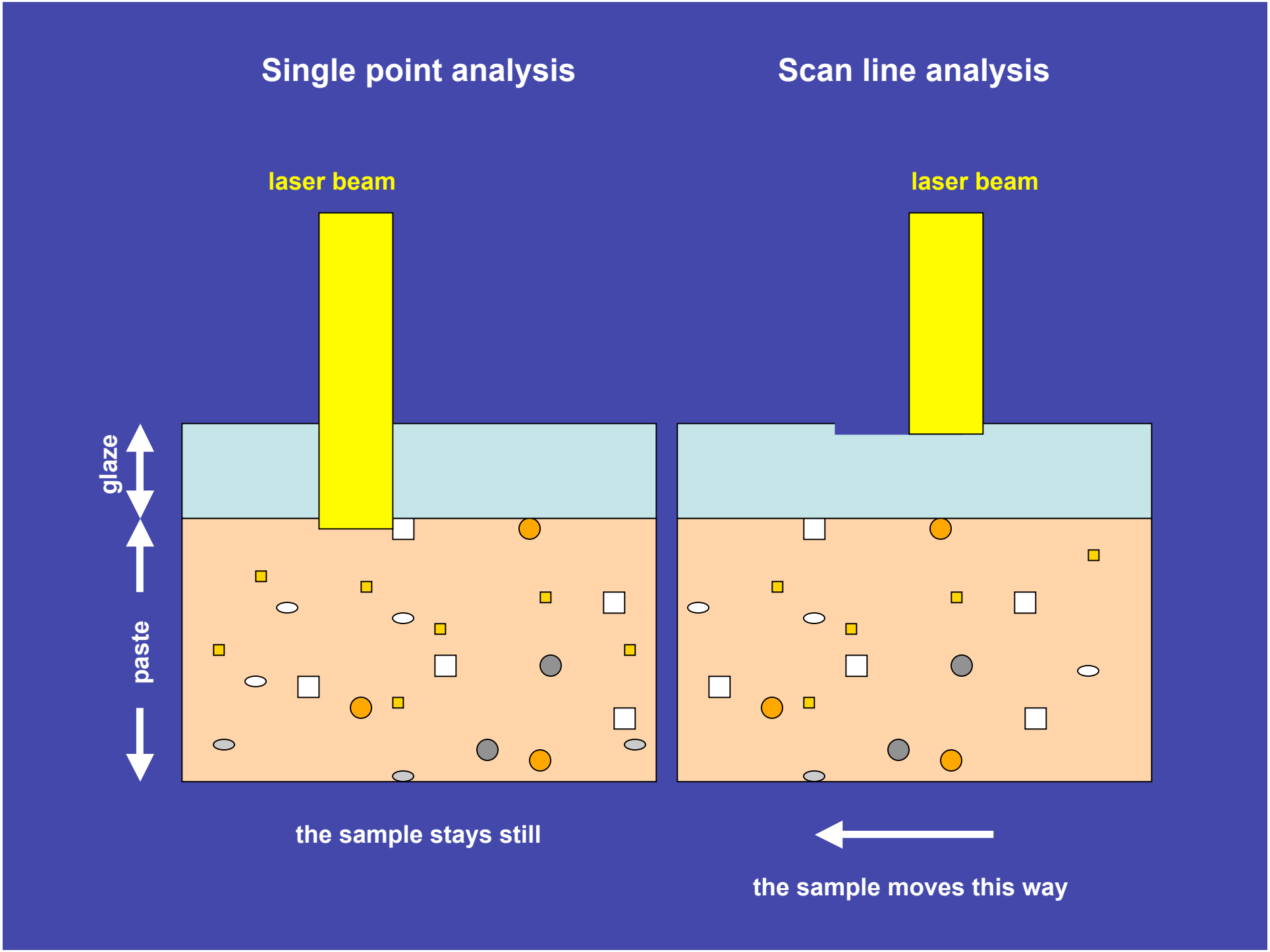
Bead producing workshop

GLAZE

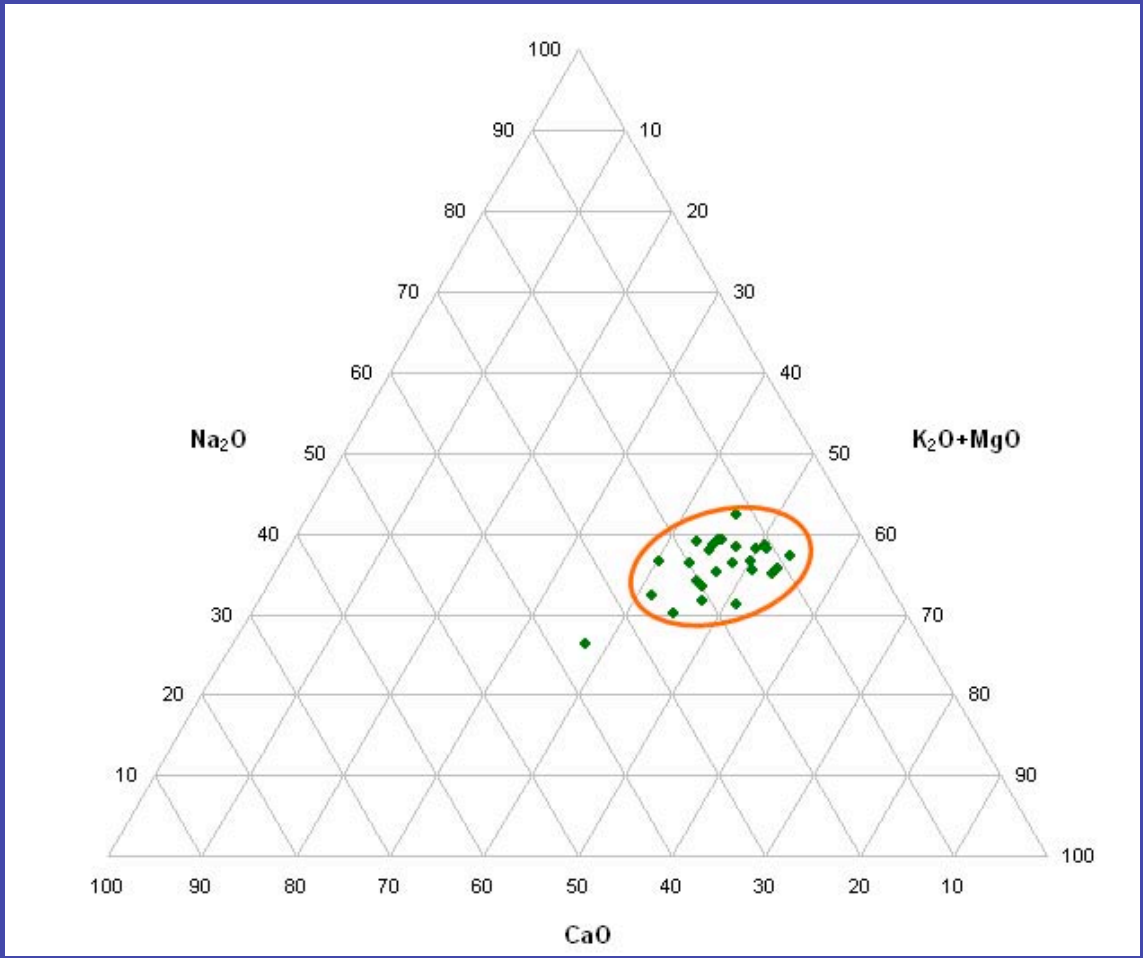
17th to 19th c. glazed ceramics from Mexico (Ronald Bishop, Jim Blackman, NMNH).

_ Comparison of the composition of the paste and of the glaze to help locating production centers in Mexico.

