The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
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IAEA
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2272-4

Joint ICTP-IAEA School on Synchrotron Applications in Cultural Heritage and Environmental Sciences and Multidisciplinary Aspects of Imaging Techniques

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Radiation for Cultural Heritage

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Radiation for Cultural Heritage

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Outline

- Scientific methods: Aims of investigations, Probes and techniques
- Comparison of different radiation probes
- X-rays: Portable spectrometers, Laboratory-SR facility
- Charged particle beams
- Neutron beams
- Imaging with UV-Vis-IR radiation
- Laser based techniques
- Dating TL-OSL

Scientific methods in Art and Archaeology

Objectives of the scientific examination

- Identification of chemical / biological constituents
- Structural characterization
- Provenance and dating. Authentication
- Manufacture Technology (metallurgy, pottery, coloring)
- Dietary habits (Human, Animal remains)
- Environmental degradation. Conservation

Scientific methods in CH: Challenges-Requirements

- **Diversity** of materials nature: - Organic, inorganic, biological materials
- **Elemental** /**Molecular** analysis /**Structural** information
- Analysis at different scales from **sub- m** particles to **cm**-size size samples
- **Quant**itative/**semi-Q** analysis/ **Quali**tative information
- Material **interactions** for environmental impact
- Optimum analytical **range-sensitivity**
- **<u>In-situ analysis</u>**
- **<u>Non-destructive or even non -invasive analysis!</u>**

Radiation Probes in Art and Archaeology

- **X-rays**

  - X-ray Tubes –unpolarized/polychromatic

  - Synchrotron radiation polarized/tunable monoenergetic

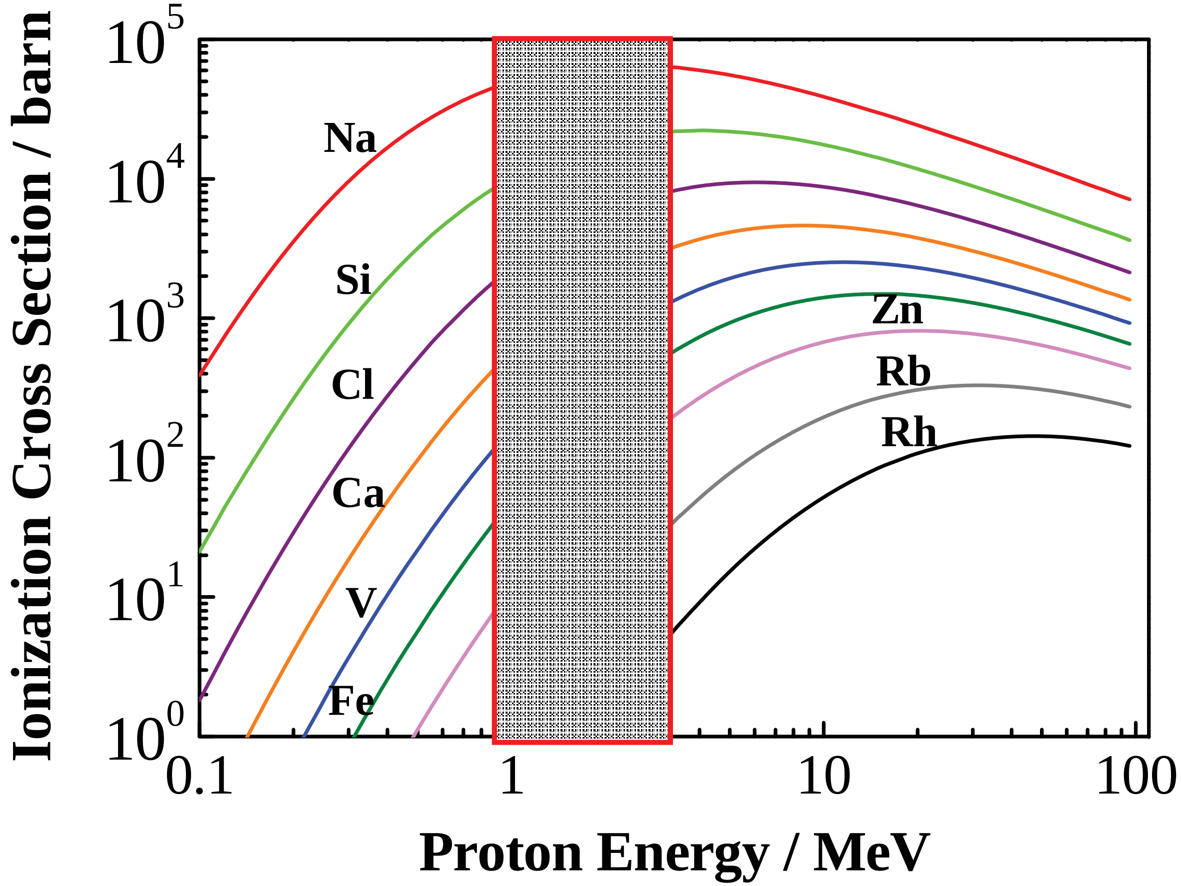
  Depth: sub-micron to mm, spot size cm to few tens of nm

- **UV, Vis-IR radiation (conventional, SR- sources)**
- **Laser Induced Techniques** (LIF, Raman, LIBS)
- **Neutrons** : Thermalized/ Fast neutrons (cm- scale)
- **Charged particle beams**

  Depth: sub-micron to mm, spot size mm to micron level

Comparison of radiation Probes: Protons (1)

Ionization cross sections

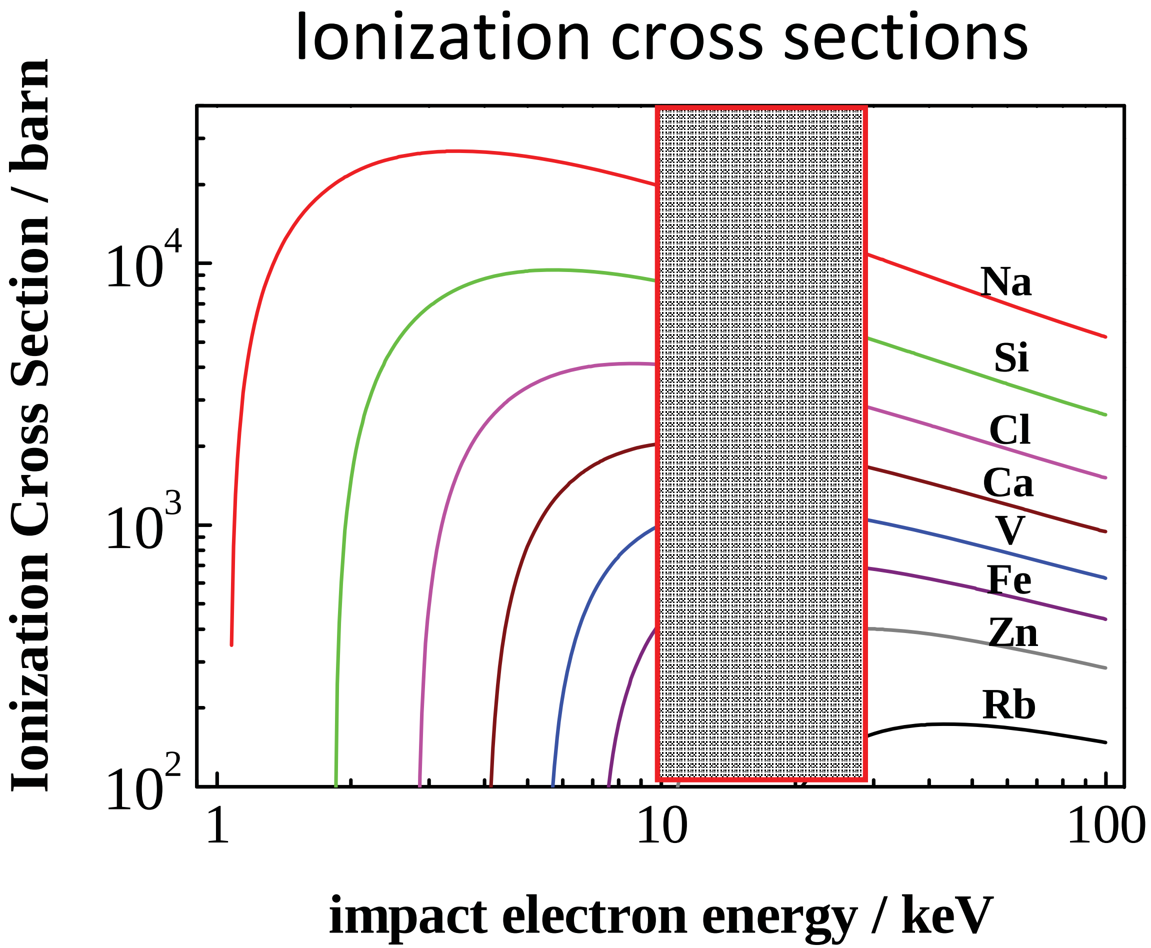


Protons

10-10^5 barns

Protons ICS through ECPSSR theory W. Brandt, G. Lapicki, *Phys. Rev. A* 23 (1981) 1717

Comparison of radiation Probes: Electrons (2)

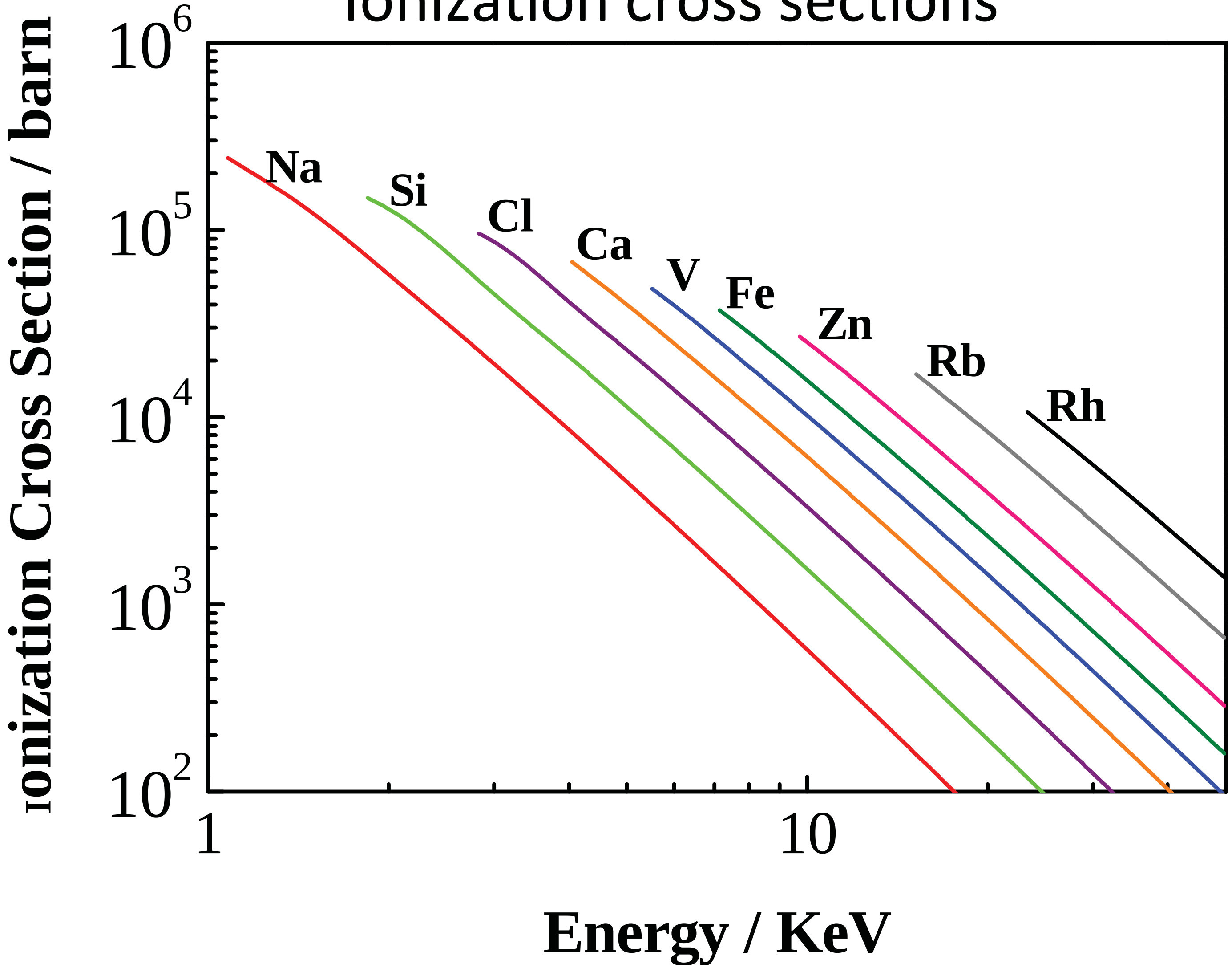


Electrons
10^2-10^4 barns

Electrons ICS through Casnati, E *et. al*, *J Phys B At Mol Phys* **15**, 155–167.

Comparison of radiation Probes: X-rays (3)

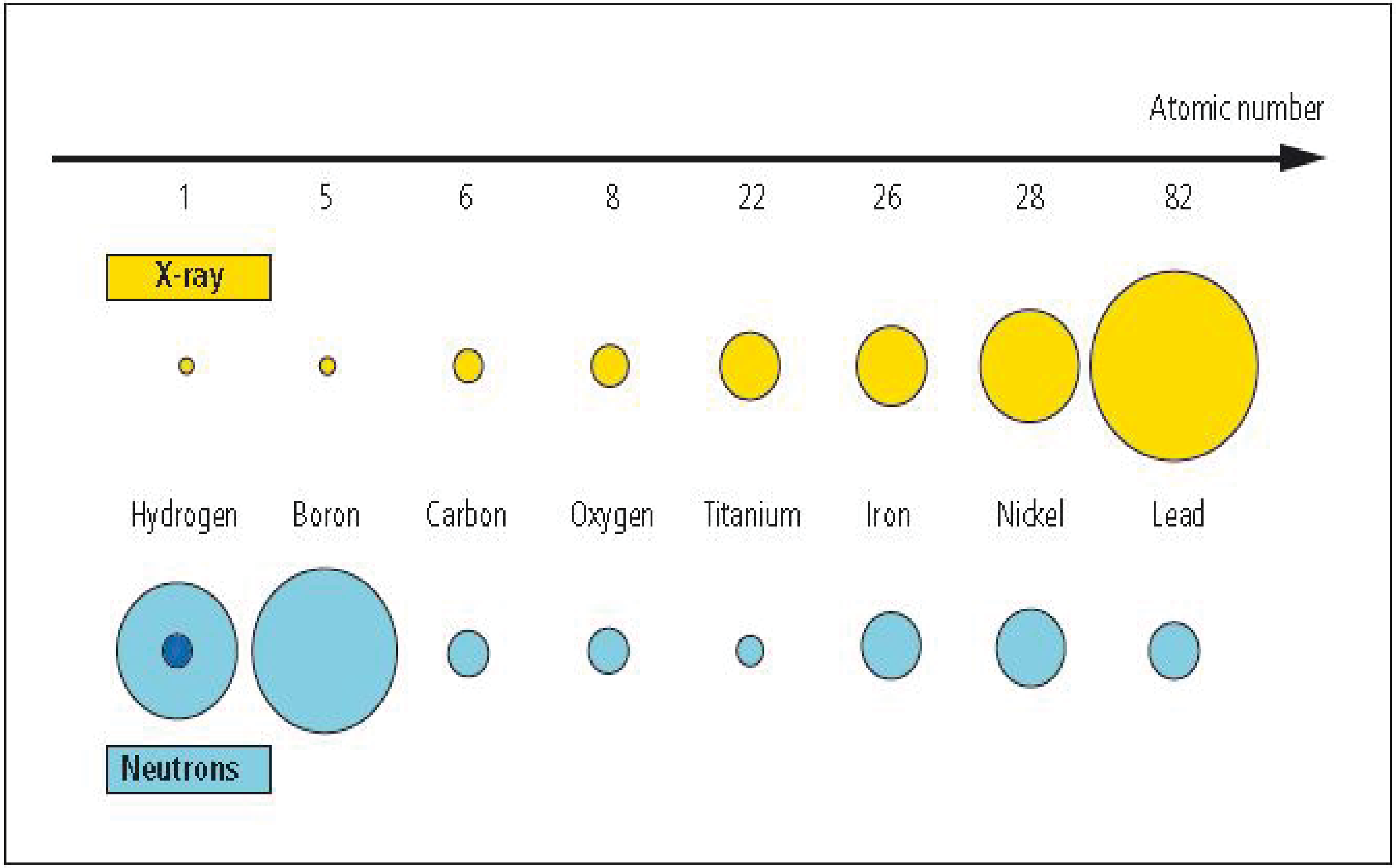
Ionization cross sections



X-rays 10^4-10^5 barns

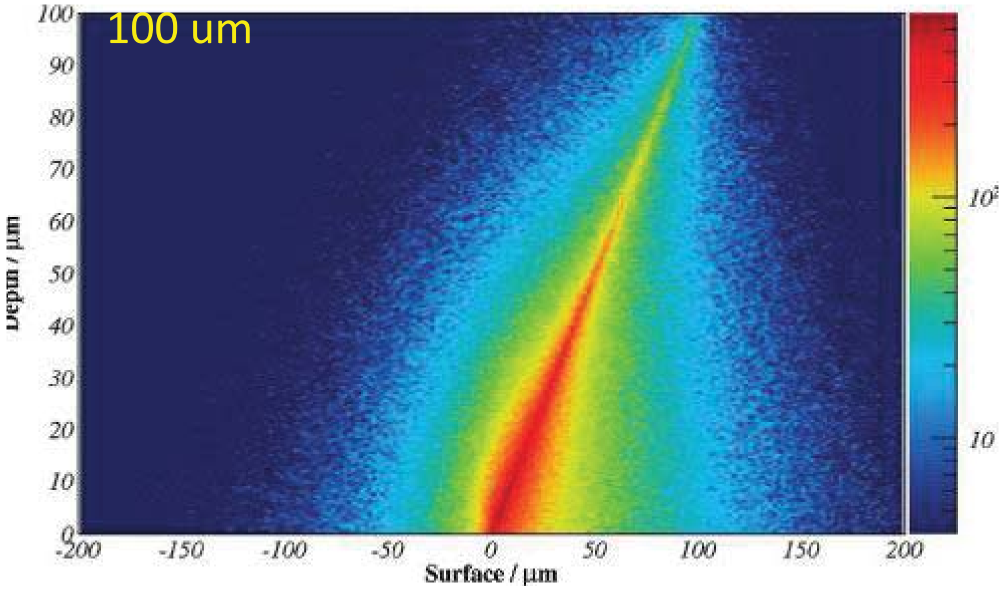
Photon ICS from "Elam database" Elam W.T. et al., *Radiat. Phys. Chem, 63,* (2002), 121