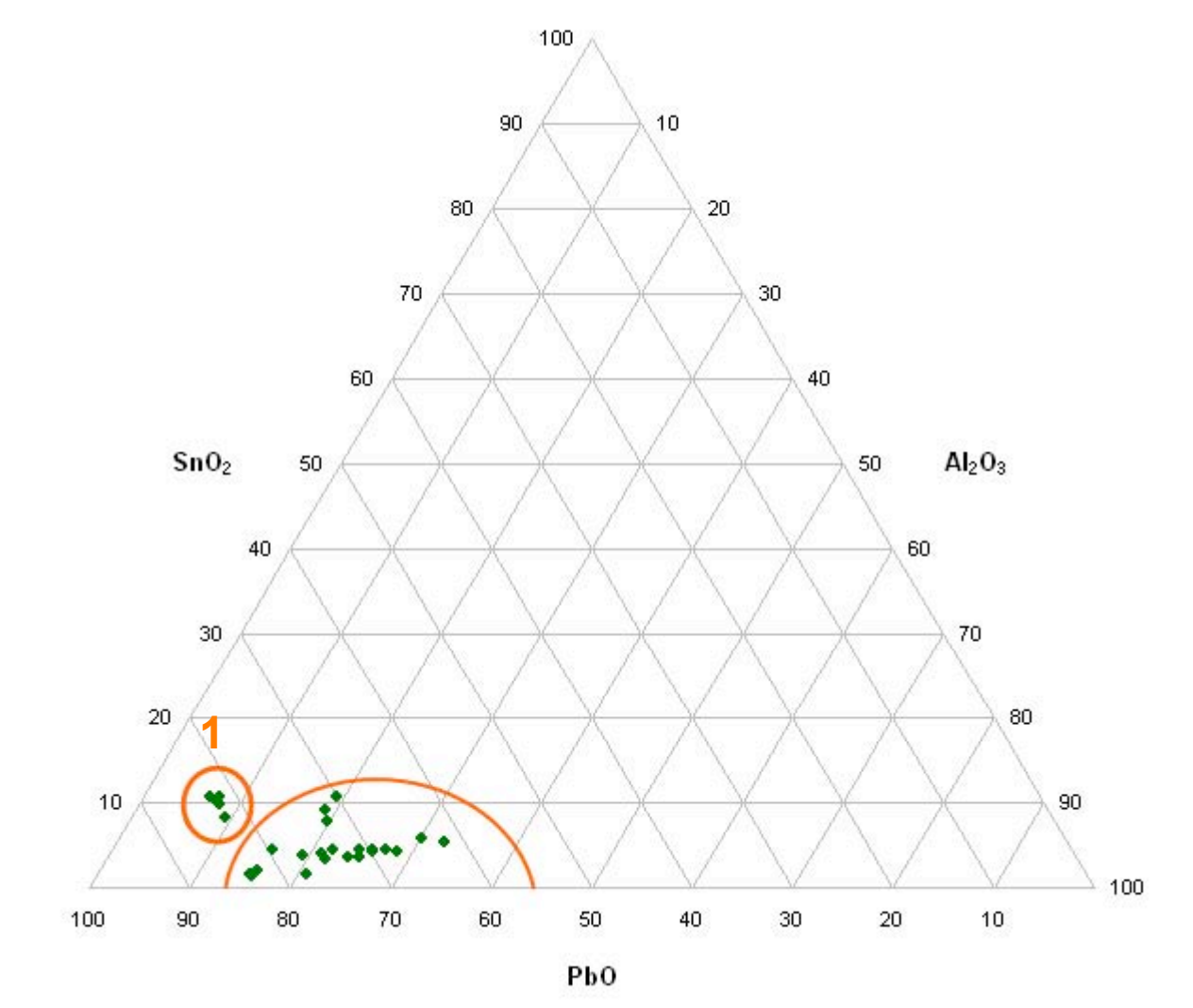



Single point analysis
Scan line analysis
laser beam
laser beam
glaze
paste
the sample stays still
the sample moves this way

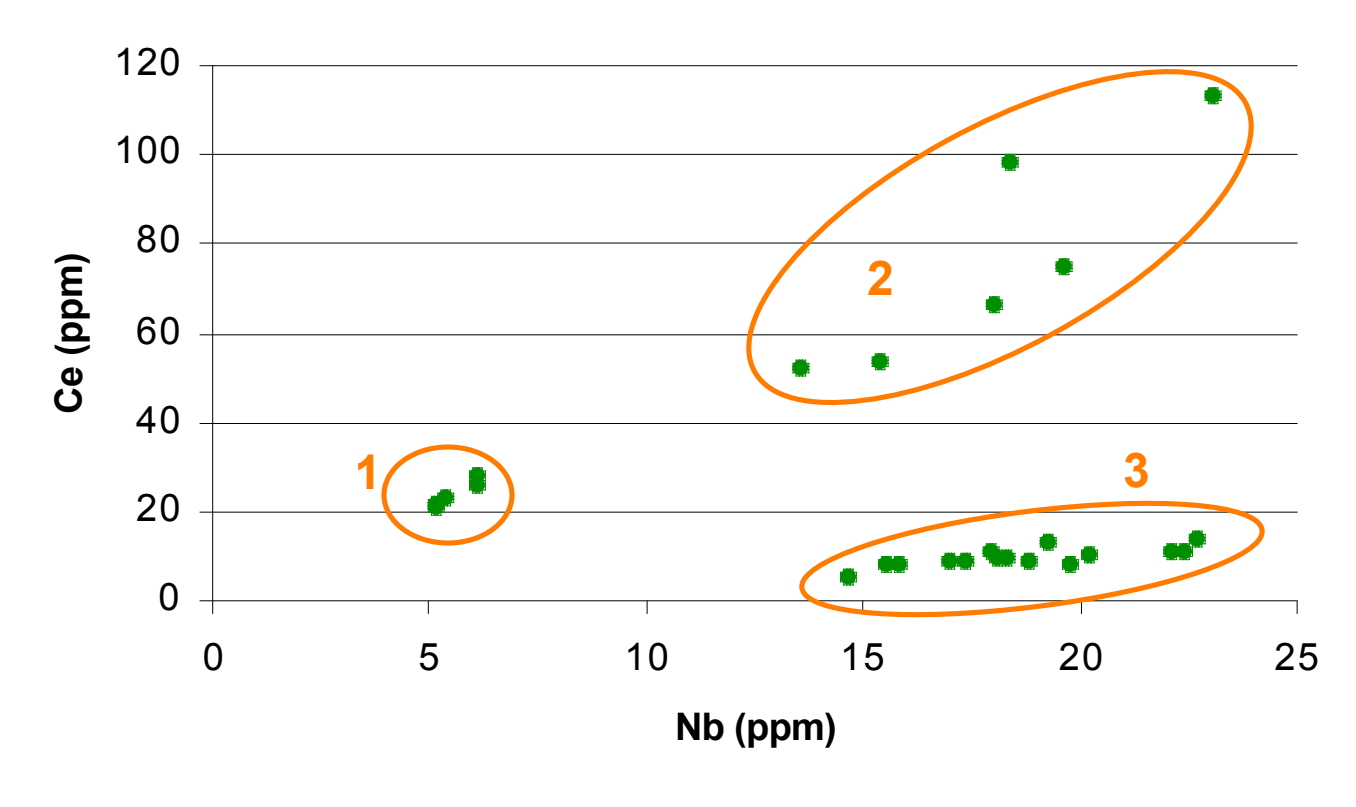
$MgO + K_2O – Na_2O – CaO$ Ternary Diagram for Majolica from Mexico

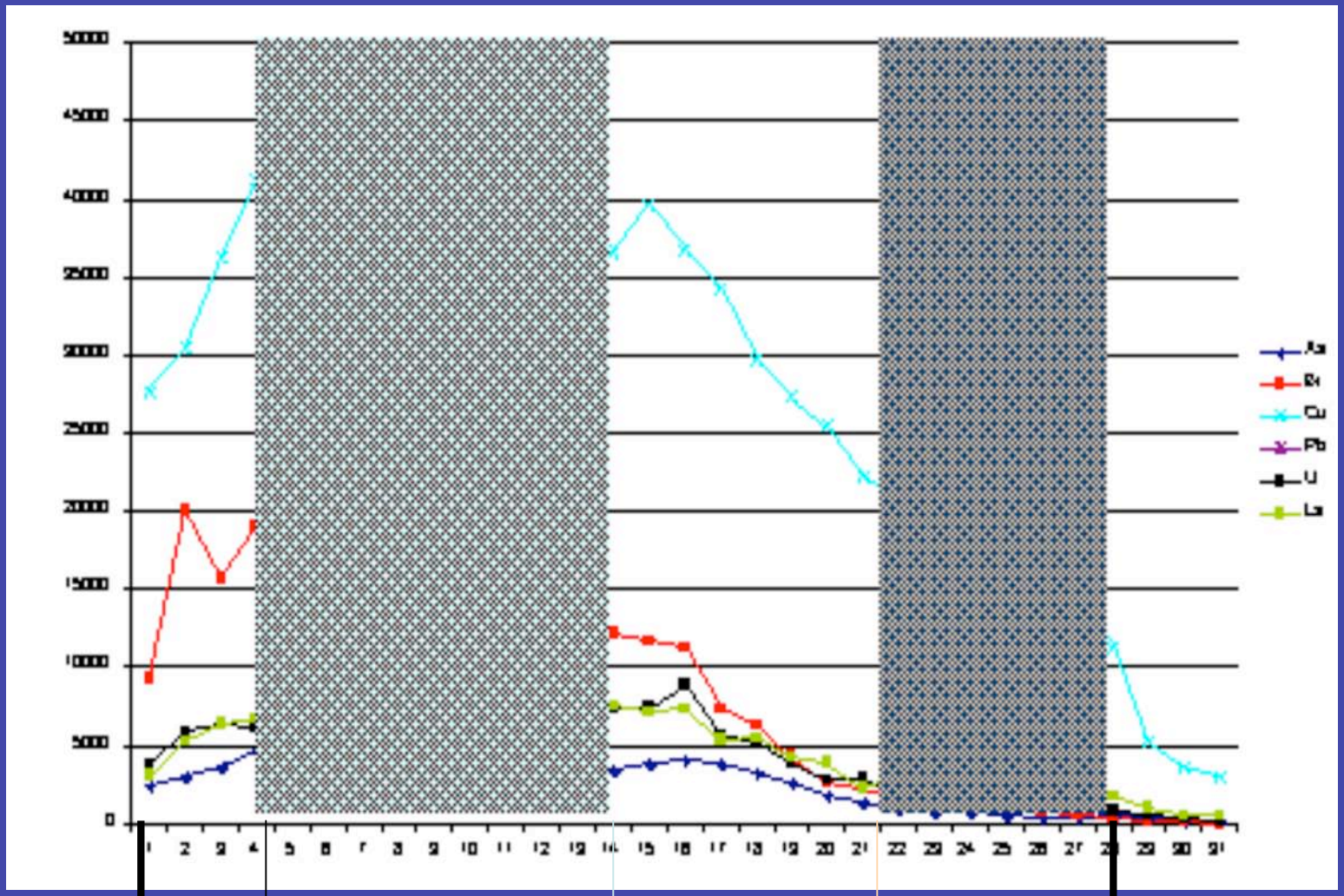


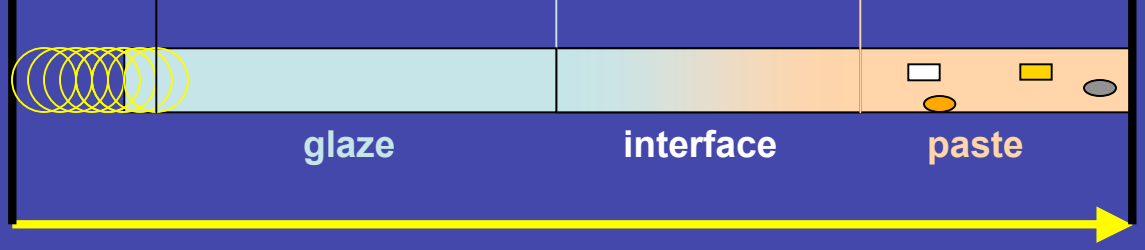
Al_2O_3 – SnO_2 – PbO Ternary Diagram for Majolica from Mexico



Nb – Ce Graph for Majolica from Mexico

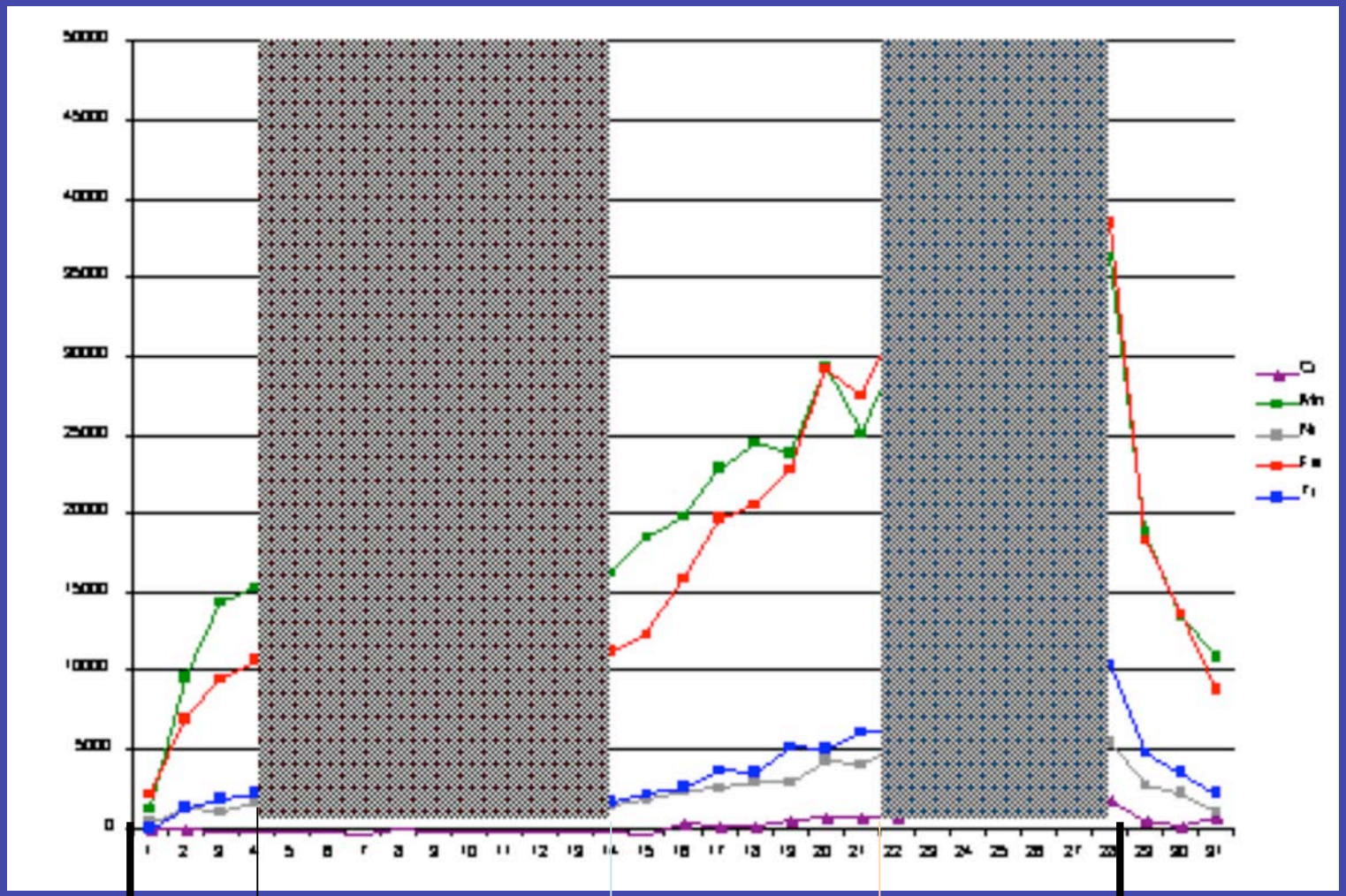


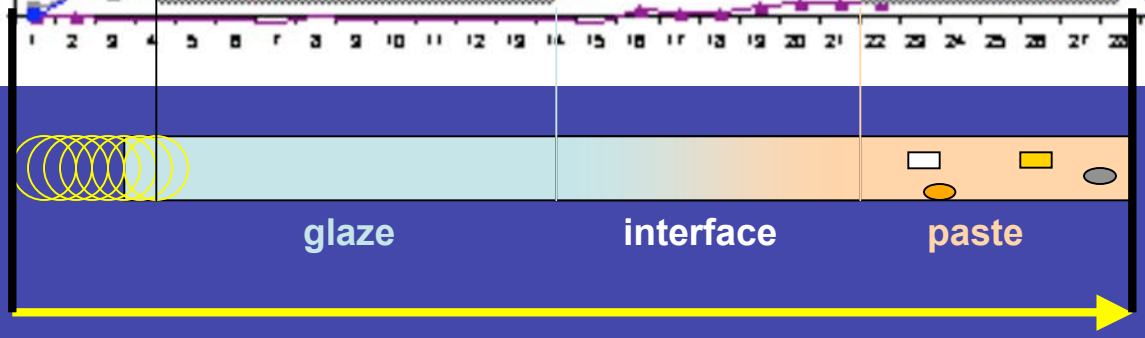




Beginning of the ablation

End of the ablation





Beginning of the ablation

End of the ablation

GOLD ALLOY

Gold ores from different parts of North, Central and South America (Paul Pohwat and Serena Sorensen, NMNH).