Thermal Neutrons cross sections



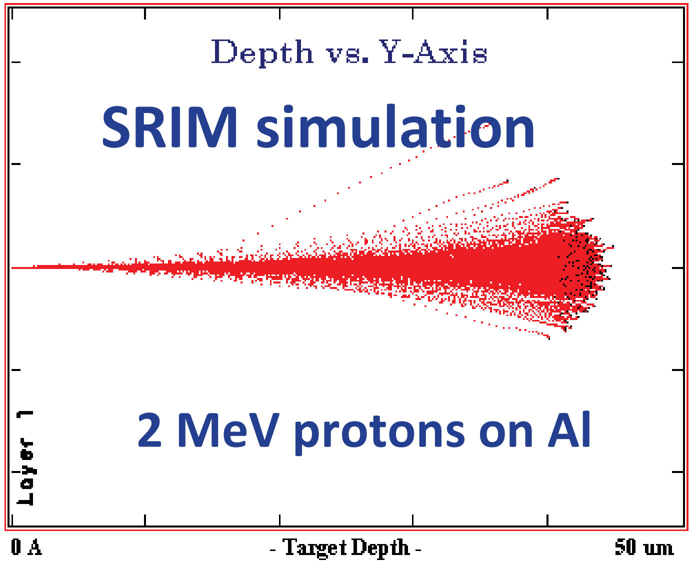
Source: Paul Scherrer Institut, PSI, Switzerland

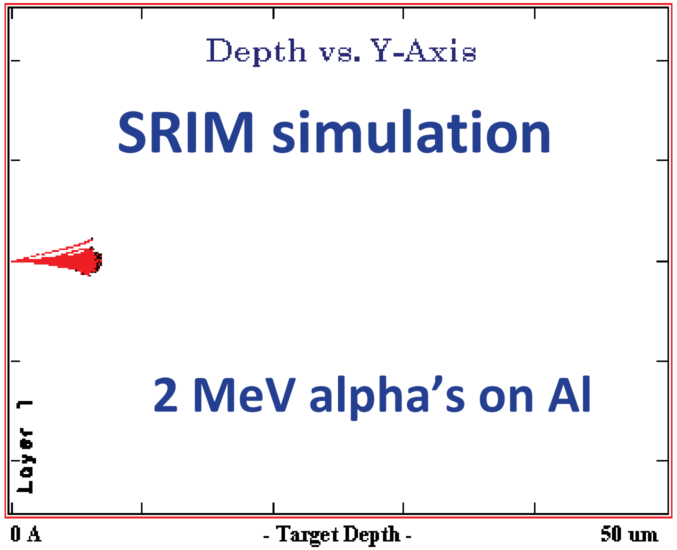
Information depths by radiation probes: Examples:



13 keV, excitation,
SiO_2 matrix, 5% Cu, 5% Fe
Topology of secondary fluorescence of Fe-K radiation

Sokaras et al, Anal. Chem. **2009,** *81,* 4946





50 m

Analytical Techniques in Art and Archaeology

- **Elemental/Isotopic analysis**

  Sy Micro X-ray Fluorescence analysis (Sy-XRF), Portable XRF

  SEM-EDX, Ion Beam Analysis (IBA): PIXE, RBS, PIGE

  Laser Induced Breakdown Spectroscopy (LIBS)

  Neutron Activation Analysis (NAA, isotope selective)

- **Structural Information**

  Molecular analysis (Raman, FTIR)

  Mineralogical/Crystalline phase analysis (TOF-ND, XRD)

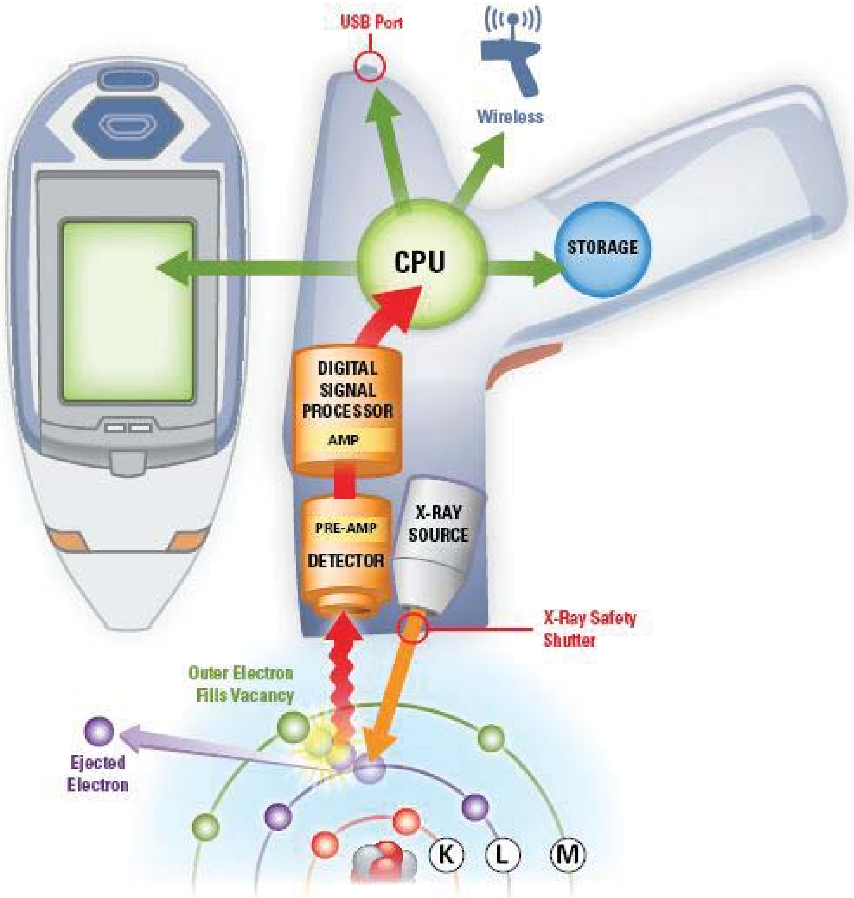
  Oxidation state, chemical environment, Coordination site: XANES - EXAFS

- **Imaging** X-ray and Neutron imaging, UV-Vis-IR

X-Ray Fluorescence Analysis - XRF

- Typically, from Z=11 or Z=12 upward.
- Sensitivity within the few ppm range (conventional x-ray sources, best excited elements) or few tens of ppb for synchrotron exciting radiation
- Spatial resolution from mm range down to few micrometers
- Portability, Handheld autonomous operation
- Quantitative information for materials presenting good preservation state
- Poor depth resolution: Confocal micro-XRF, micro-PIXE analysis

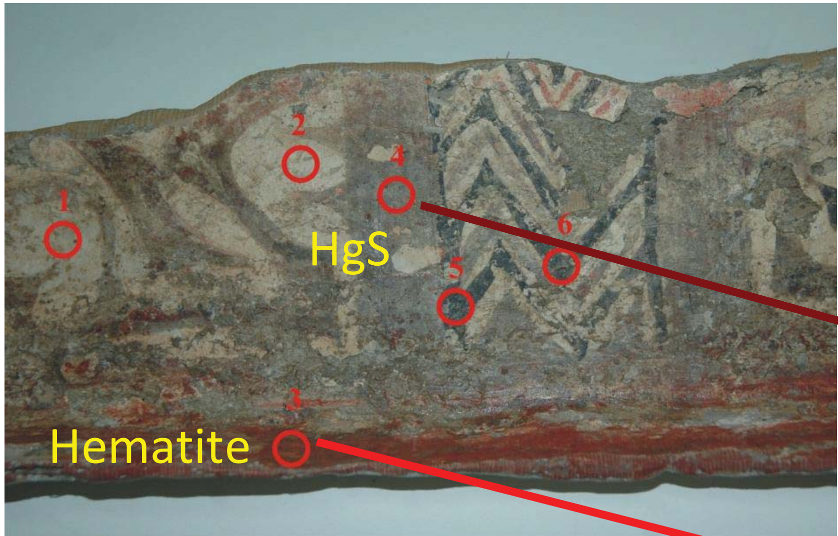
New Developments in XRF: Hand-held analyzer

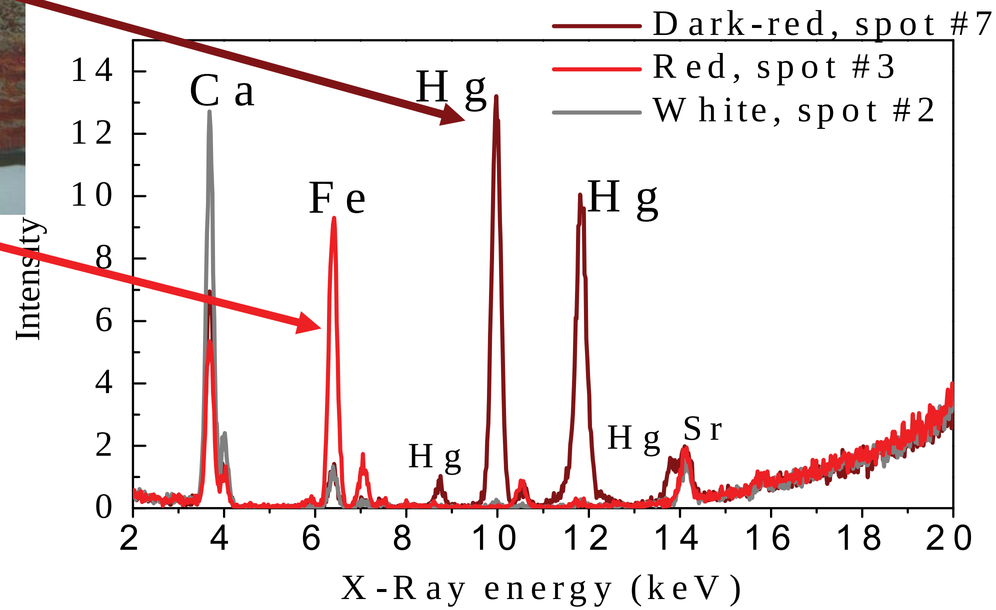


Ankara, Anatolian Civilization Museum, 2007

ÇATALHÖYÜK 7000-8000 B.C. Wall-Painting pigments

✓Dark Red
✓Red
✓White
✓Black

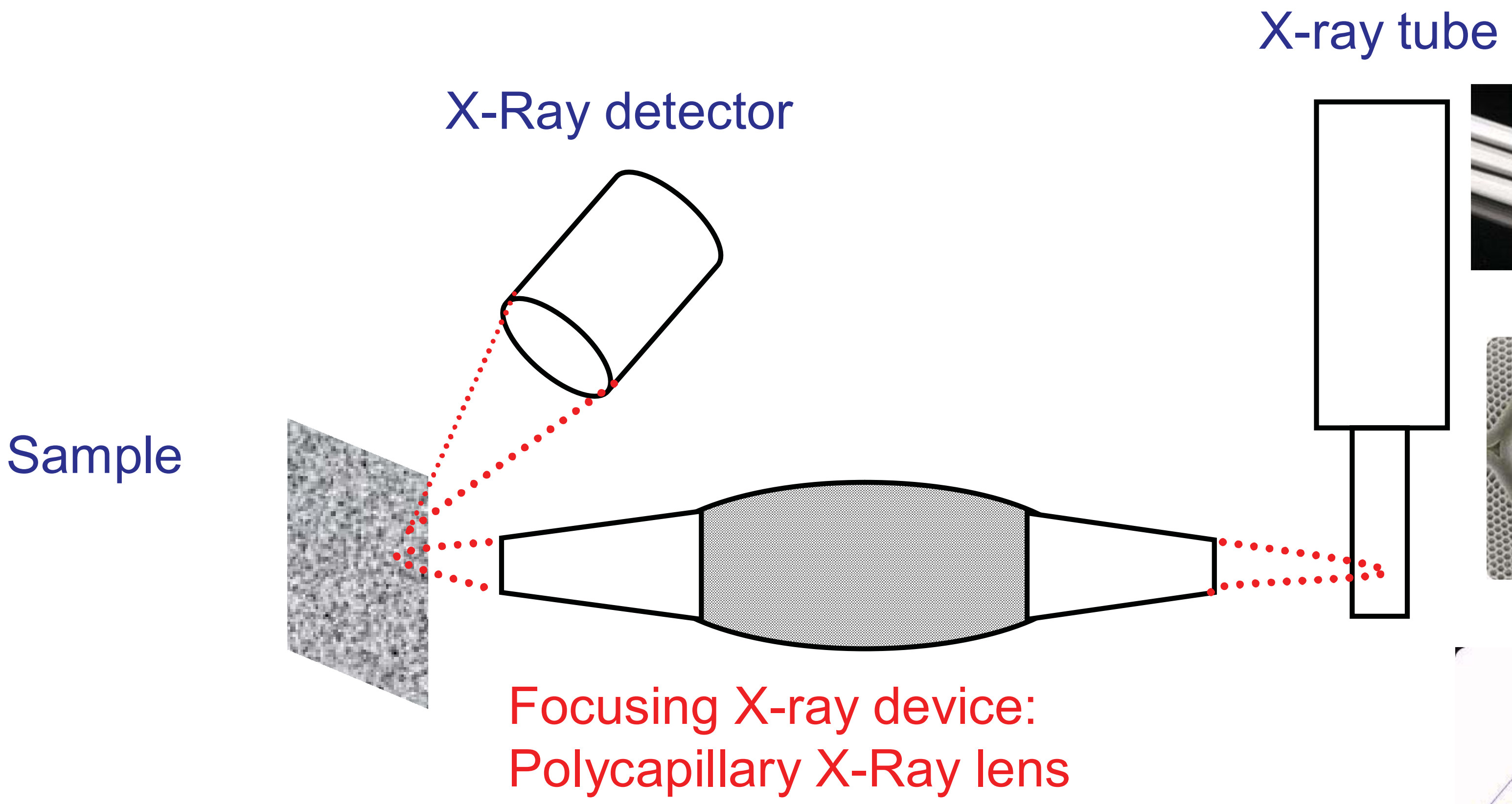


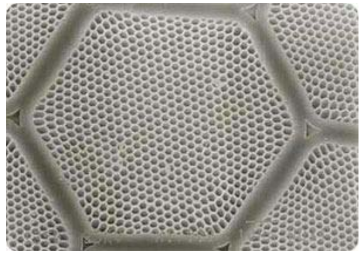


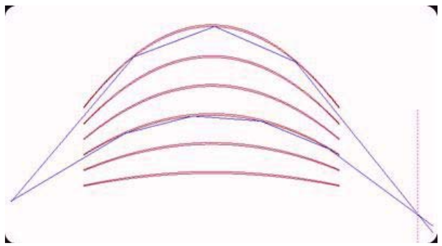
Hand-held XRF analysis, A. Zararsiz et *al*. 2008

Developments in Micro-XRF spectroscopy

X-ray lenses

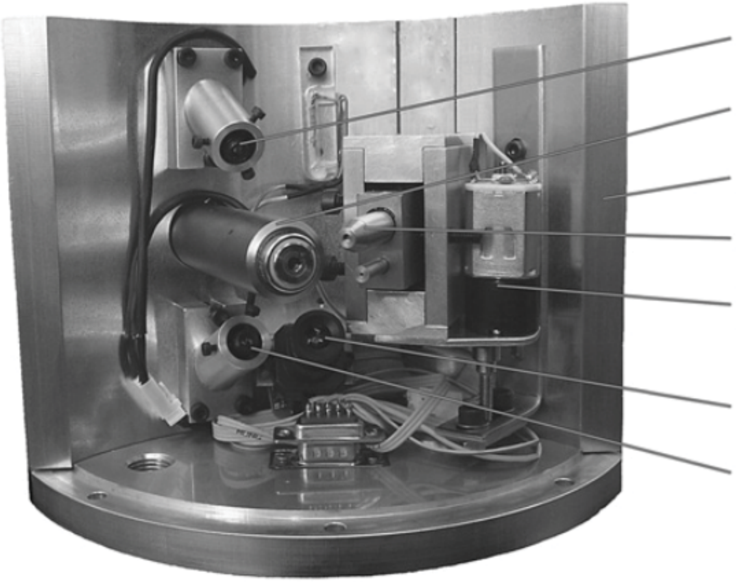


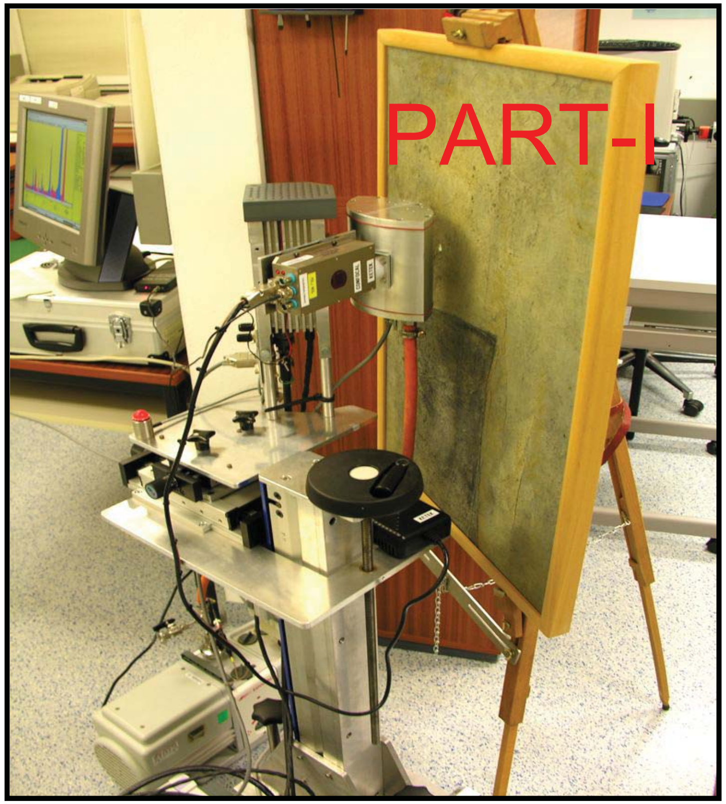




The Portable IAEA XRF prototype

- ✓ Pd-anode X-ray tube (50W)
- ✓ Pollycapillary lens
- ✓ silicon drift detector
- ✓ 2 laser pointers
- ✓ CMOS camera with
- ✓ Mechanical positioning system

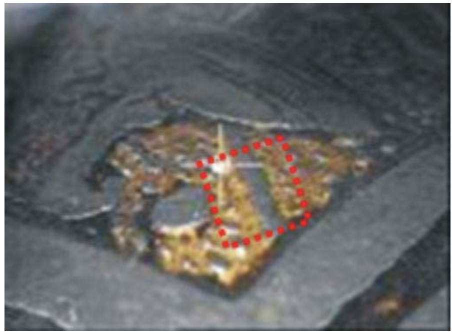




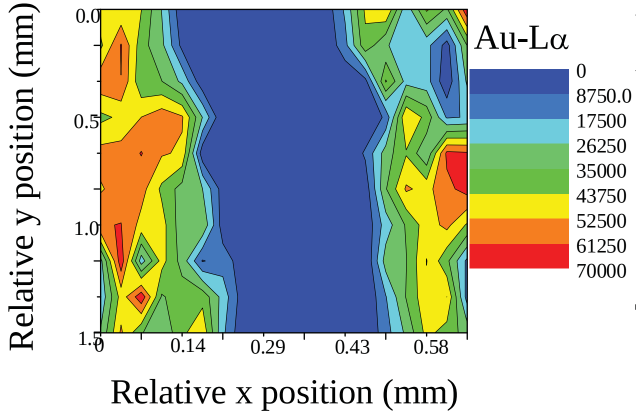
Buzanich et al, SAB 62 (2007) 1252
Uhlir et al, XRS, 37 (2008) 450

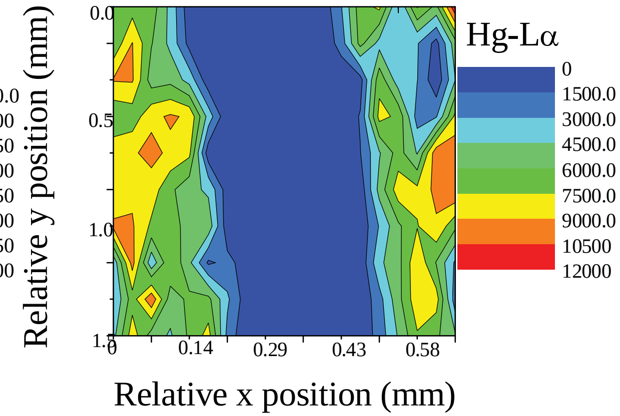
Analytical possibilities: Gilding technique

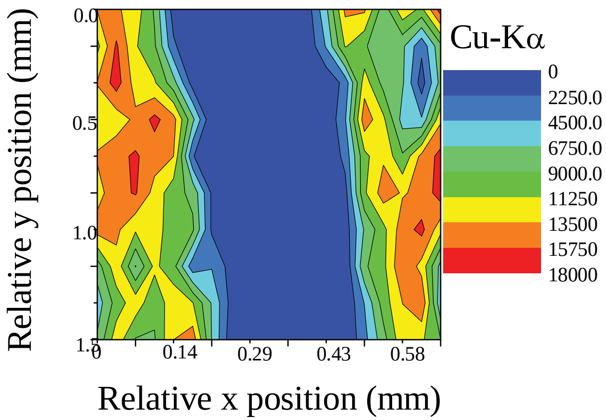
Palace Armoury, Malta

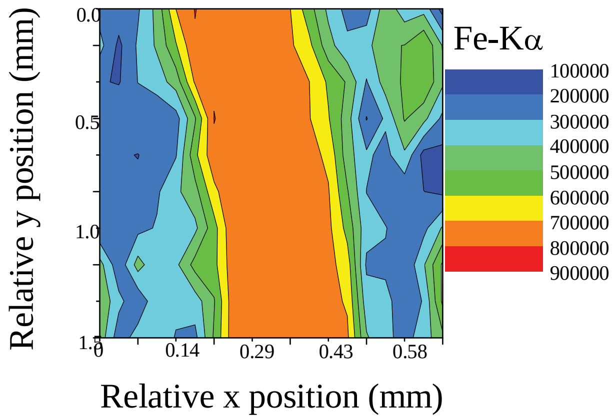


Area scanned:1.9×1.0mm²
Step size used: 0.1mm
Time per step: 20 s.









A.G. Karydas, D. Anglos and M.A. Harith, In Metals and Museums in the Mediterranean: Protecting, Preserving and Interpreting, ed. Argyropoulos, (2008) 141-177

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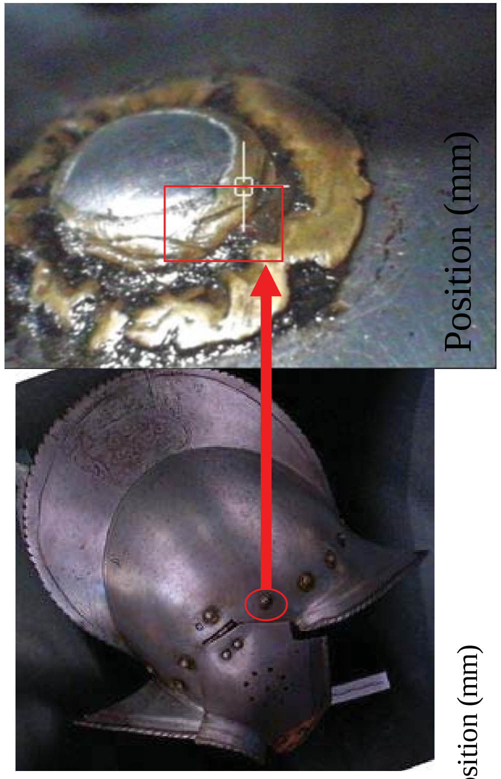
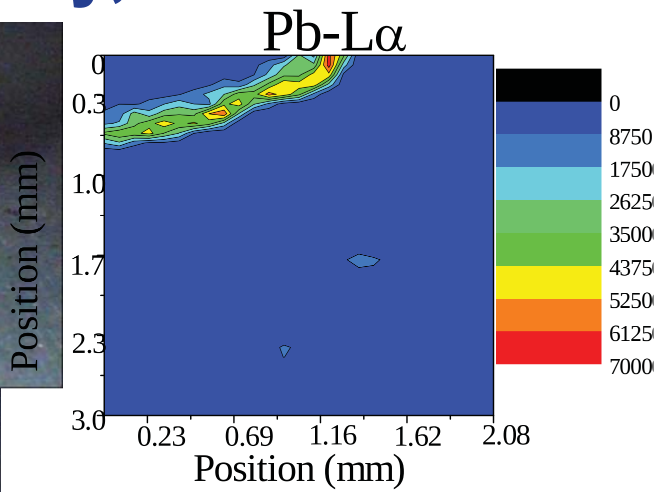
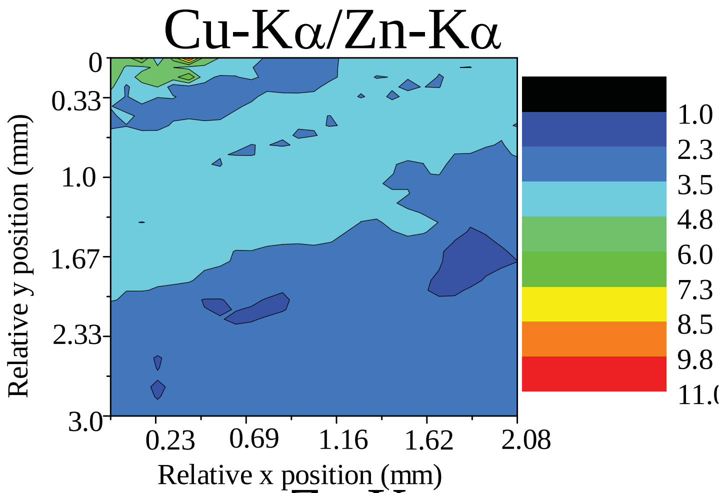
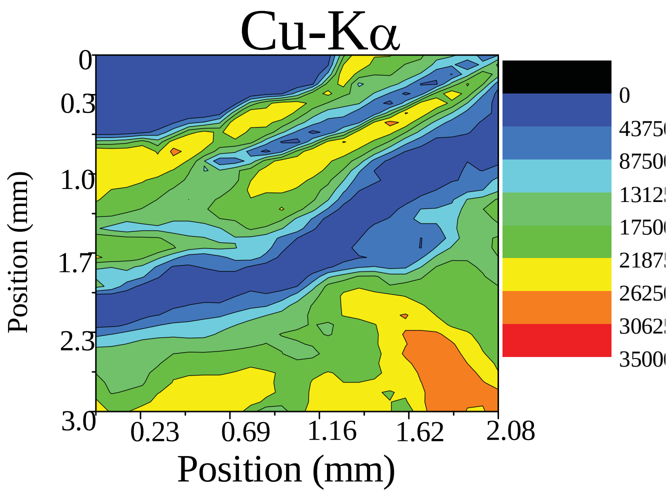
Alteration of brass rivets plating

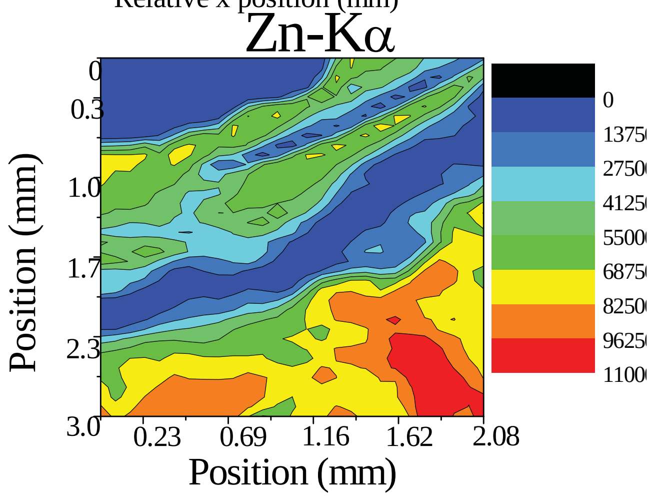
Palace Armoury, Malta











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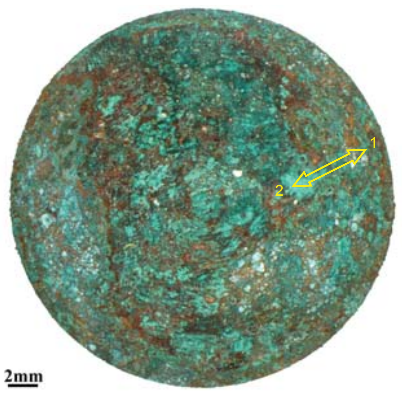
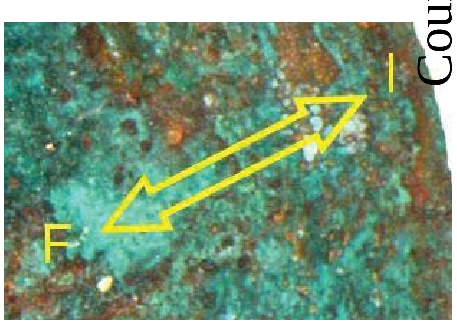
A.G. Karydas, ICTP-IAEA SR-CH school, 21-11-2011

Analysis of copper coupon corrosion products

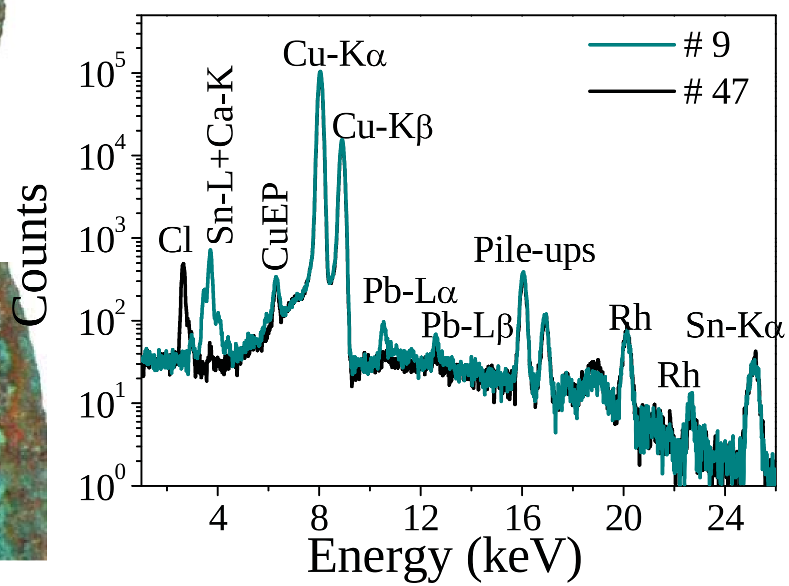
Artificially and naturally aged bronze coupon: **(Cu: 91.3%, Sn: 7.5%, Pb: 1.0%)**

#9 : green area
#47: pale green area

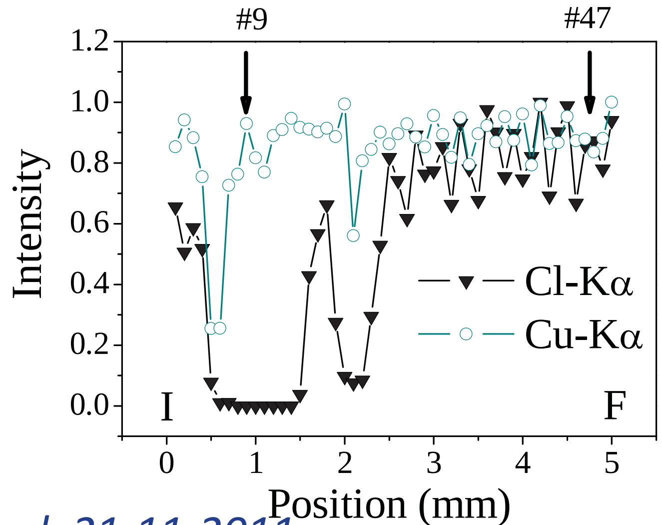




50kV, 600μA,
30s/step,0.1mm/step,
50 measurements



A.G. Karydas, D. Anglos and M.A. Harith, In Metals and Museums in the Mediterranean: Protecting, Preserving and Interpreting, ed. Argyropoulos, (2008) 141-177



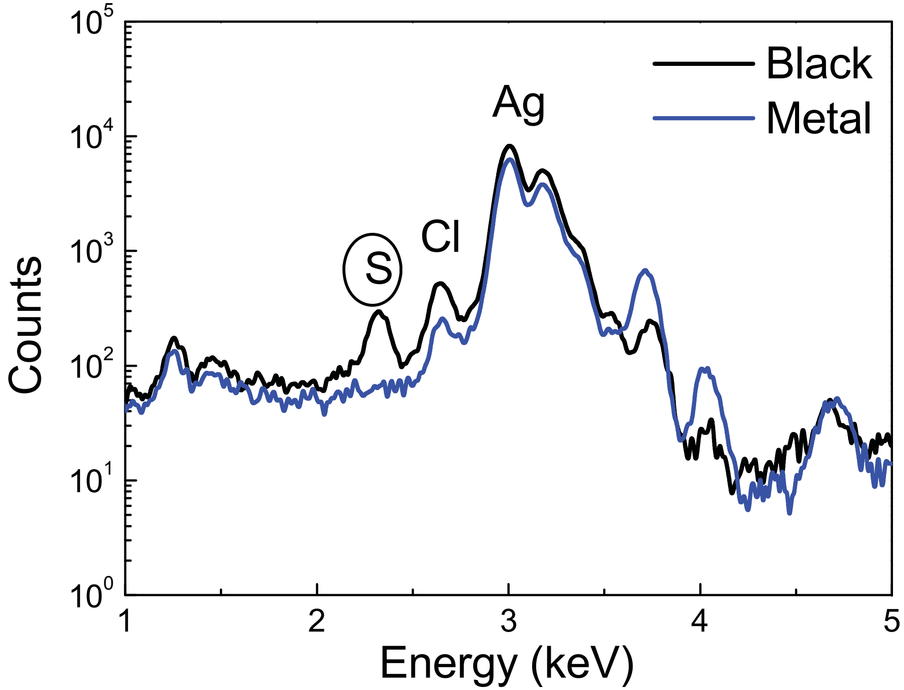
Monitoring of tarnishing layer

Damascus Archaeological museum

Silver Bowl 1400 -1300 BC   Late Bronze Age

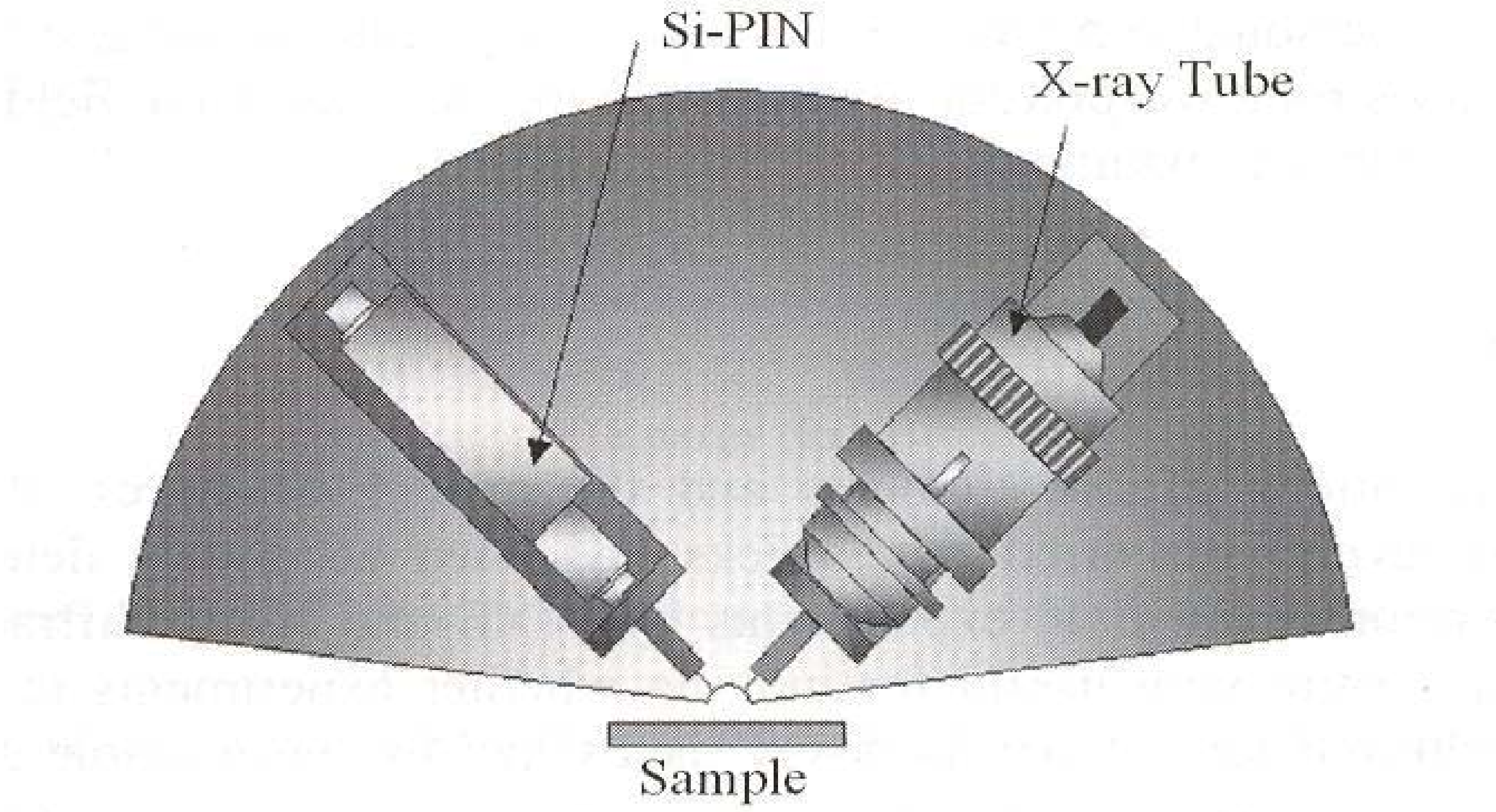
Thickness of the layer: ~ 0.5 μm

Detection limit: 20 nm



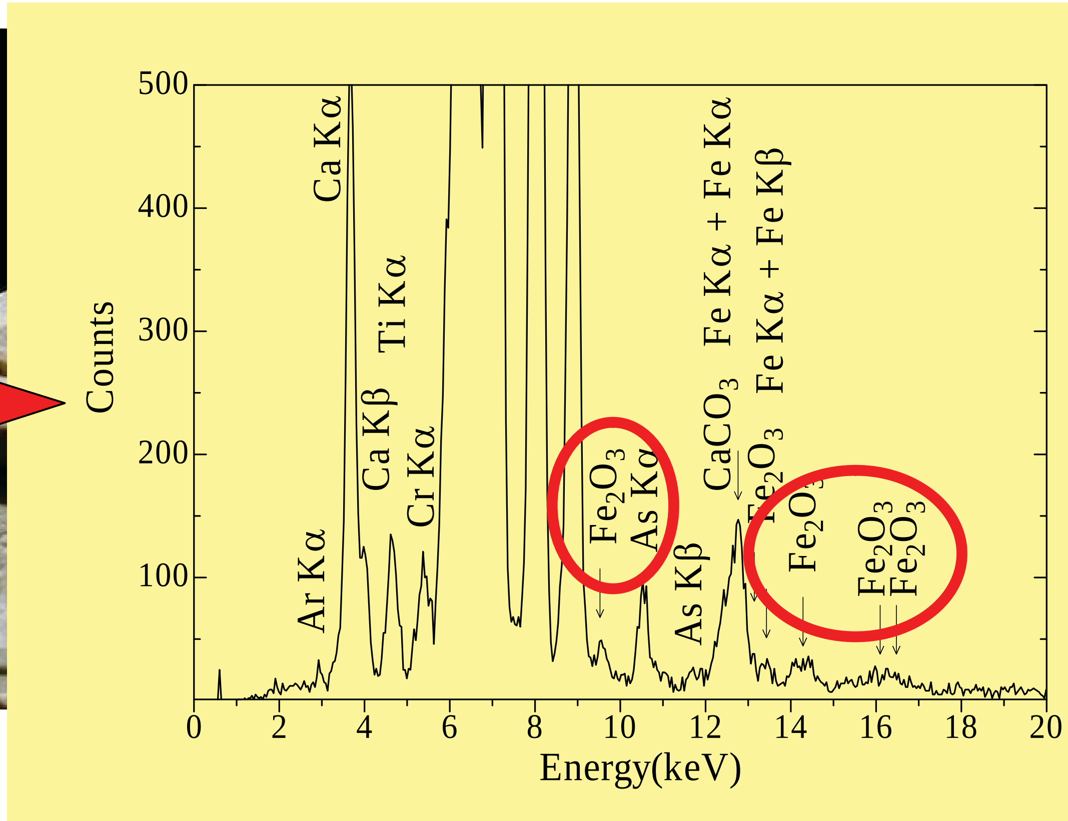
Tarnish: corrosion mainly caused by the sulfur in the air