_ Are there specific trace element patterns according to area?

Gold plaques and foils from China, dated from the 6th c. BC. (Paul Jett, FGA-DCSR)

_ Is it possible to discriminate gold alloy with similar composition using trace element concentrations?

No specific trace element patterns exist for gold ore from the Americas according to the area, except for Brazilian gold that contains high Pd contents.

Implication: It is not possible to trace the origin of gold by comparing trace element patterns in gold object and gold ores except for some very specific cases.

GOLD ALLOY

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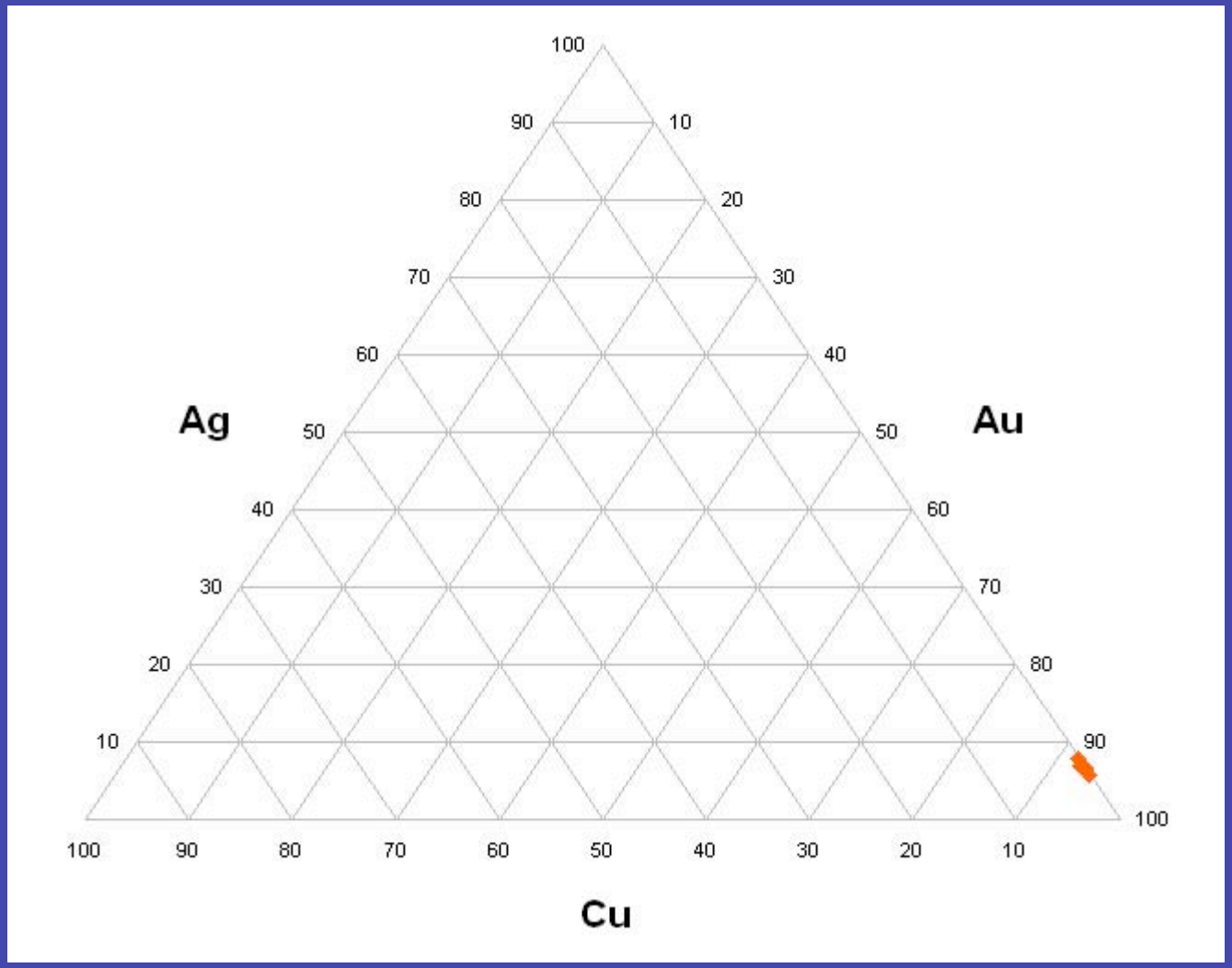
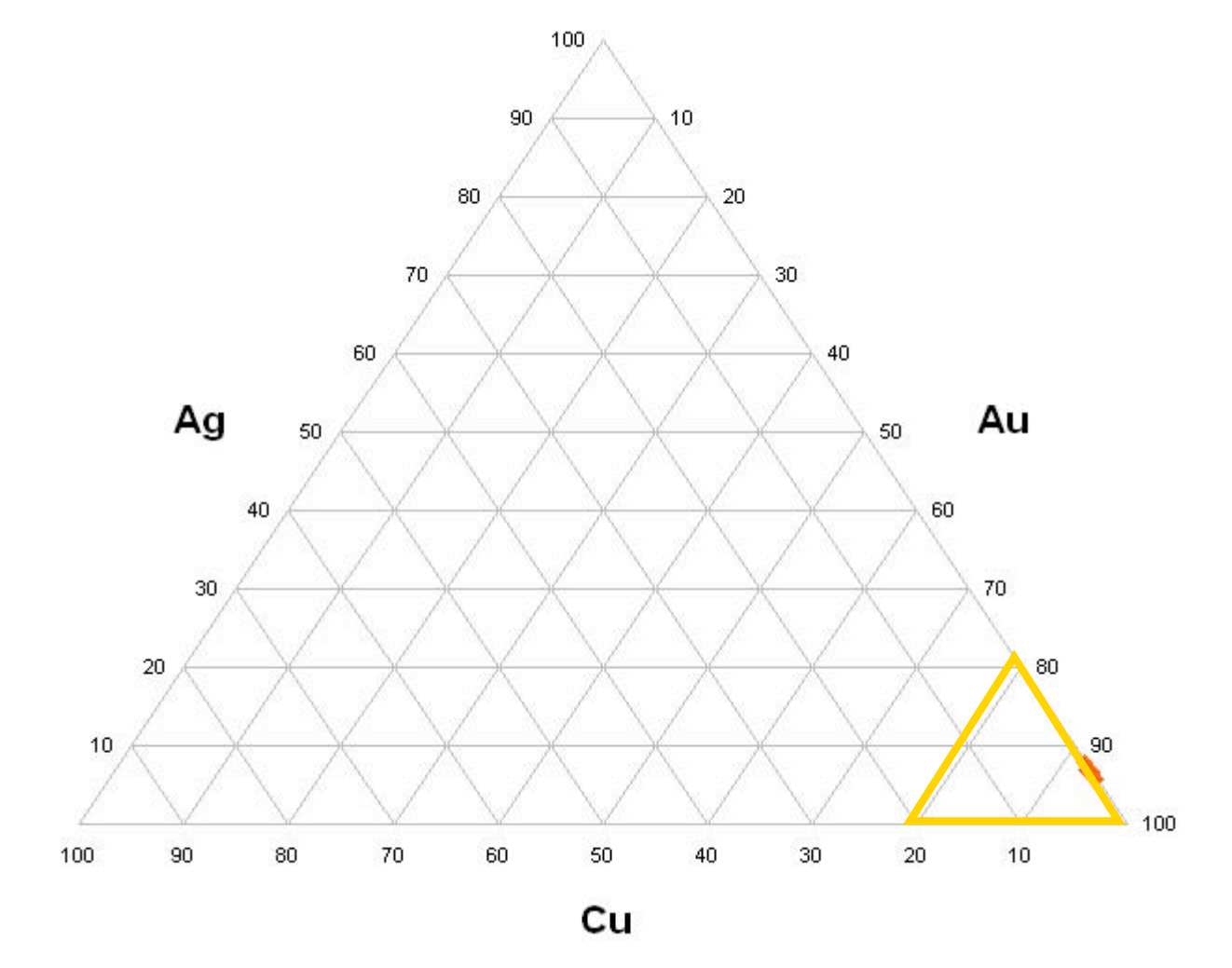
Ag – Au – Cu Ternary Diagram for Chinese gold samples