Combined XRF-XRD Analysis

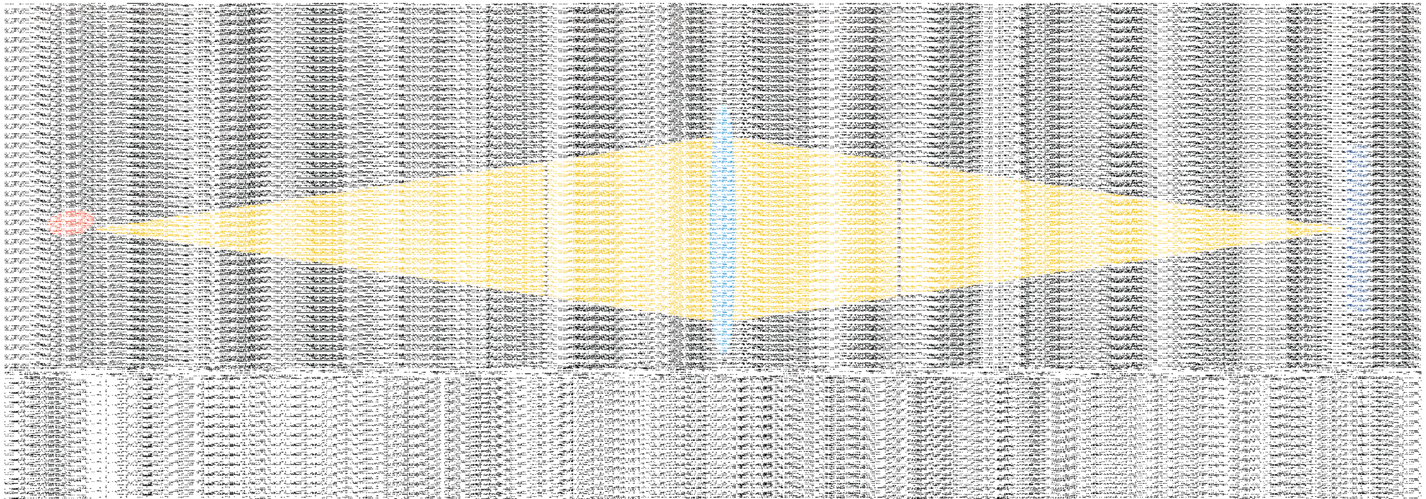


M. Uda, X-rays for Archaeology, 2005

XRF-XRD, Pigments on Macedonia stele



Synchrotron radiation features/techniques



- High brilliance
- Wide spectral range, IR- hard X-ray energy region
- Wavelength/energy tunability
- High degree and selection of polarization
- Well-defined time-space structure and coherence

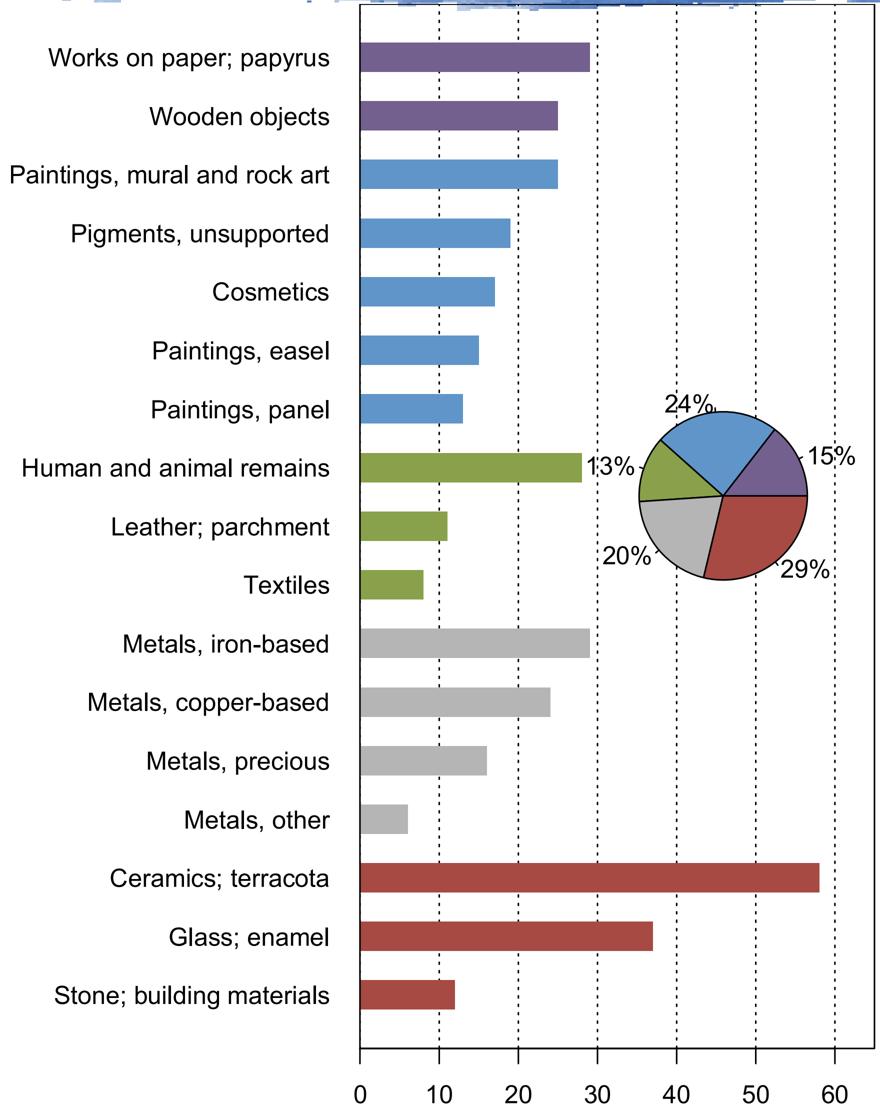
Advantages of SR techniques

- Low destructiveness allowing protocols involving complementary characterization
- Integrated analytical information (from the atomic to the structural levels), due to the synergistic application of different techniques on the same experimental set-up
- Rapid analysis on a limited quantity of matter;
- The high spatial resolution offered by the beam spot size, in particular for micro-imaging, which allows a selective analysis;
- Some methods are non-invasive and allow for internal inspection of entire objects (hard X-ray, THz);
- The capability to perform real-time in-situ analyses.

Limitations of SR techniques

- Objects and people need to be transferred;
- Most techniques are invasive (sampling required);
- There is a limited access to beam time, and skills in getting beam time may not always be accessible to new users;
- Communication and knowledge transfer between physical scientists and specialists in the fields of Cultural Heritage, Archaeology and Forensics

CH materials studied by SR techniques.



Data by L. Bertrand, SOLEIL

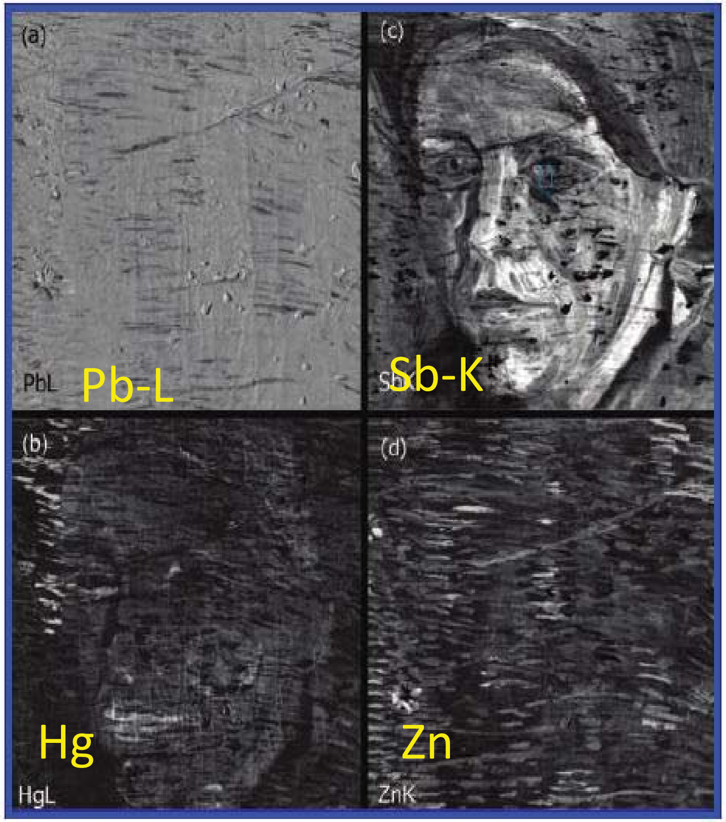
Applications in CH of SR technqiues

- Provenance
- Ancient technology
- Visualization of hidden/vanished art and historical documents,
- Study of degradation phenomena and products
- Evaluation, monitoring, optimization of consolidation, stabilization and conservation procedures

Examples : Elemental mapping by Micro-XRF

DORIS at DESY:

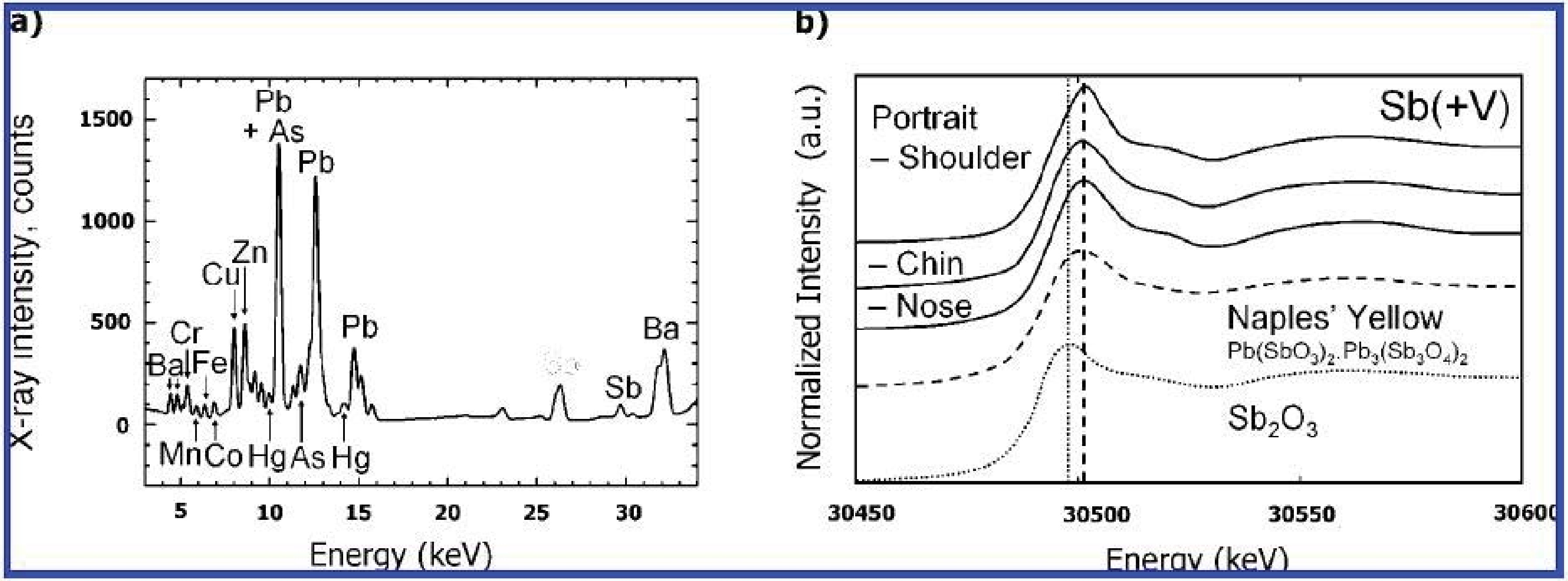
38.5 keV, 0.5x0.5 mm^{2,} 2s, 17.5x17.5 cm^2



Dik et *al*., Anal. Chem., **2008**, 80 (16)

Vincent van Gogh, *Patch of Grass*, Paris, Apr-June 1887, oil on canvas, 30 cm × 40 cm, Kro¨ ller-Mu¨ ller Museum, Otterlo, The Netherlands

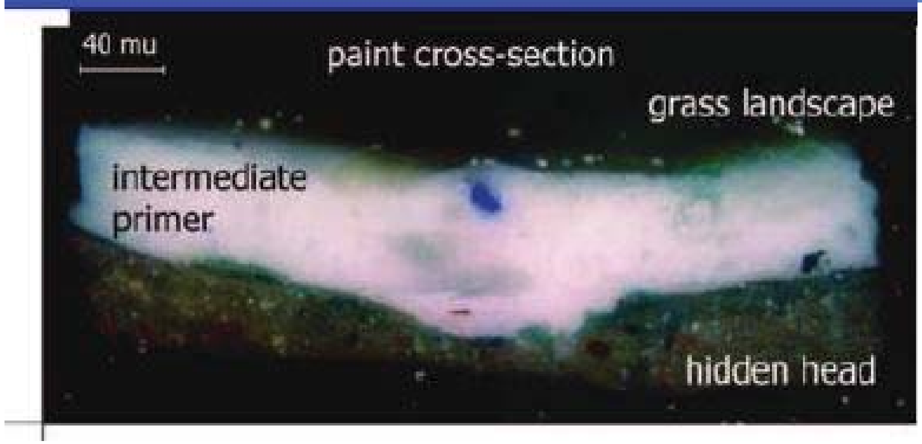
XANES: Identification of chemical compound



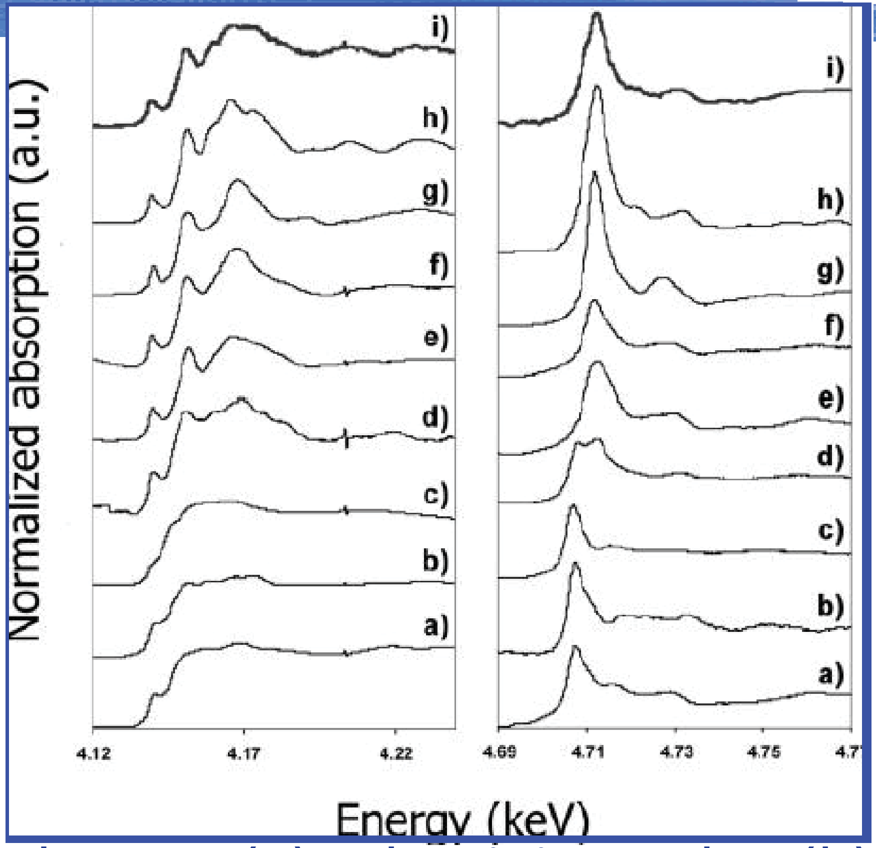
Comparison of Sb K- edge XANES spectra from three positions on the painting to reference XANES spectra of Naples yellow [$Pb(SbO_3)2 \cdot Pb_3(Sb_3O_4)2$] and antimony white ($Sb_2O3$). All spectra were recorded in the **fluorescent mode**.

Dik et *al*., Anal. Chem., **2008**, 80 (16)

XANES: Identification of chemical compound



XANES spectra at the Sb-LIII edge and at the Sb-LI edge).



Reference antimony compounds: Sb_2O_3 as (a) valentinite and as (b) senarmontite; (c) Sb_2S_2O, kermesite; (d) Sb_2O_4; (e) Sb_3O_6OH, stibiconite; (f) $KSbO_3 \cdot 3H_2O$; (g) $NaSbO_3OH \cdot 3H_2O$; (h) Naples yellow; and (i) Sb pigment in the cross section of the Van Gogh painting

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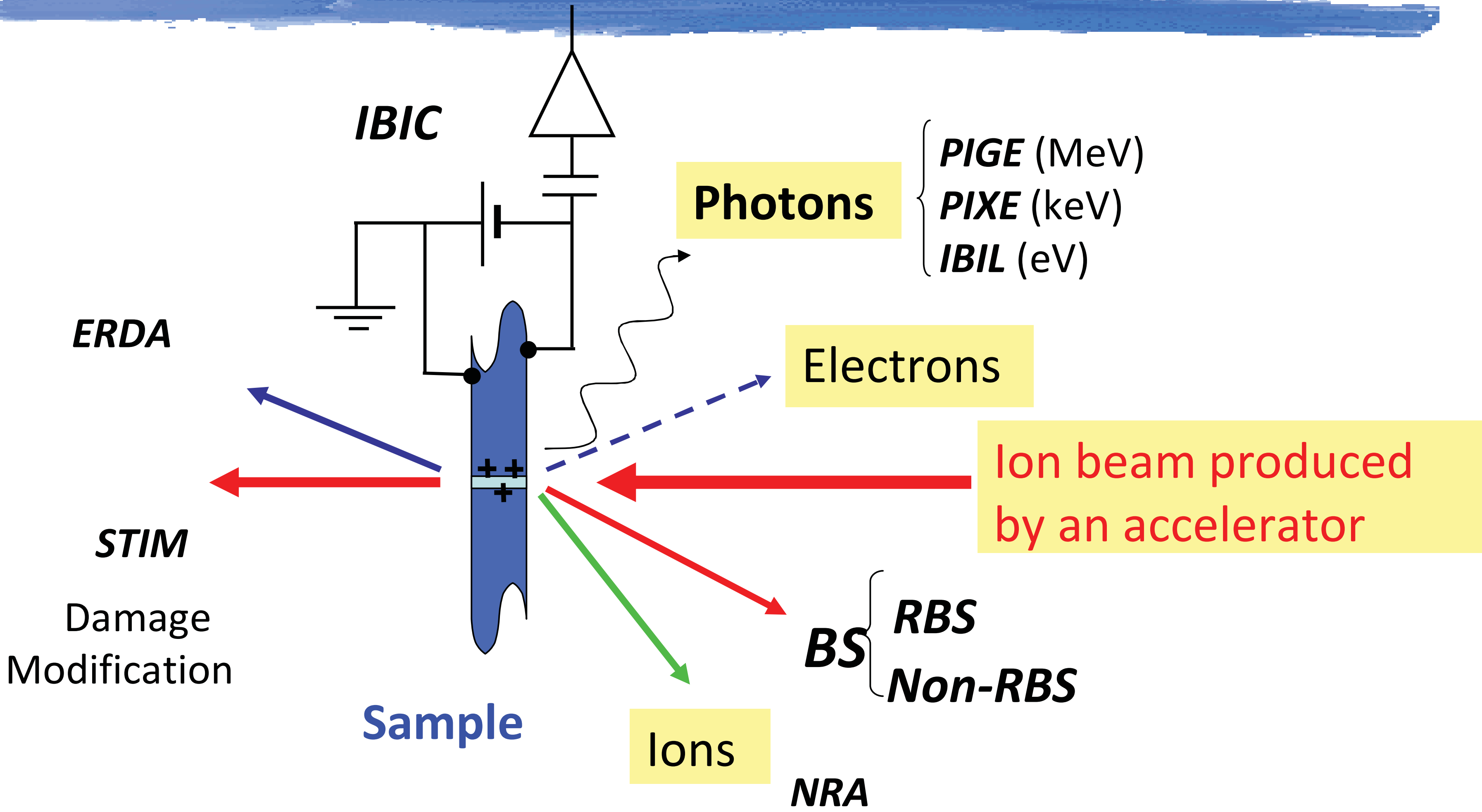
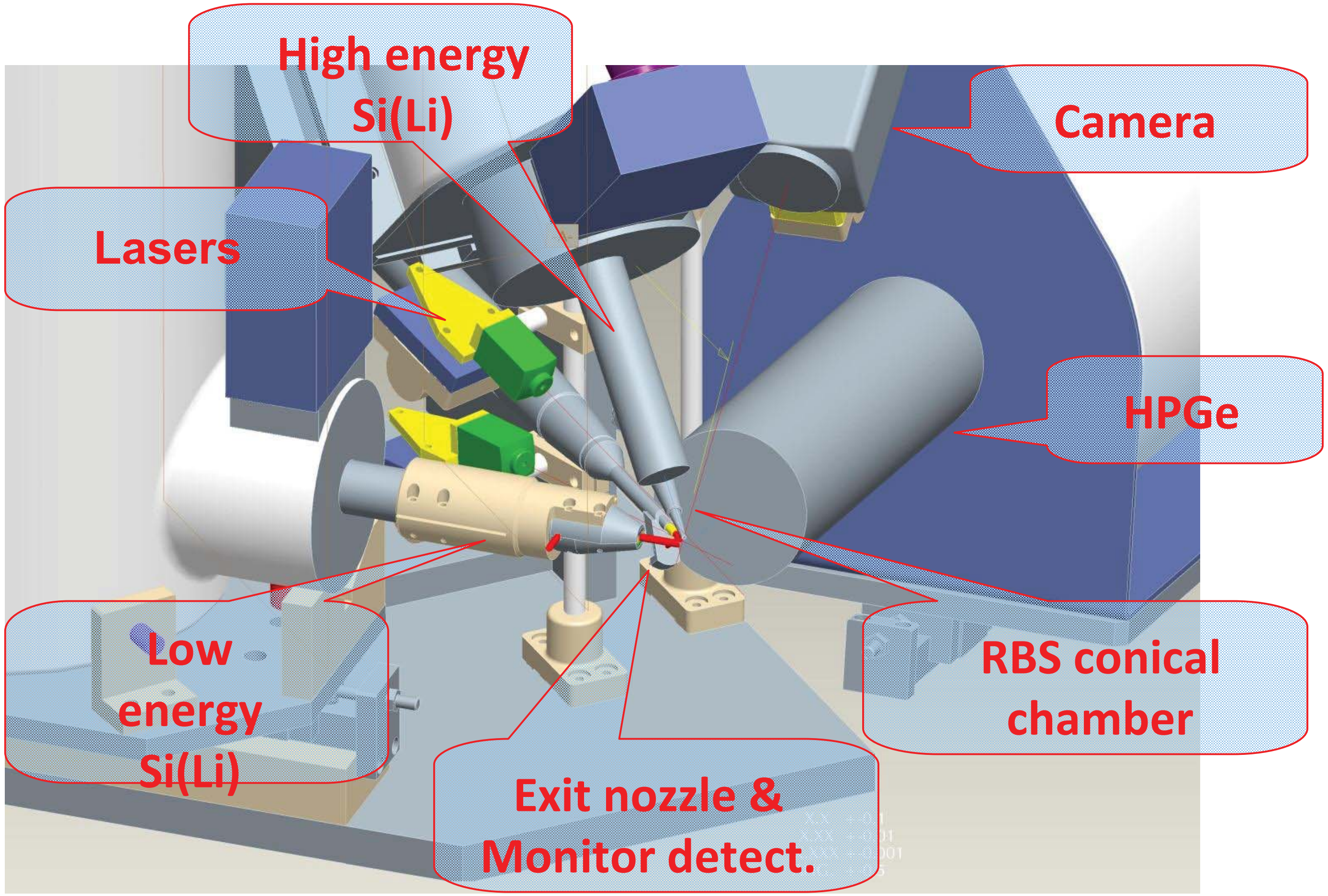
Ion Beam Analysis



MeV ion beam based techniques constitute a powerful tool for the quantitative determination of the composition and structure of matter

External Ion-Beam Analysis set-up



Sokaras et *al*, NIM B, 2011 NCSR "Demokritos", Athens

External Ion-Beam Analysis Set-up

Gkikas, 1921-1922, oil-painting

Synergy of Ion Beam Analysis Techniques

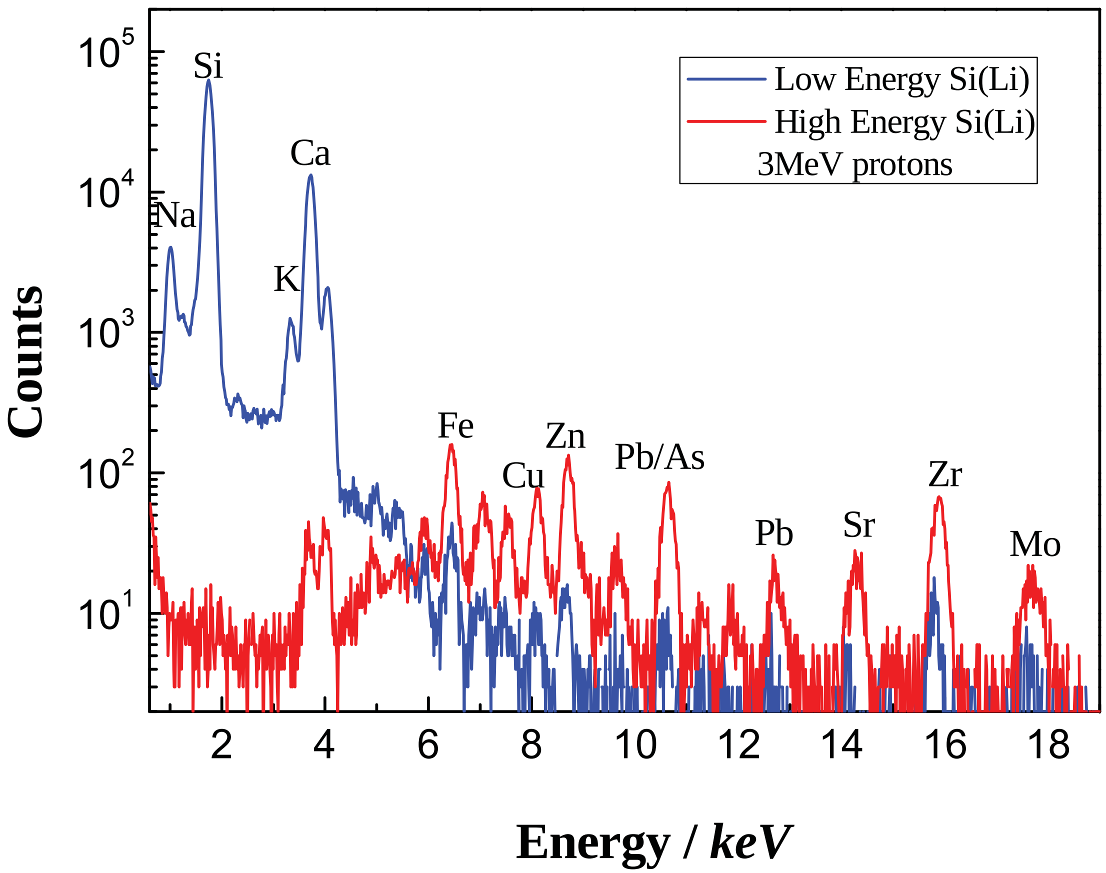
- Multi-elemental and near-surface depth resolved analysis of samples/artifacts.
- Analytical range: Lithium (Z=3) to Uranium (Z=92)
- Analytical sensitivity: From μg/g (ppm) to % level

External Ion-Beam

- Non destructive
- No limitations (in general) for the size or shape of the object
- No heating, reduce damage
- No sampling, no charging, no preparation
- Easy sample positioning

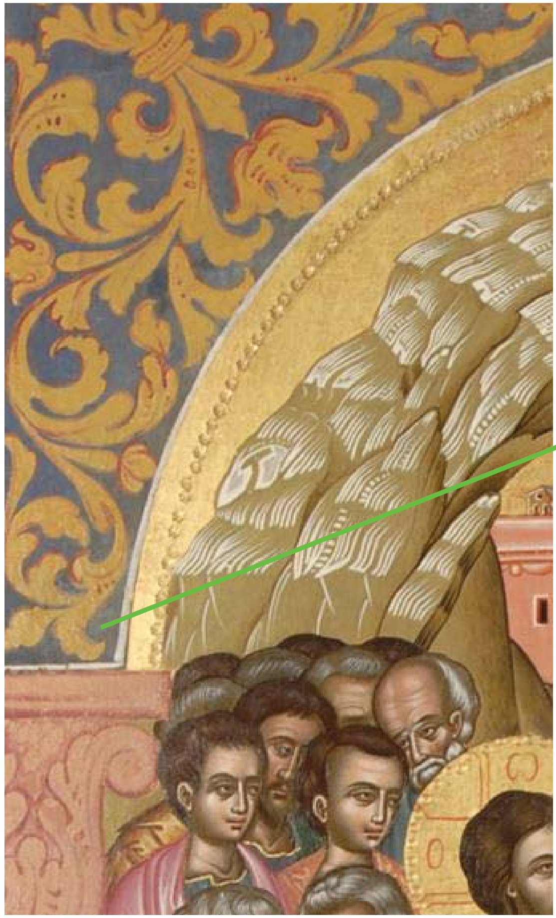
PIXE1: Multi-elemental analysis

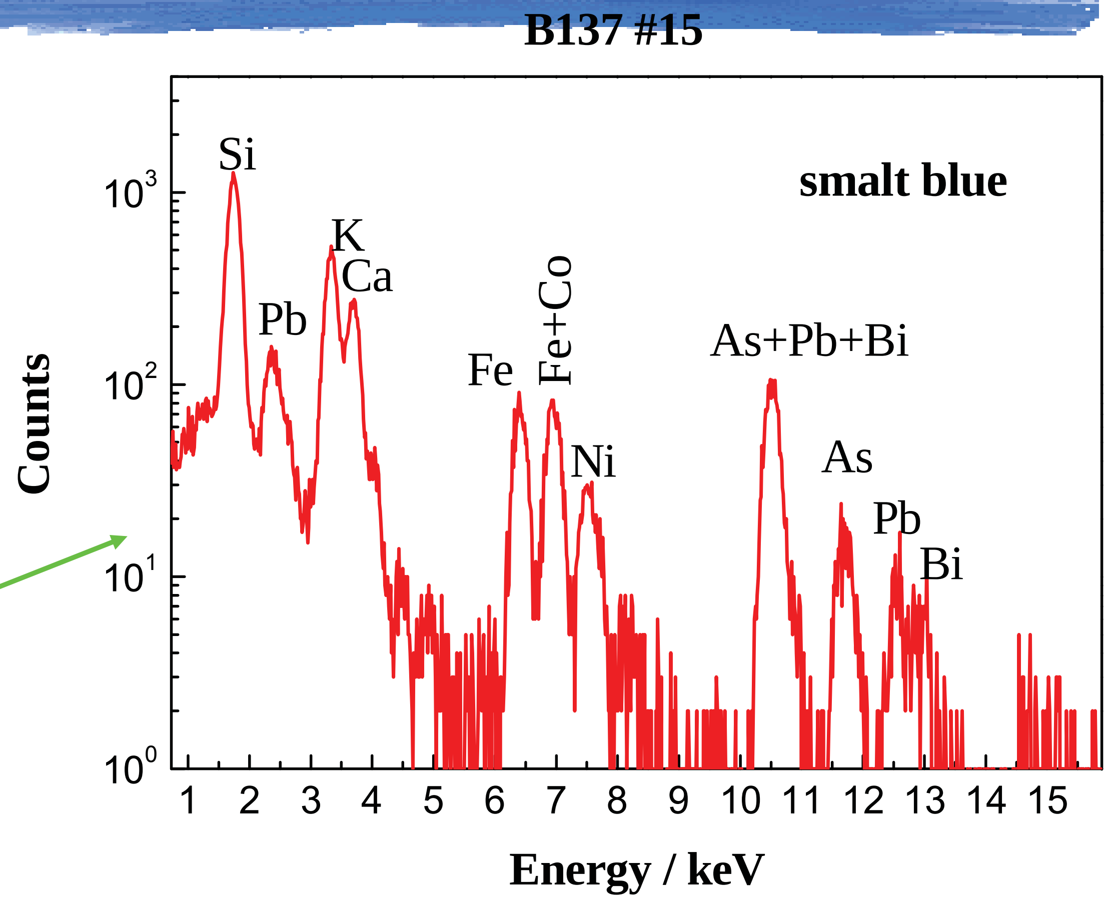
PIXE spectra, SRM Glass BAM-S005B



Sokaras et *al*, ABC, 20O9

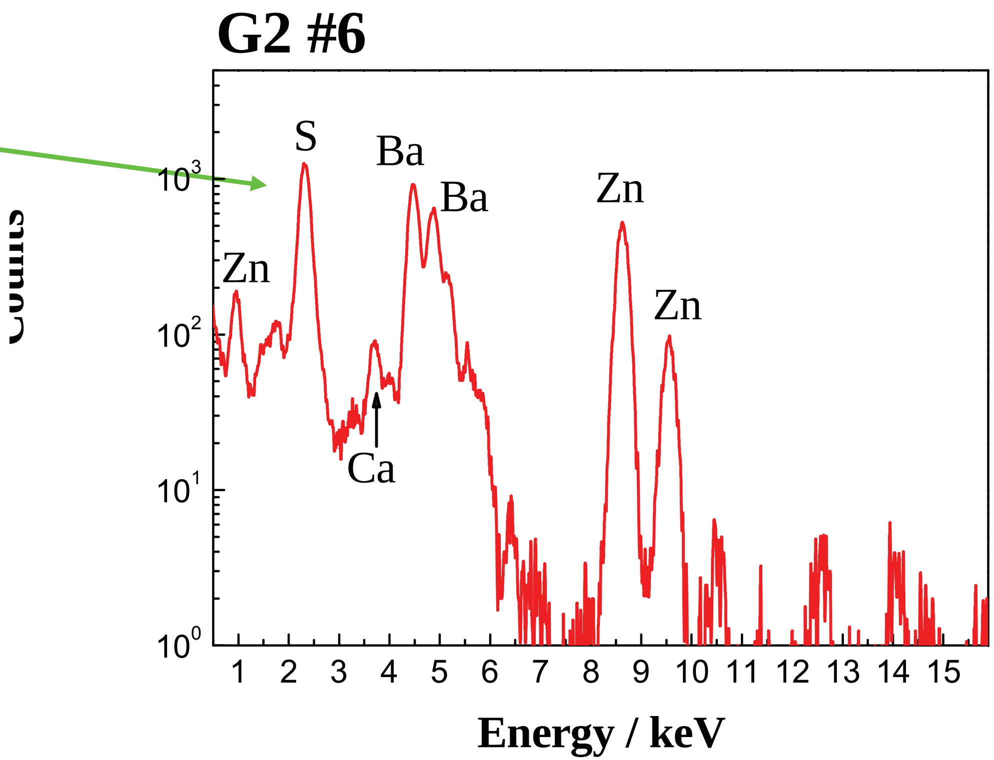
PIXE: Elemental Analysis of smalt





Smalt Blue: Quartz,
Smalt minor elements
Fe, Co, Ni, As Pb, Bi

PIXE: Analysis of modern painting pigment



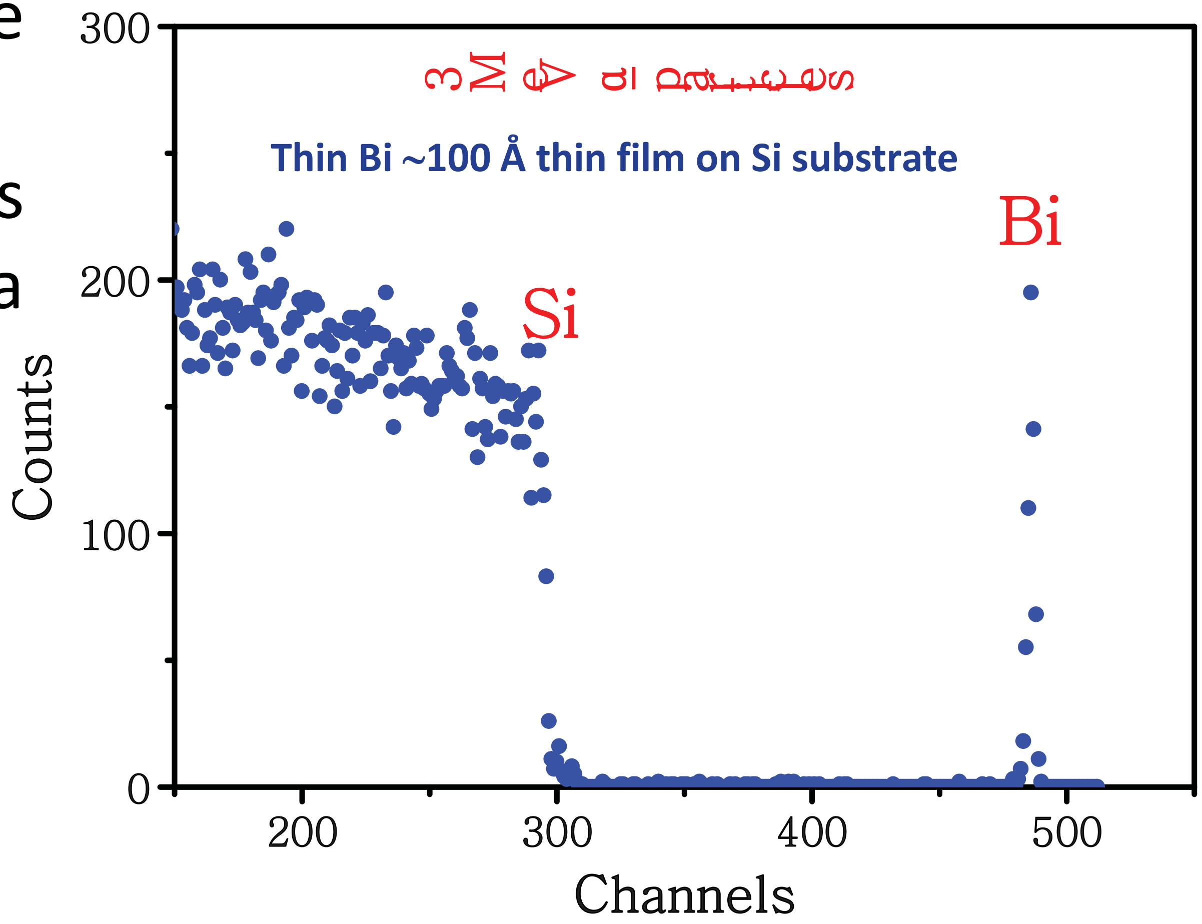
- ➢ **Lithopone, mixture of ZnS and $BaSO_4$**