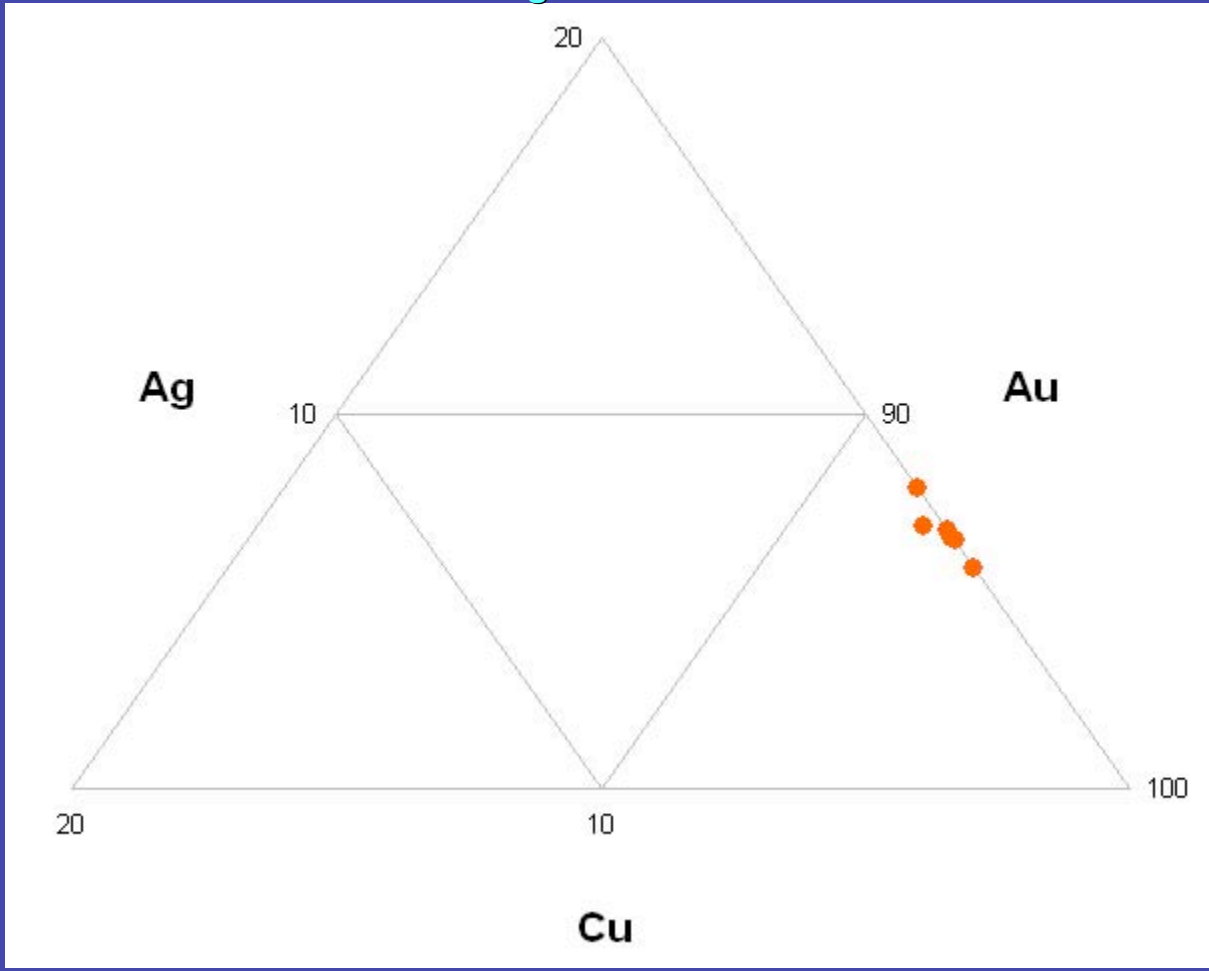
Ag – Au – Cu Ternary Diagram for Chinese gold samples

Area that will be magnified

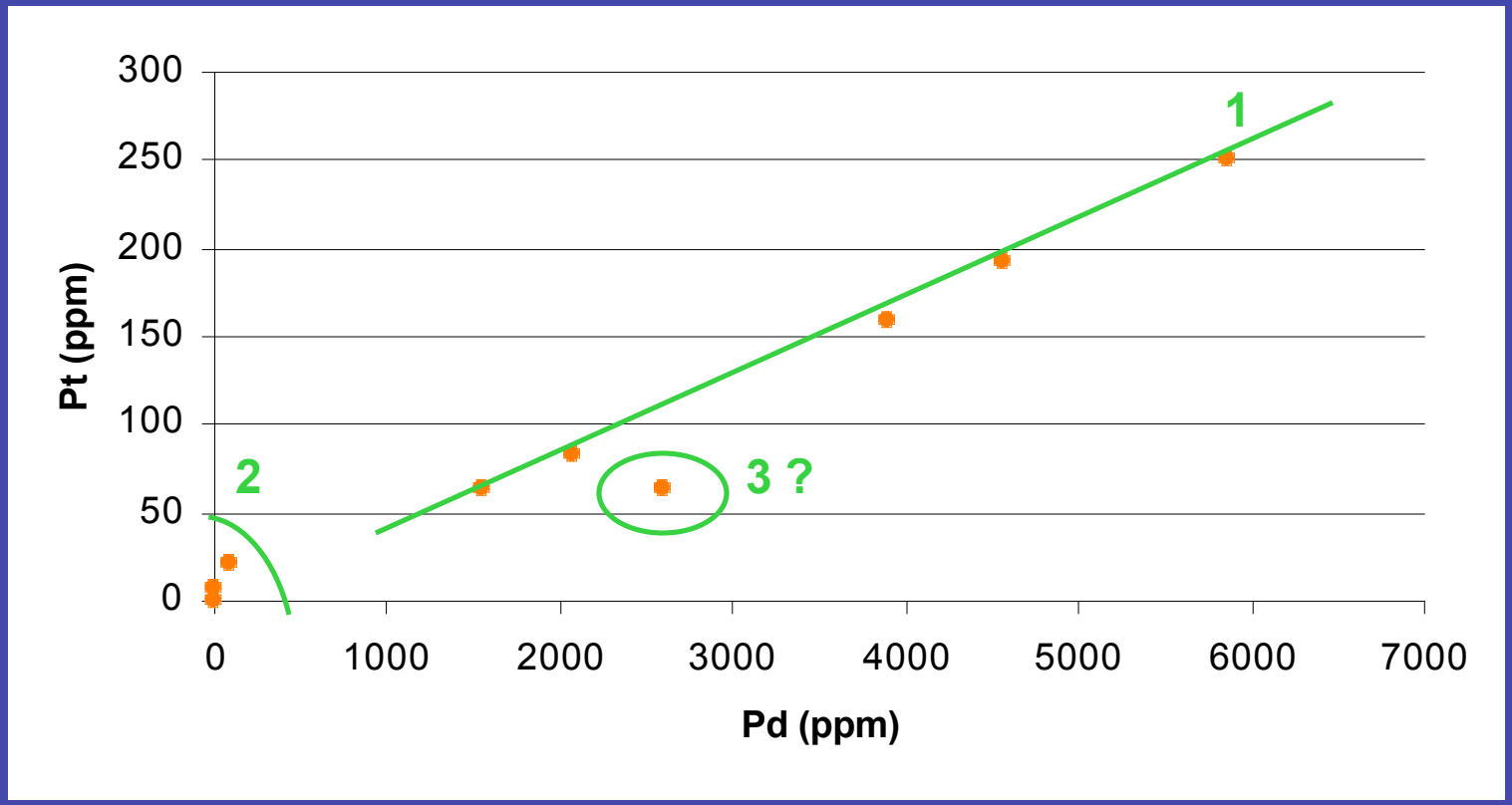


Ag – Au – Cu Ternary Diagram for Chinese gold samples

Magnified area



Pd - Pt Graph for the Chinese Gold Samples



A least two different gold sources were used to manufacture the gold objects.

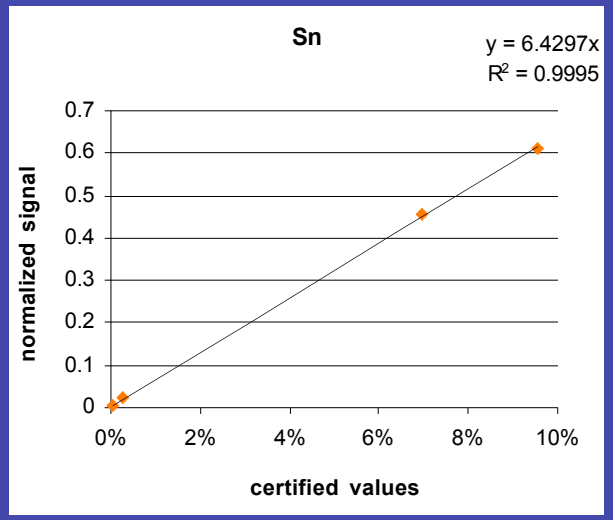
COPPER ALLOY

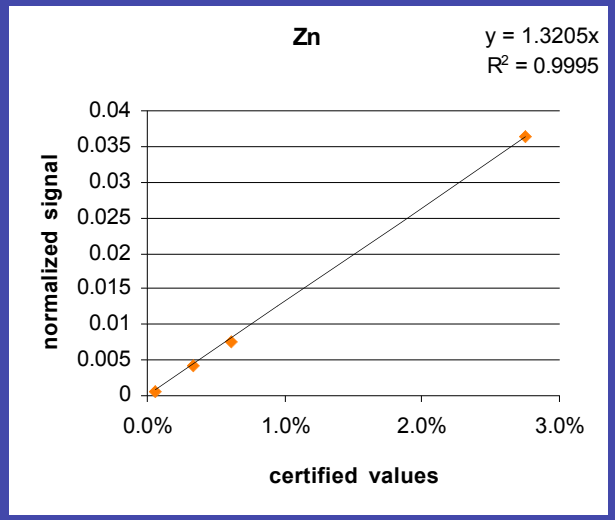
Matisse bronzes from the Baltimore Museum of Art analyzed using the Handheld XRF (Jia-Sun Tsang, Charles Tumosa, Sarah Pinchin, SCMRE)

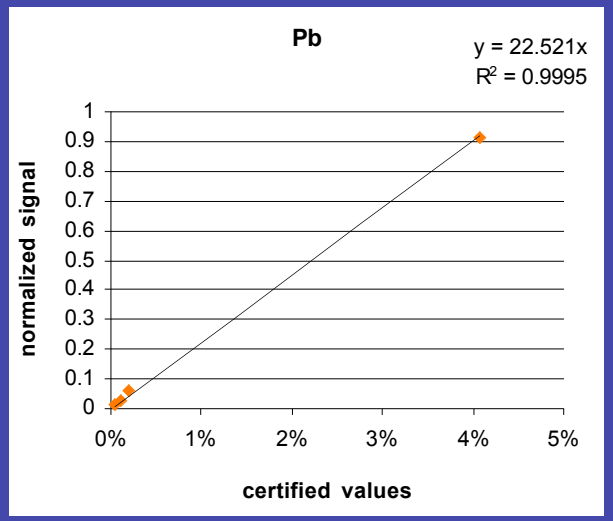
_ Comparison of analytical results provided by the handheld XRF and by LA-ICP-MS

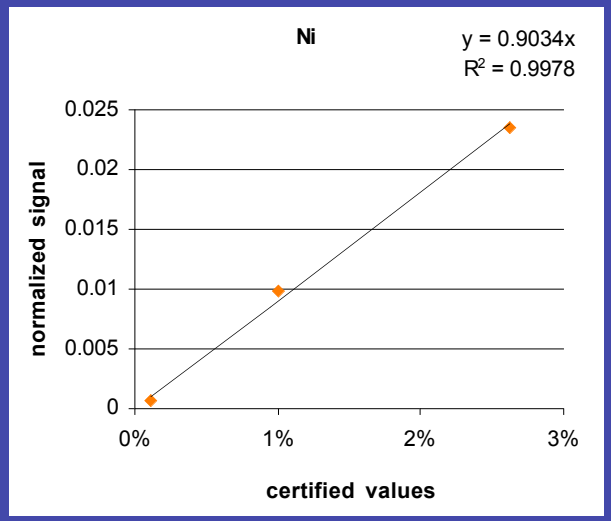
Handheld XRF: surface analysis
LA-ICP-MS: "core" analysis

Calibration curves

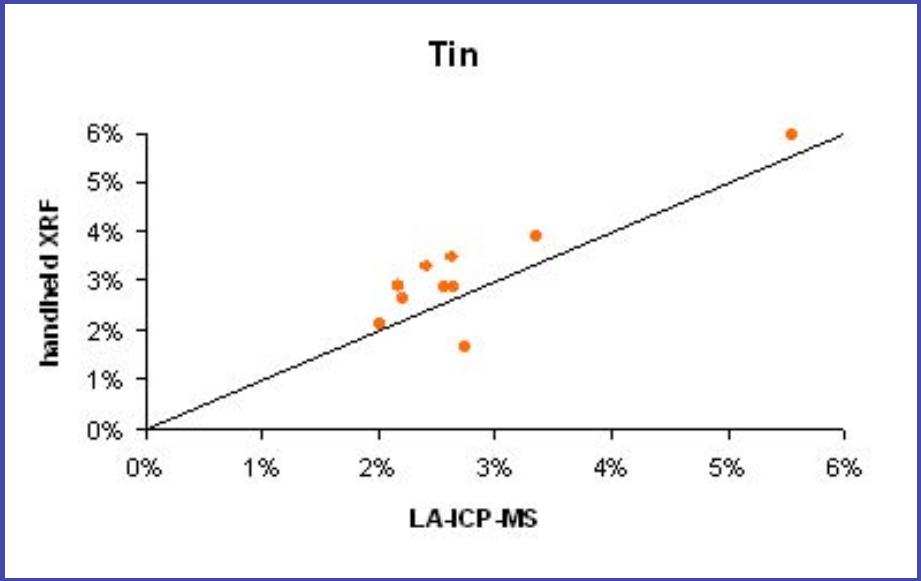


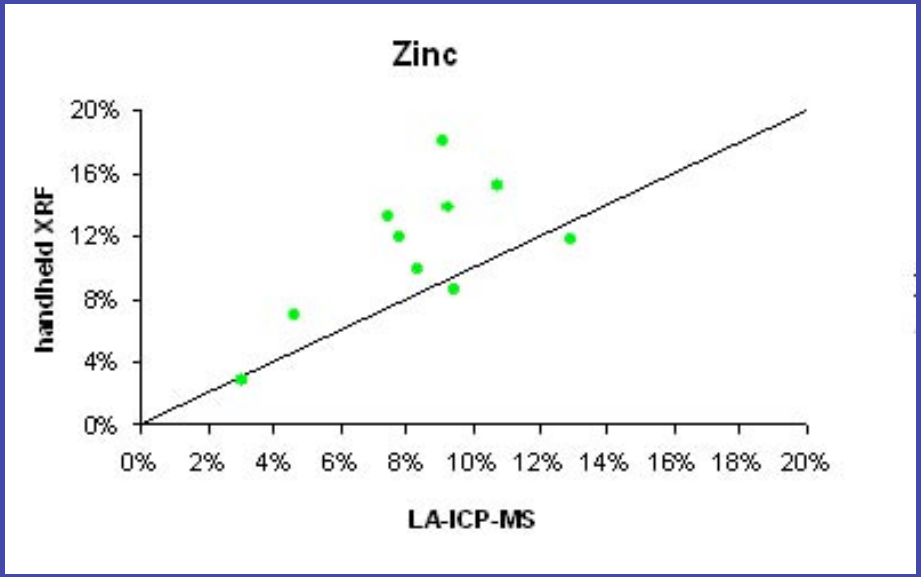






Comparison for the Tin and Zinc Concentrations between handheld XRF and LA-ICP-MS