Greek contemporary painter, Nikos Chatjikyriakos-Gkikas, Benaki museum

Rutherford-Back Scattering (RBS) Spectroscopy

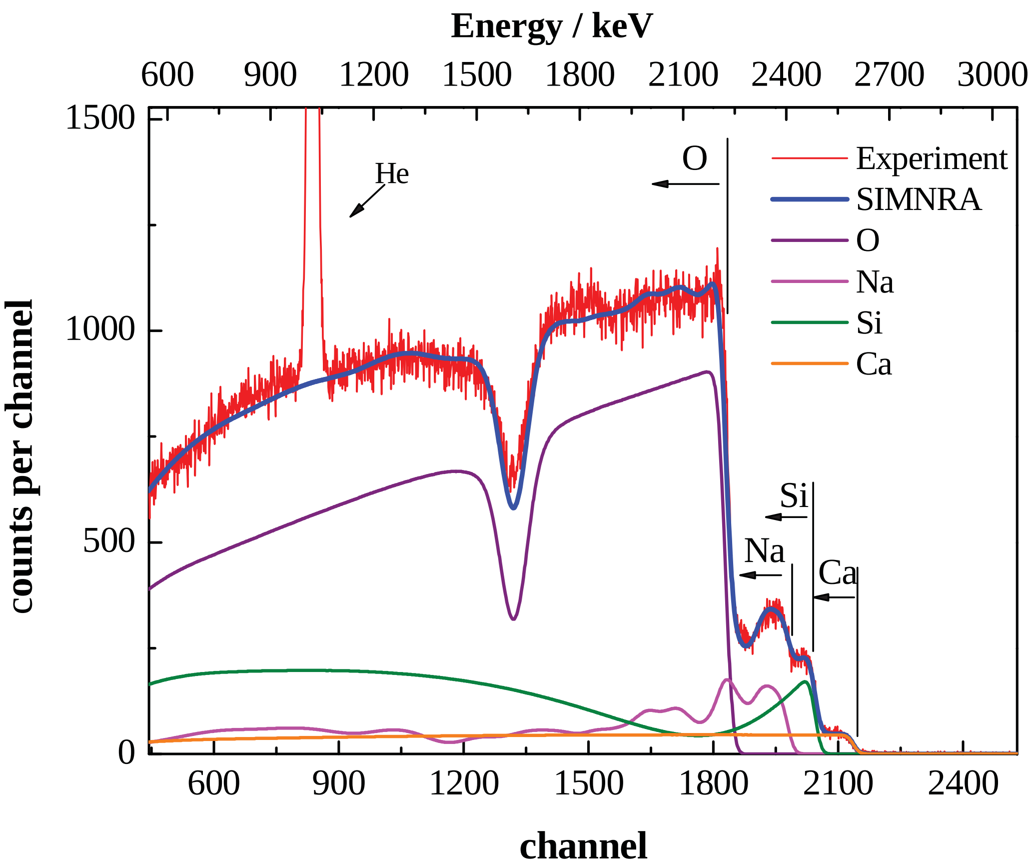
RBS: Near-surface depth resolved elemental analysis in the range of a few micrometers.

Detection:
Energy of the elastically back-scattered charged particles



➢ Concentration profile versus depth is provided by the energy loss of the BS particles

RBS: Elemental analysis – Homogeneous sample

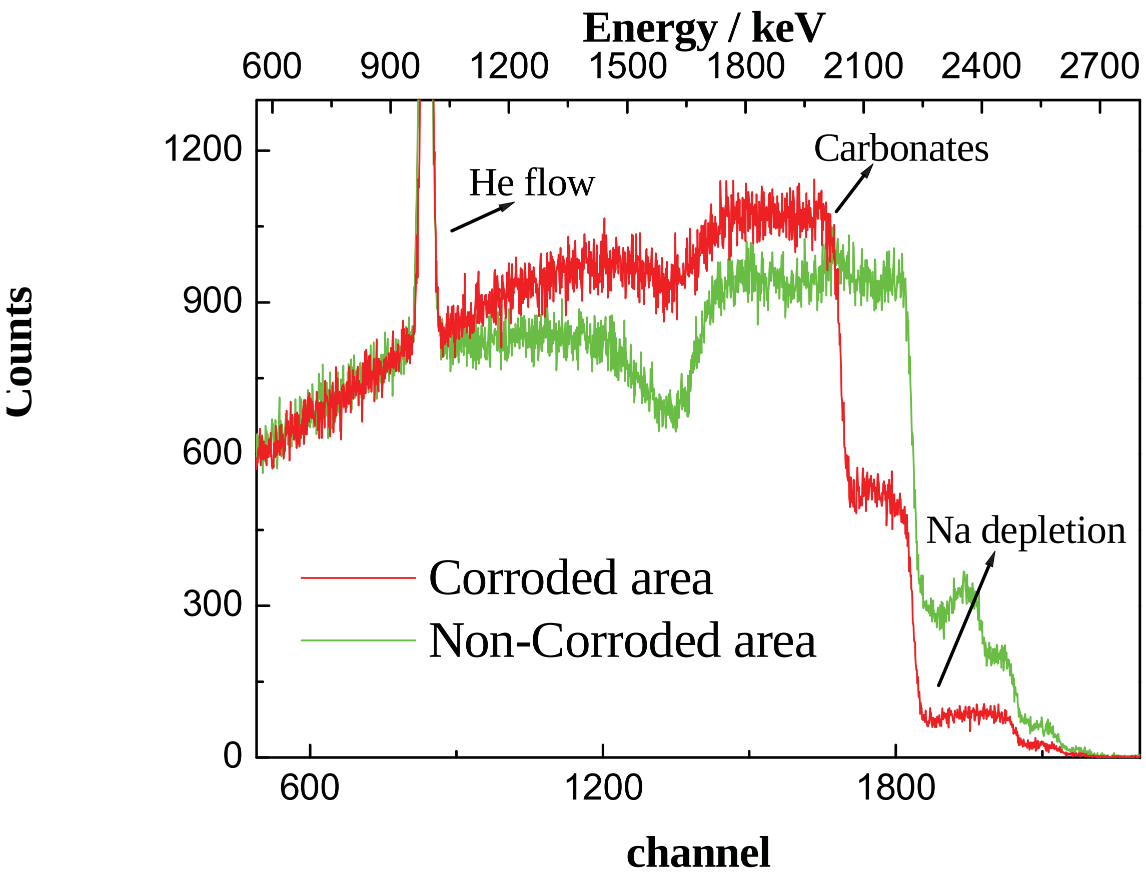


NIST Soda Lime glass 620

- Protons *3MeV*
- Angle 161°

Element	PIXE	RBS	Certified
O		45.3	47.0
Na	10.6	7.2	10.7
Si	36.5	39.1	33.8
Ca	5.05	6.4	5.08

RBS: Depth elemental profiling - Corrosion



PIGE: Particle Induced gamma-ray emission

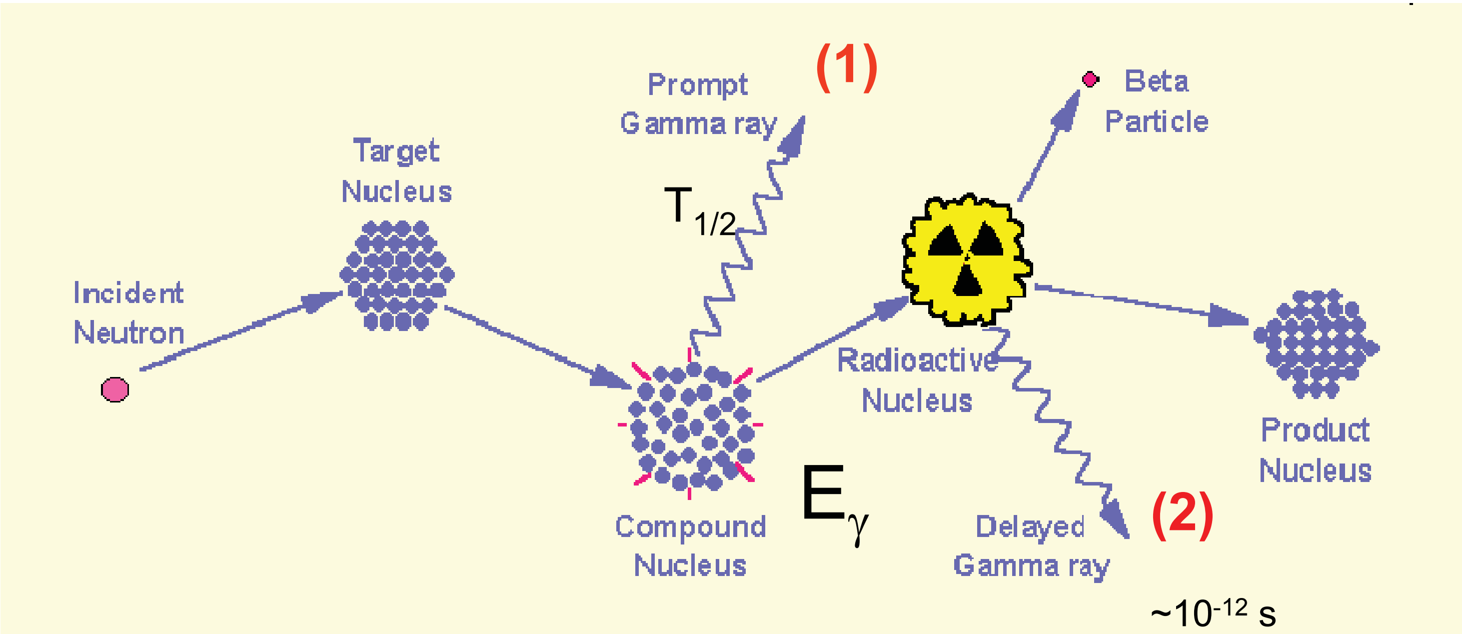
Nuclear Reactions may induce isotope specific characteristic γ-rays emission.

Light elements: Li, B, Na, Mg, Al, Si

Element	$E_p = 1.77$ MeV		$E_p = 4.0$ MeV	
	γ-Ray (keV)	Reaction	γ-Ray (keV)	Reaction
Li	478	$^{7}Li(p, p'\gamma)^{7}Li$	478	$^{7}Li(p, p'\gamma)^{7}Li$
B	429	$^{10}B(p, \alpha\gamma)^{7}Be$	718	$^{10}B(p, p'\gamma)^{10}B$
F	6129	$^{19}F(p, \alpha\gamma)^{16}O$	197	$^{19}F(p, p'\gamma)^{19}F$
Na	440	$^{23}Na(p, p'\gamma)^{23}Na$	440	$^{23}Na(p, p'\gamma)^{23}Na$
Mg	585	$^{25}Mg(p, p'\gamma)^{25}Mg$	585	$^{25}Mg(p, p'\gamma)^{25}Mg$
Al	1779	$^{27}Al(p, \gamma)^{28}Si$	1014	$^{27}Al(p, p'\gamma)^{27}Al$
Si			1779	$^{28}Si(p, p'\gamma)^{28}Si$
P			1266	$^{31}P(p, p'\gamma)^{31}P$

Neutron Activation Analysis -NAA

Neutron capture by a target nucleus followed by emission of gamma rays



(1) Prompt-gamma neutron activation analysis (PGNAA)

(2) Delayed-gamma neutron activation analysis (NAA)

Instrumental (INAA), *minimum sample preparation*

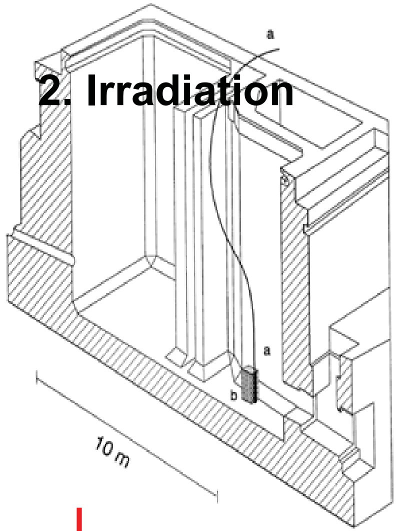
Radiochemical (RNAA), *chemical analysis of the sample*