Determination of inorganic constituents in organic materials

_ Inorganic mordants or dyes on textile

_ Lead in lichen

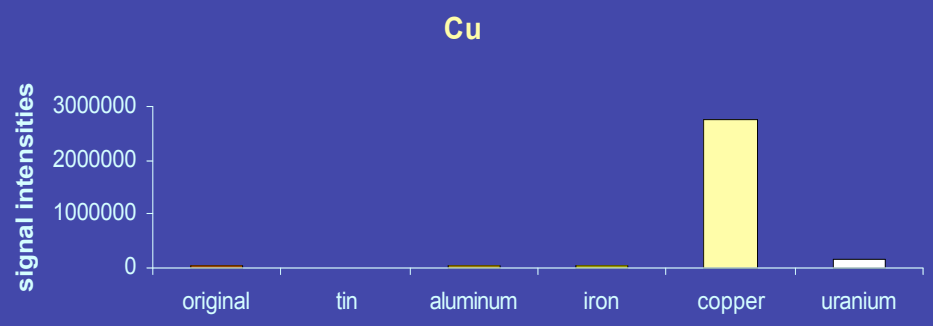
_ and also…

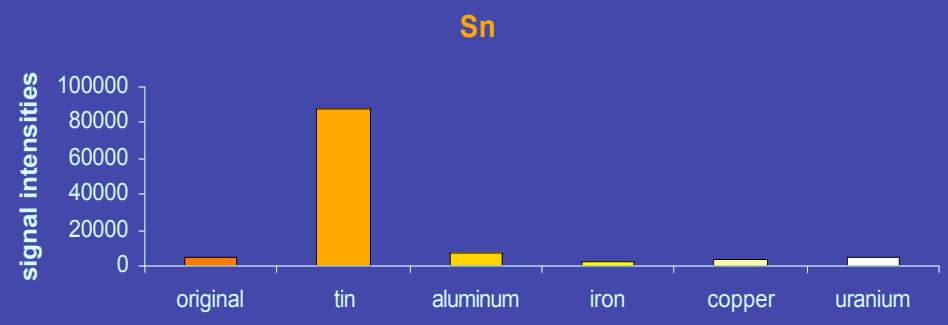
… Arsenic in bone or tanned skin

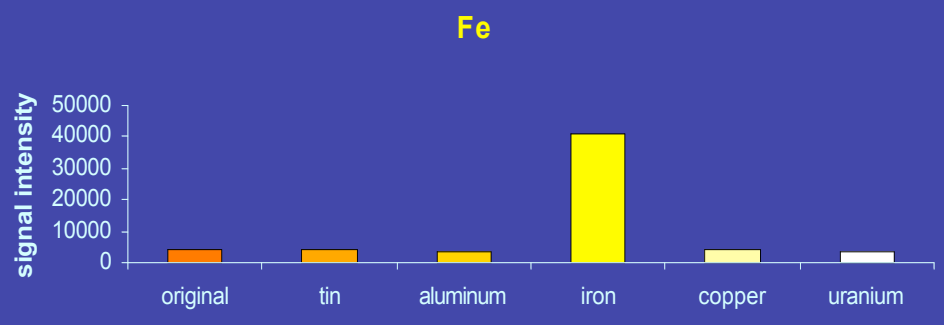
MORDANTS AND DYES ON TEXTILES

Modern and Ancient textiles (Mary Ballard, SCMRE)

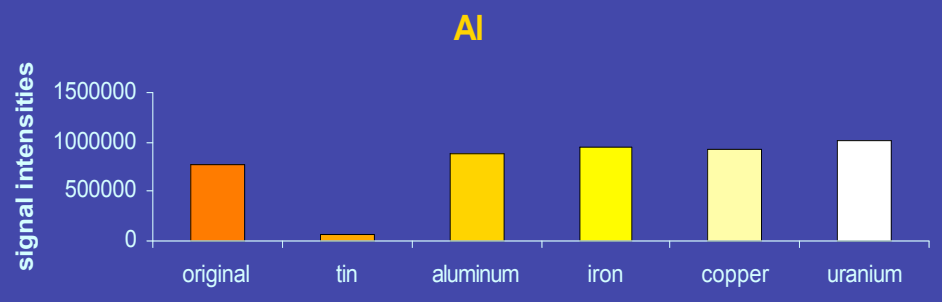
_ Testing of the feasibility of determining mordants using ICP-MS.

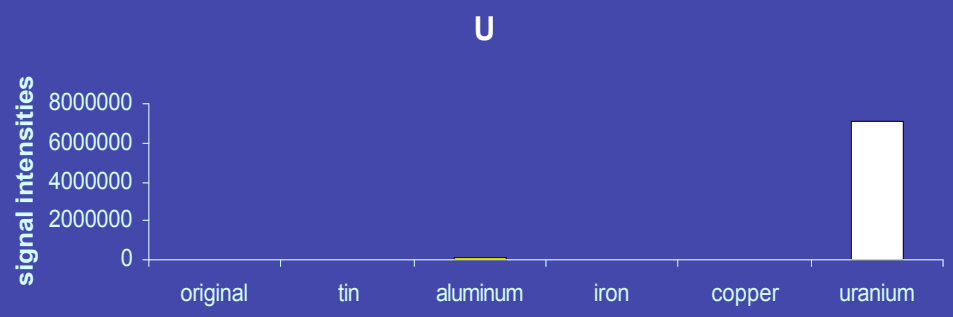

Cu
signal intensities
3000000
2000000
1000000
0
original
tin
aluminum
iron
copper
uranium


Sn
signal intensities
100000
80000
60000
40000
20000
0
original
tin
aluminum
iron
copper
uranium


Fe
signal intensity
50000
40000
30000
20000
10000
0
original
tin
aluminum
iron
copper
uranium

Original Sn Al Fe Cu U


Al
signal intensities
1500000
1000000
500000
0
original
tin
aluminum
iron
copper
uranium


U
signal intensities
8000000
6000000
4000000
2000000
0
original
tin
aluminum
iron
copper
uranium