INAA procedure

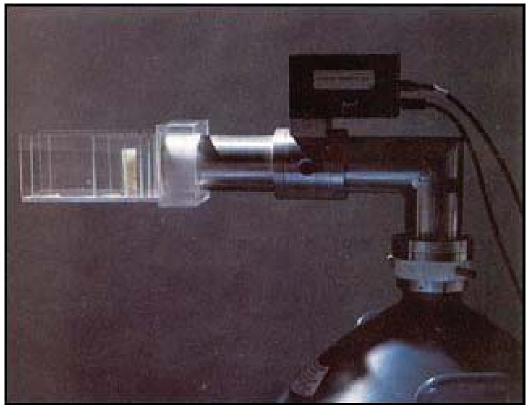
Sample

1. Sample encapsulation

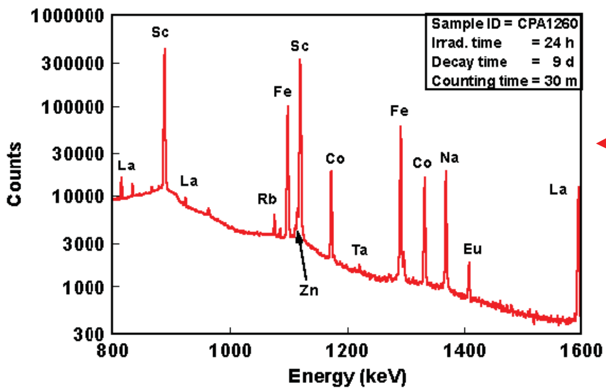
2. Irradiation



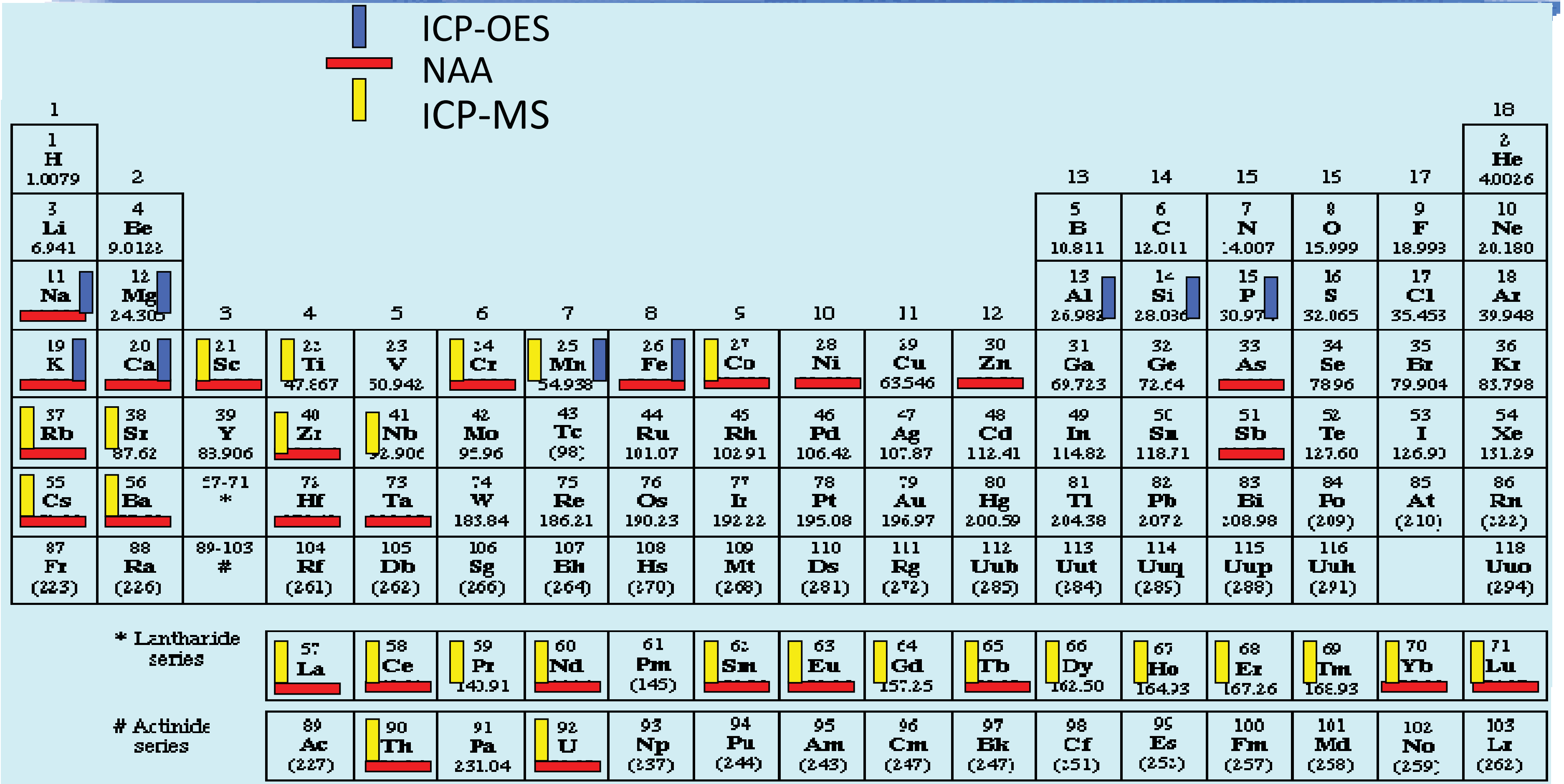
3. Gamma ray counting



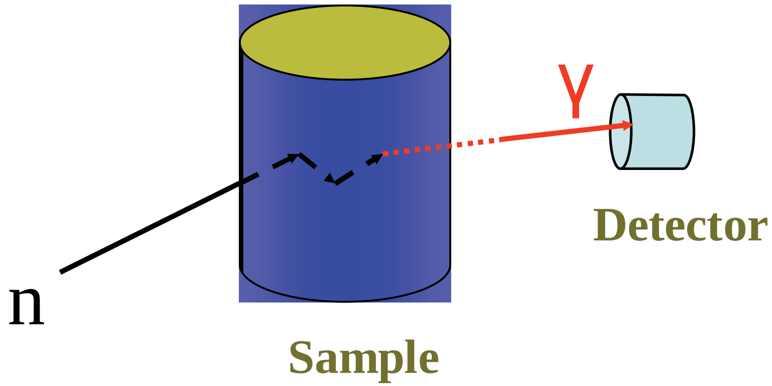
4. Spectrum analysis



Analytical features/Advantages of NAA



Large Sample NAA

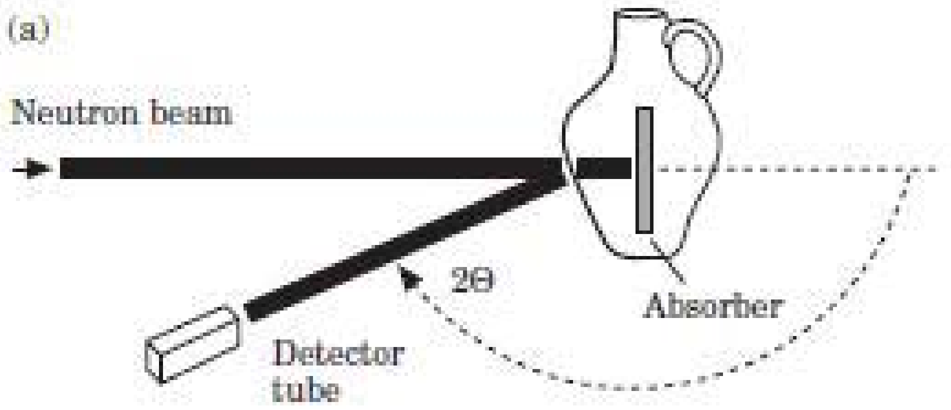


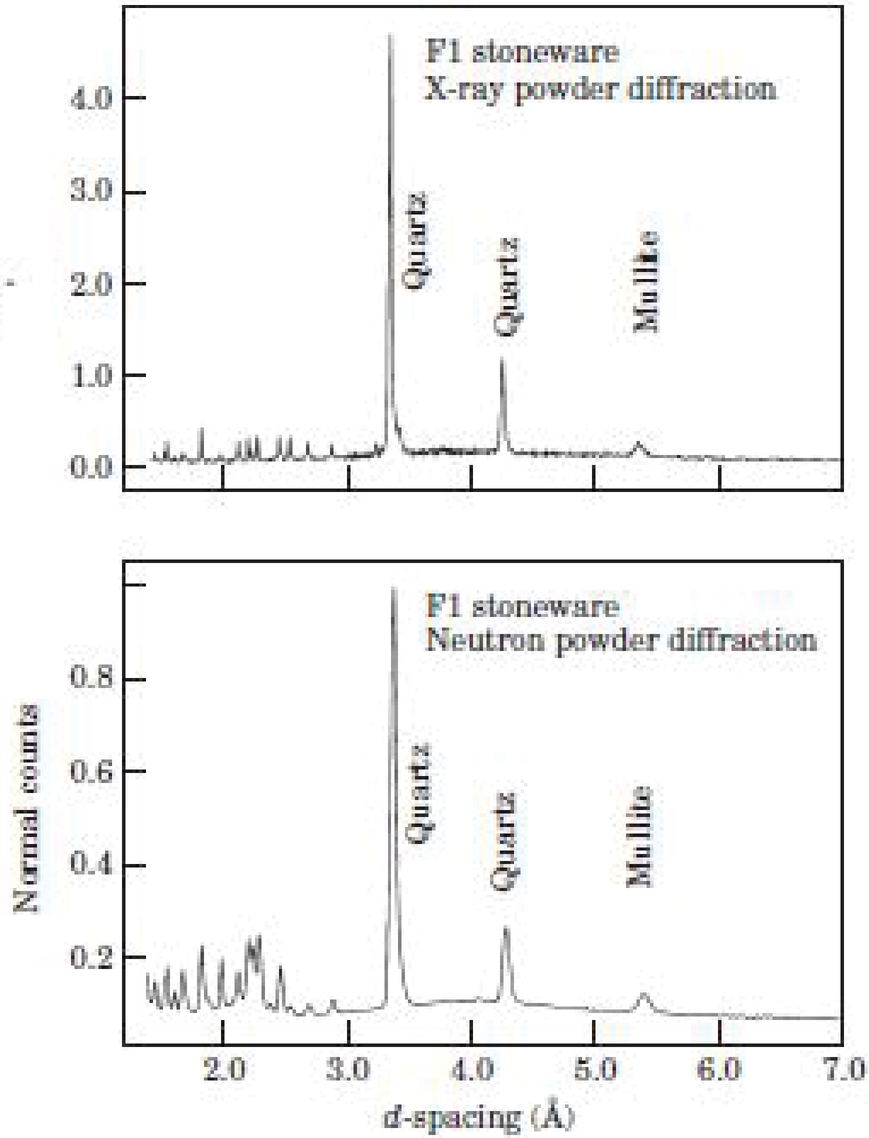
Neutrons and gamma-rays have mean free paths of several centimeters within materials

Neutron Activation an “ideal” tool for Analysis of Large Volume Samples (≥1 L)

IAEA CRP on Harmonization of LSNAA methodology (2009 -), Stamatelatos-Tzika, NCSR “Demokritos”

Time Of Flight Neutron Diffraction



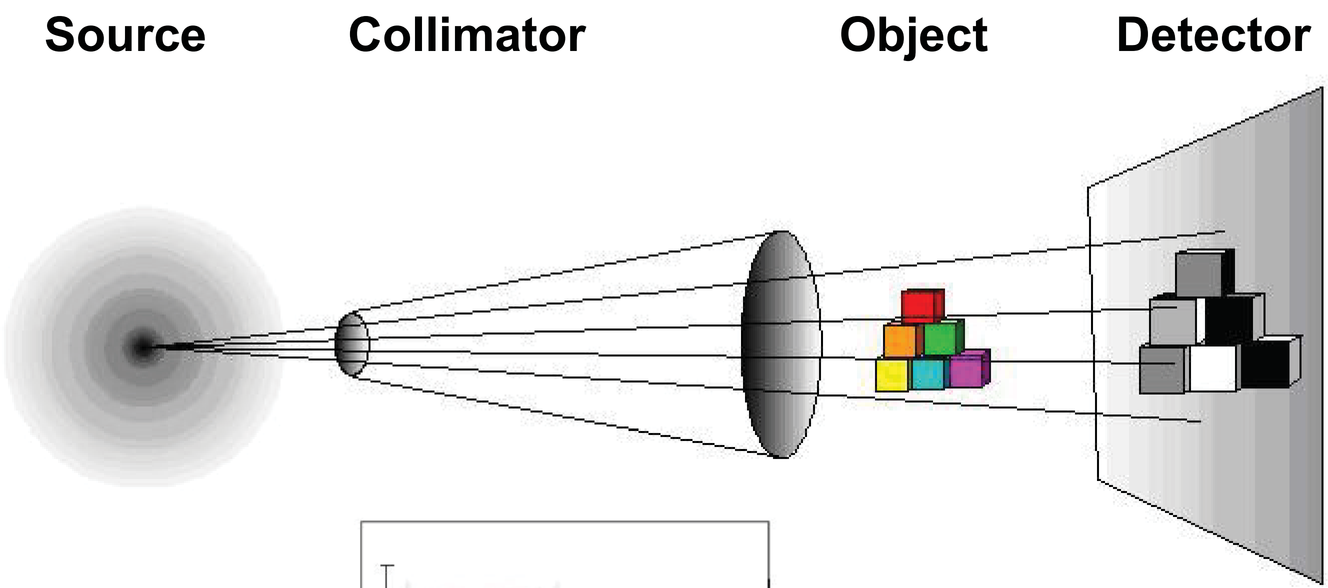


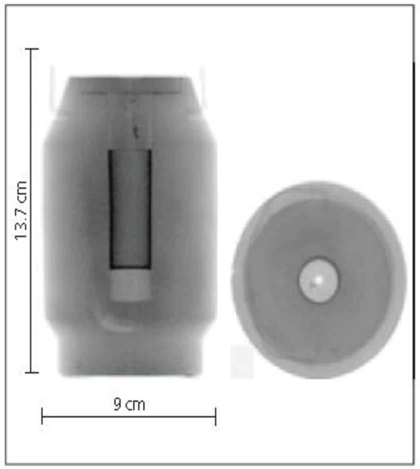
Bragg Equations:

$\lambda = 2 * d_{hkl} * \sin\Theta$

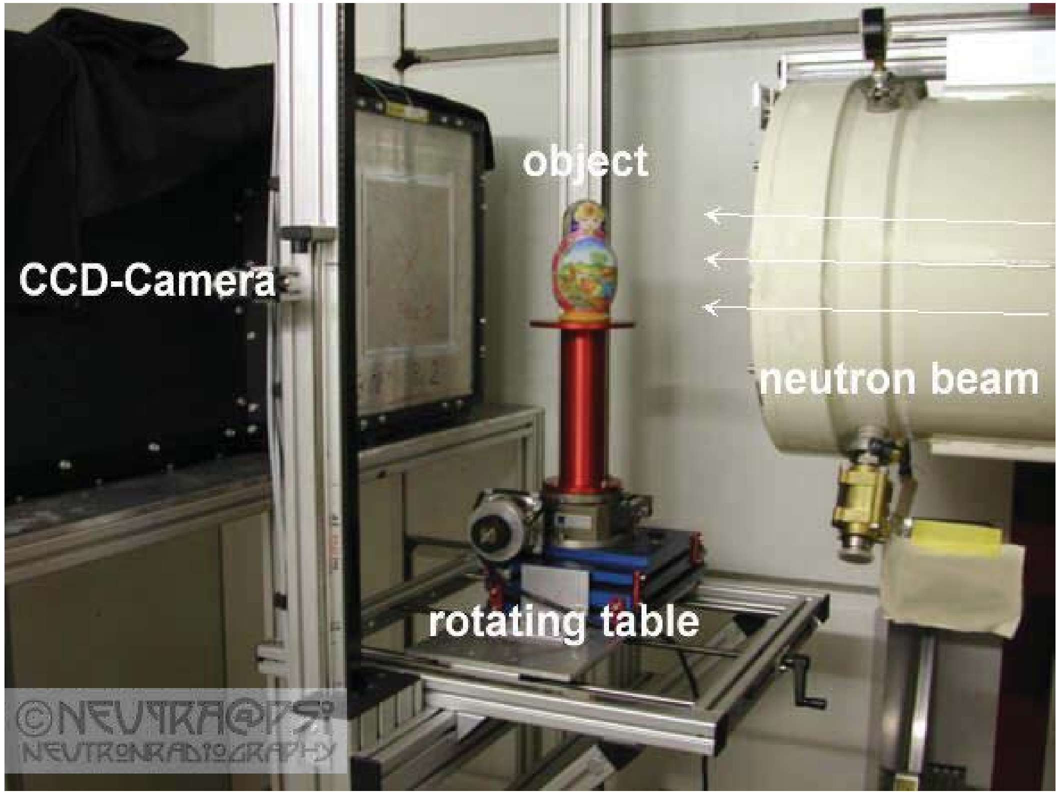
Time (μs)=505.56 L(meters)* d_{hkl}(Angstron)*sinΘ

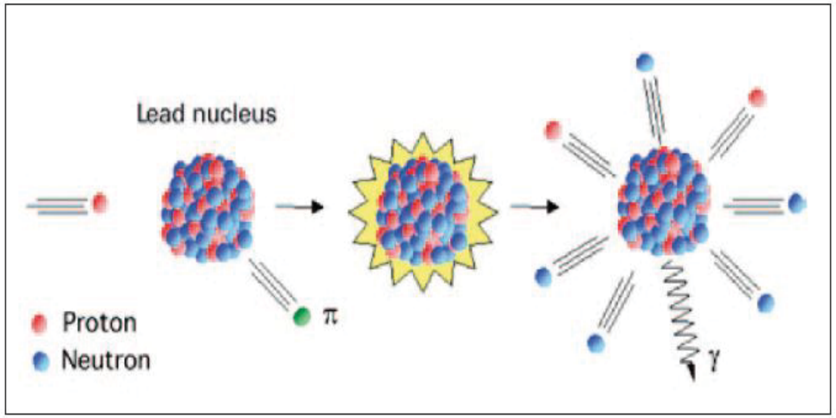
Neutron imaging techniques





Experimental facility at Paul Scherrer Institut

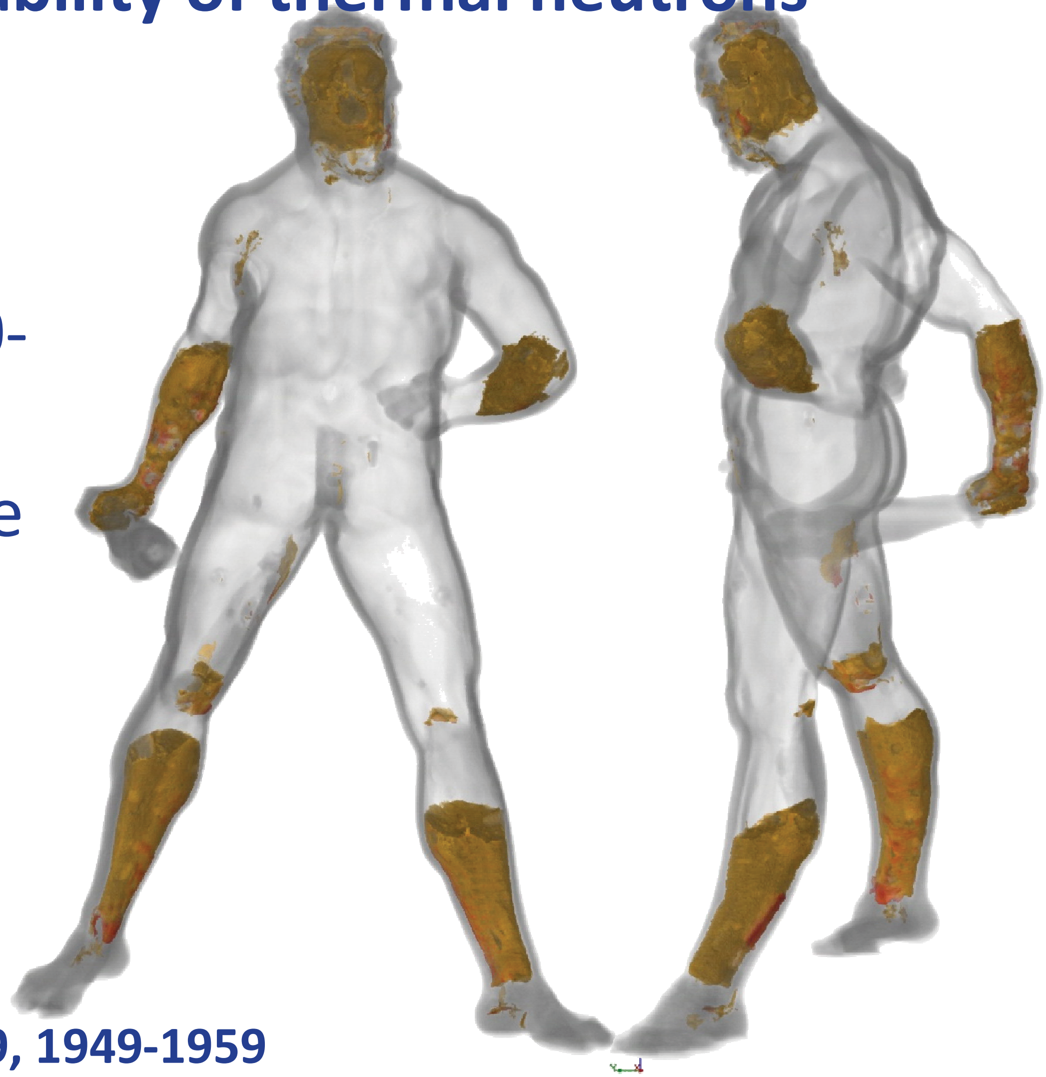




. **NEUTRA set-up:** Swiss spallation source for research purposes
Neutrons are produced by a 590 MeV proton beam of 1.3 mA current on Pb target. D_2O moderator to produce 25 meV thermal neutrons

Neutrons tomography image

Very high interaction probability of thermal neutrons with H, C and O



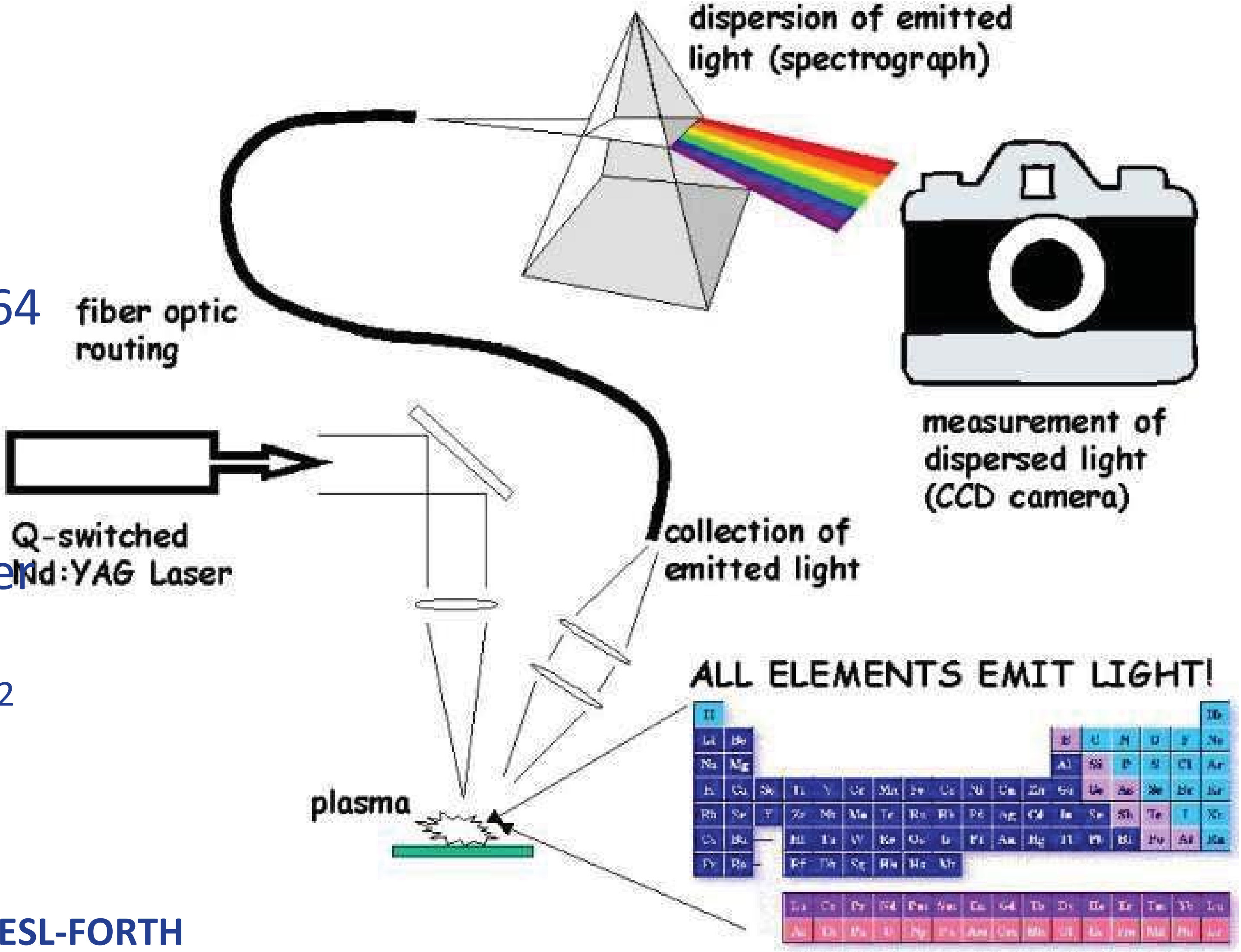
Hercules Pomarius,
Willem van Tetrode's, 1520-1588
Renaissance bronze figurine

Grey color: Bronze
Yellow color: Core material (silicate based, clay)

R. Van Lang et al. , ABC, 395, 7, 2009, 1949-1959

Laser Induced Breakdown Spectroscopy - LIBS

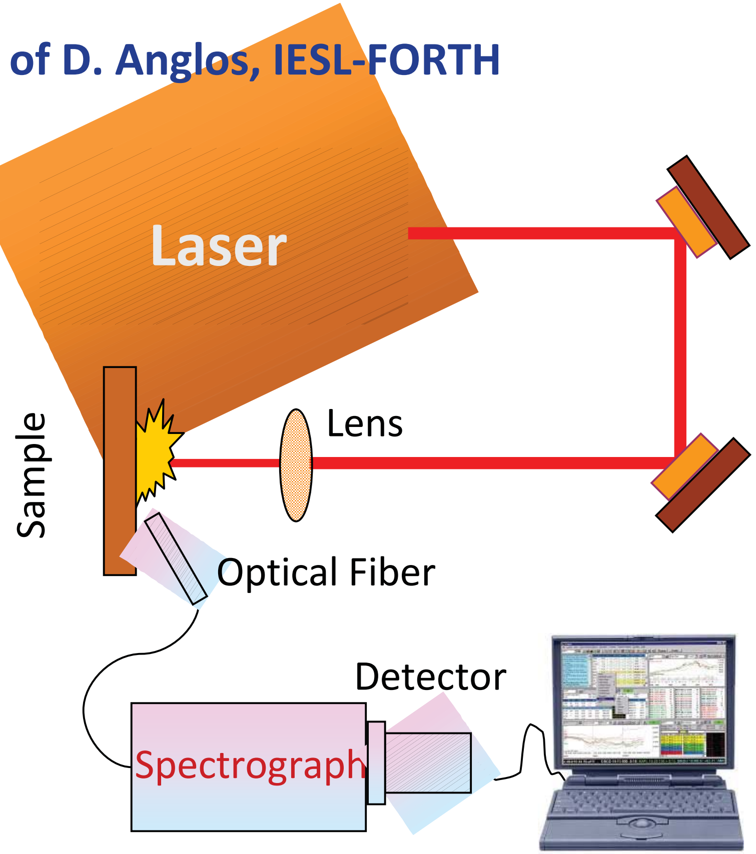
Near infrared region of the electromagnetic spectrum, with a wavelength of 1064 nm. The pulse duration is in the region of 10 ns generating a power density which can exceed 1 GW·cm^{-2} at the focal point



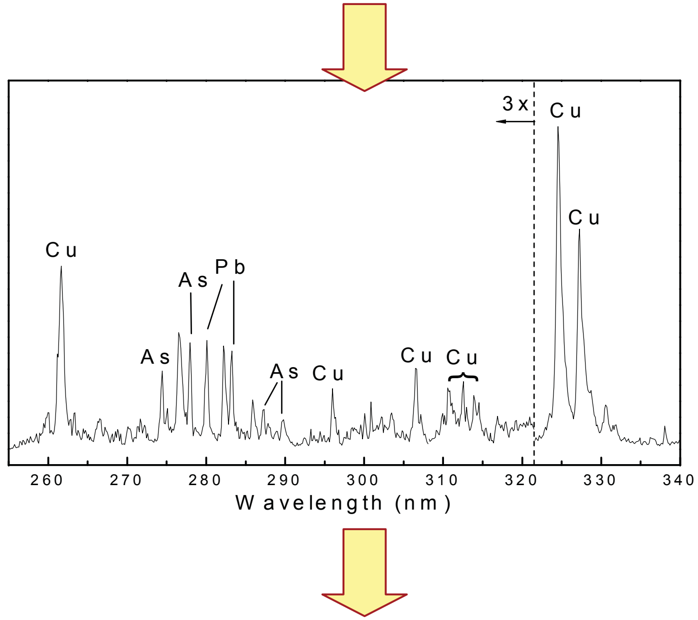
Courtesy of D. Anglos, IESL-FORTH

Laser Induced Breakdown Spectroscopy - LIBS

Courtesy of D. Anglos, IESL-FORTH



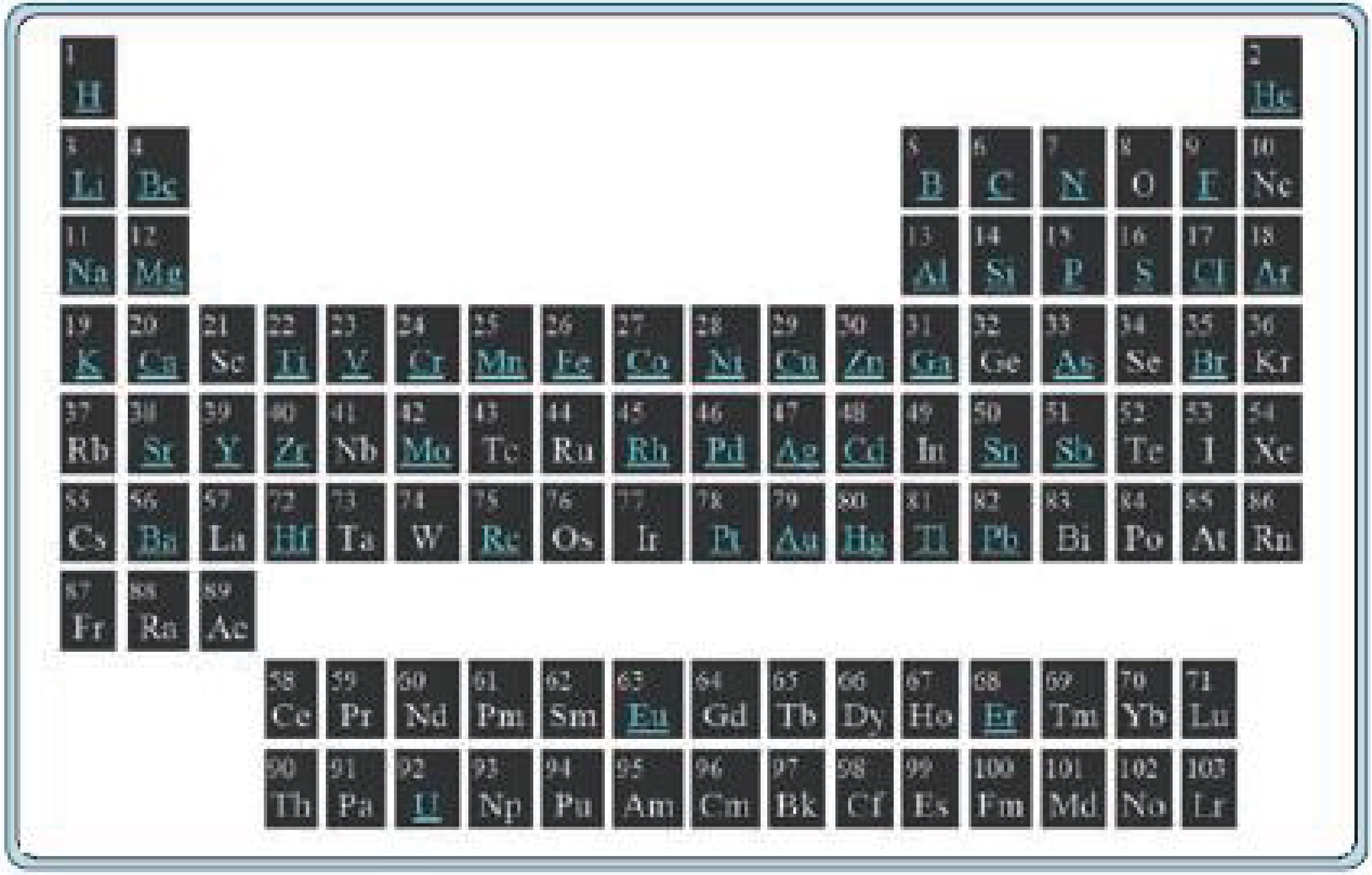
Spectral information from *micro-plasma* generated when a *laser pulse* probes the sample/object surface



Characteristic Spectral Lines ⇒ Which elements?

Line Intensity ⇒ How much of each?

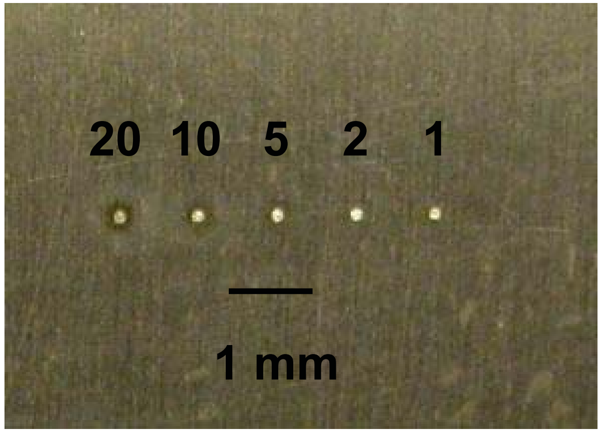
Laser Induced Breakdown Spectroscopy - LIBS

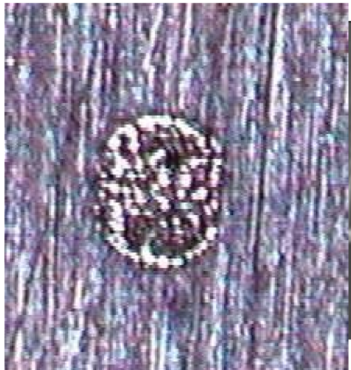


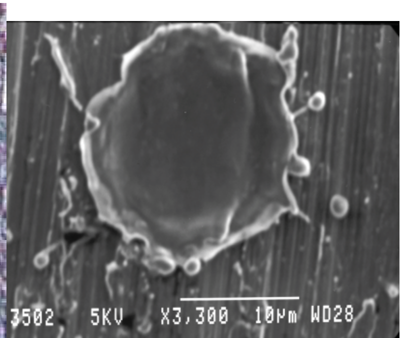
Courtesy of D. Anglos, IESL-FORTH

Laser Induced Breakdown Spectroscopy - LIBS

Typical craters on brass







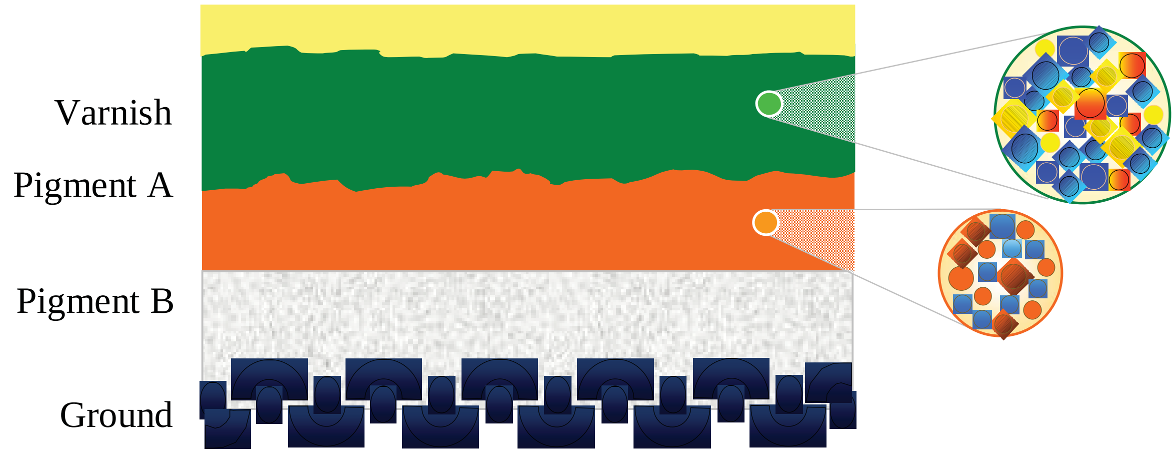
Portable LIBS @ IESL-FORTH

Laser pulse : **10 ns**

Plasma emission: **1 us**

Courtesy of D. Anglos, IESL-FORTH

Stratigraphic analysis by LIBS



Stratigraphic analysis

with increasing number of laser pulses

Courtesy of D. Anglos, IESL-FORTH

Raman spectroscopy

Laser (Visible or near IR) + Matter

↓

Excitation

↓

Inelastic scattering of light

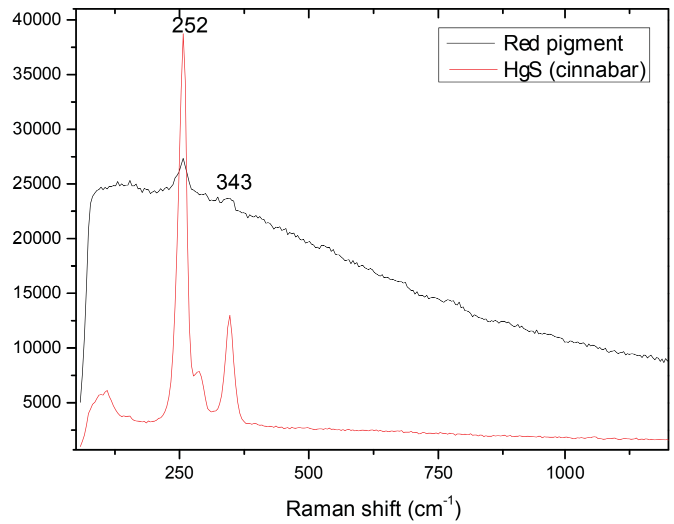
↓

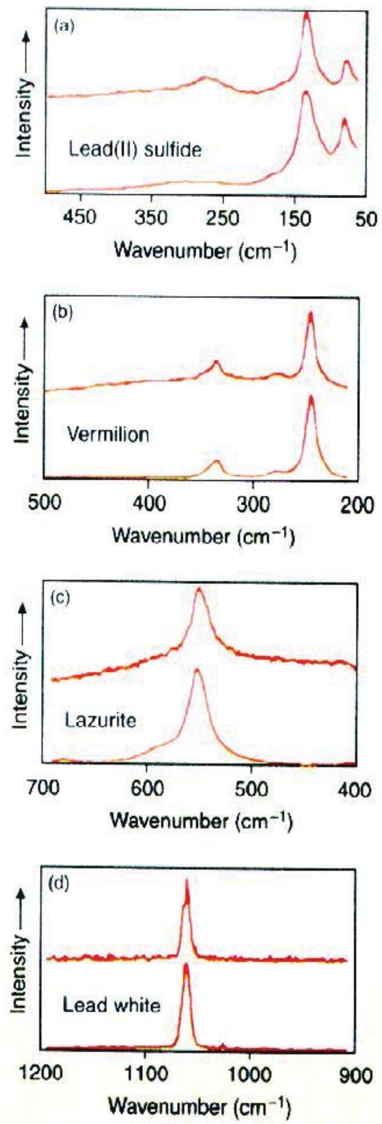
Raman Spectrum

↓

Chemical information
(molecular vibrations – chemical bonds)

JY Micro-Raman system





Detecting pigments on Byzantine icon @ **IESL-FORTH**

Courtesy of D. Anglos, IESL-FORTH

UV Photography, Délos, Musée, Aphrodite



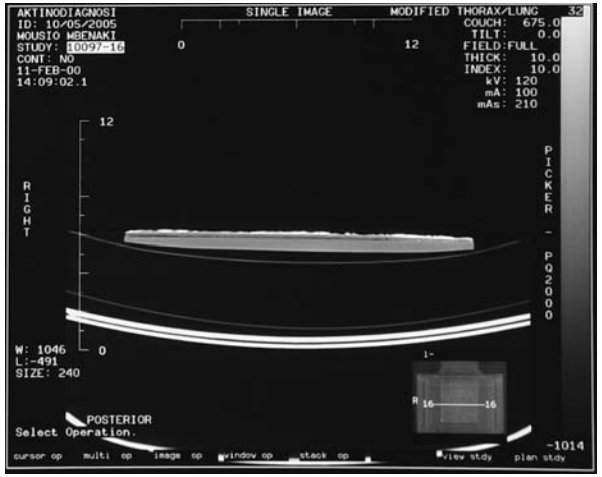
El-Greco: The Baptism of Christ

- nd techniques before cleaning
  - CT scan
  - X-ray radiography
  - UV,VIS, IR examination with a multi-spectral imaging
  - Holographic interferometry (1)
  - Stereoscope
  - nd XRF (analysis of 30 spots in 4 hours at 15 and 40 KeV)

Aloupie et al, Benaki, Journal, 2006

- nd techniques after cleaning
  - FT n-IR
  - LIBS
  - Holographic interferometry (2)

El-Greco: The Baptism of Christ



Computer Aided Tomography (CAT)

X-Radiography

Digital holographic speckle interferometry by IESL-FORTH

Aloupie et al, Benaki, 2006

Practically UV radiation allows the study of the state of preservation of the varnish and the detection/location of interventions on the varnish (cleaning or over-paintings which not fluoresce). Recognition of certain pigments based on their characteristic fluorescence under UV radiation.

Penetrates the varnish and surface paint layers (depending on the pigments). Study of the under-drawing, and changes over-paintings by the painter? Recognition of certain pigments based on their characteristic reflectance in the IR.

Paintings: UV fluorescence for varnishes

14th C. Italian panel painting with varying levels of repainting and varnishing, as evident from UV examination using a wood lamp (emission at approximately 360 nm)

Different varnishes can be discriminated on the basis of their emission spectra even with the same wavelength of excitation

De la Rie, Studies in Conservation, 1982 & M. Thoury et al, Applied Spectroscopy, 2008

Conclusions

- The complexity of cultural heritage related materials due to their heterogeneity at different scale of magnitude and diversity of contained materials requires the optimized synergistic application of different analytical techniques based on radiation probes

- The big advantage of radiation probes in Ch is that in several cases the analysis and full characterization can be conduced in a fully non-invasive way and some times in-situ

Thank you for your Attention!!!!