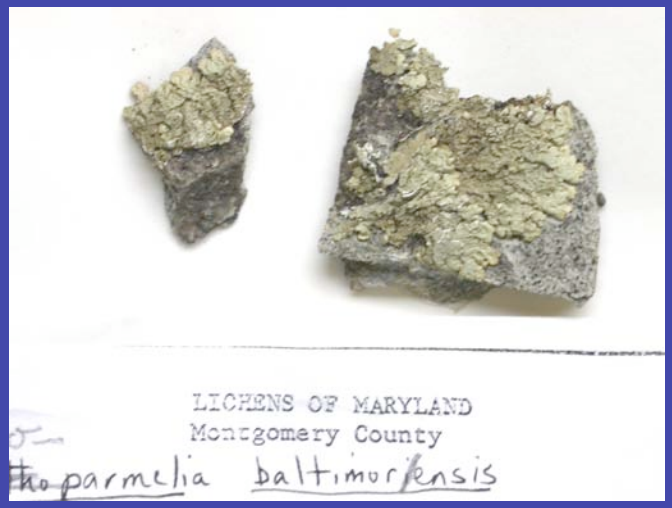
Original Sn Al Fe Cu U

LEAD IN LICHEN

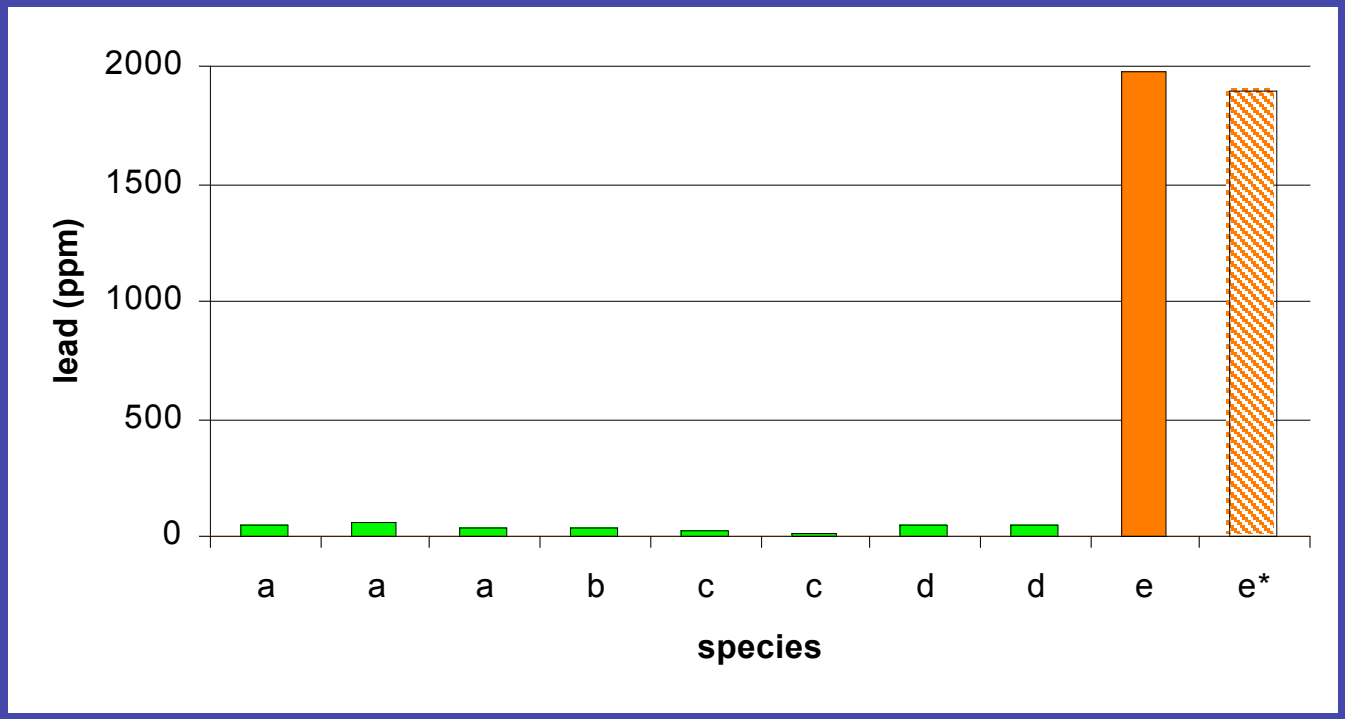
Lichens from Turkmenistan (Paula DePriest, Abdurahimova, Z., NMNH)

_ To correlate level of lead contamination with morphological changes in lichens.

_ To determine feasibility of using lichens to determine atmospheric pollution levels in Turkmenistan.



Lead Content According to the Provenance of the Lichen



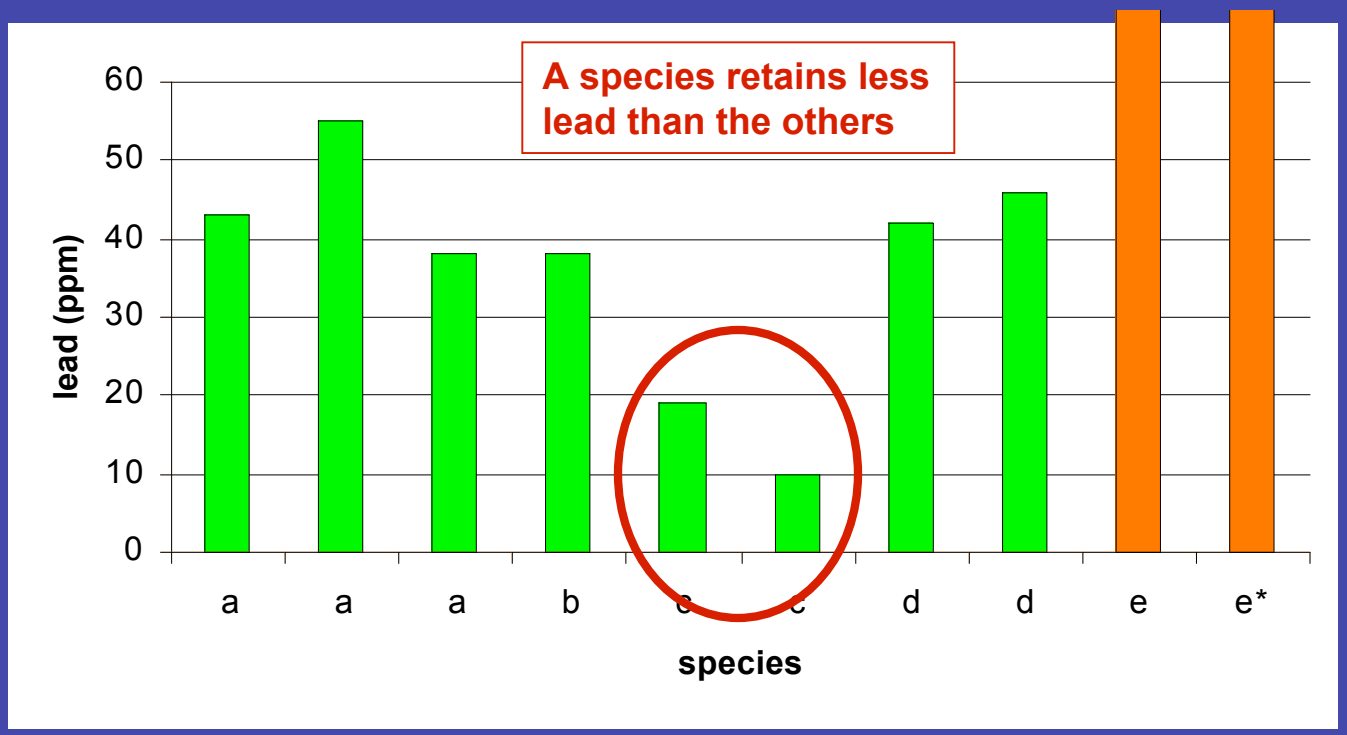
Turkmenistan

Maryland

* Lawrey and Mason, 1981

a = *Physconia pulverulenta* ; b = *Placolecanora peltata* ; c = *Dermatocarpon miniatum* ; d = *Teloschistes brevier* ; e = *Parmelia baltimorensis*

Lead Content According to the Lichen Species



Turkmenistan

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Materials that can be routinely analyzed using:

LA-ICP-MS:

Siliceous materials (glass, glaze)

Metals (gold, copper alloys)

ICP-MS:

Organic materials containing inorganic constituents

Questions that can be addressed:

Provenance studies

Trade exchanges

Technical skills

Authenticity verification

Level of contamination…..

Article:

DUSSUBIEUX, L., VAN ZELST, L., 2004, LA-ICP-MS analysis of platinum group elements and other elements of interest in ancient gold, *Applied Physics A79*, *Materials Science & Processing*, pp. 353-356.

Conferences:

DUSSUBIEUX, L., Analyses of Indonesian Glass Beads Using LA-ICP-MS, 10th International Conference of the European Association of Southeast Asian Archaeologists, London, 13-17th September 2004.

DUSSUBIEUX, L., VAN ZELST, L., LA-ICP-MS analysis of platinum group elements and other elements of interest in ancient gold, European Materials Research Society Meeting, June, 2003.

Accepted Papers:

DUSSUBIEUX, L., PINCHIN, S.E., TSANG, J-S., TUMOSA, C., Immediate on-the-spot non-destructive analysis: applications and reliability of the handheld XRF in the museum field, ICCOM-CC Triennial Meeting, The Hague, 2005.

DUSSUBIEUX, L., NAEDEL, D., CUNNINGHAM, R., ALDEN, H., BALLARD, M., Accuracy, precision, and investigation: mordant analysis on antique textiles by various methods, ICCOM-CC Triennial Meeting, The Hague, 2005.

DUSSUBIEUX, L., NAEDEL, D., CUNNINGHAM, R., ALDEN, H., BALLARD, M., Using ICP-MS to detect inorganic elements in organic materials: a new tool to identify mordants or dyes on ancient textiles, Materials Research Society Fall Meeting, Boston, MA.,December, 2004.

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At the Bead Museum, Washington, DC: Said, T., Director.

I surely forget somebody. Please accept my apologizes!