

Non Destructive Investigation

X-Ray Fluorescence Analysis (XRF)



Astrik Gorghinian

STEPS OF EXAMINATION

- **Inspection:** for example by means of an electromagnetic radiation
- **Assessment:** comparison to a model



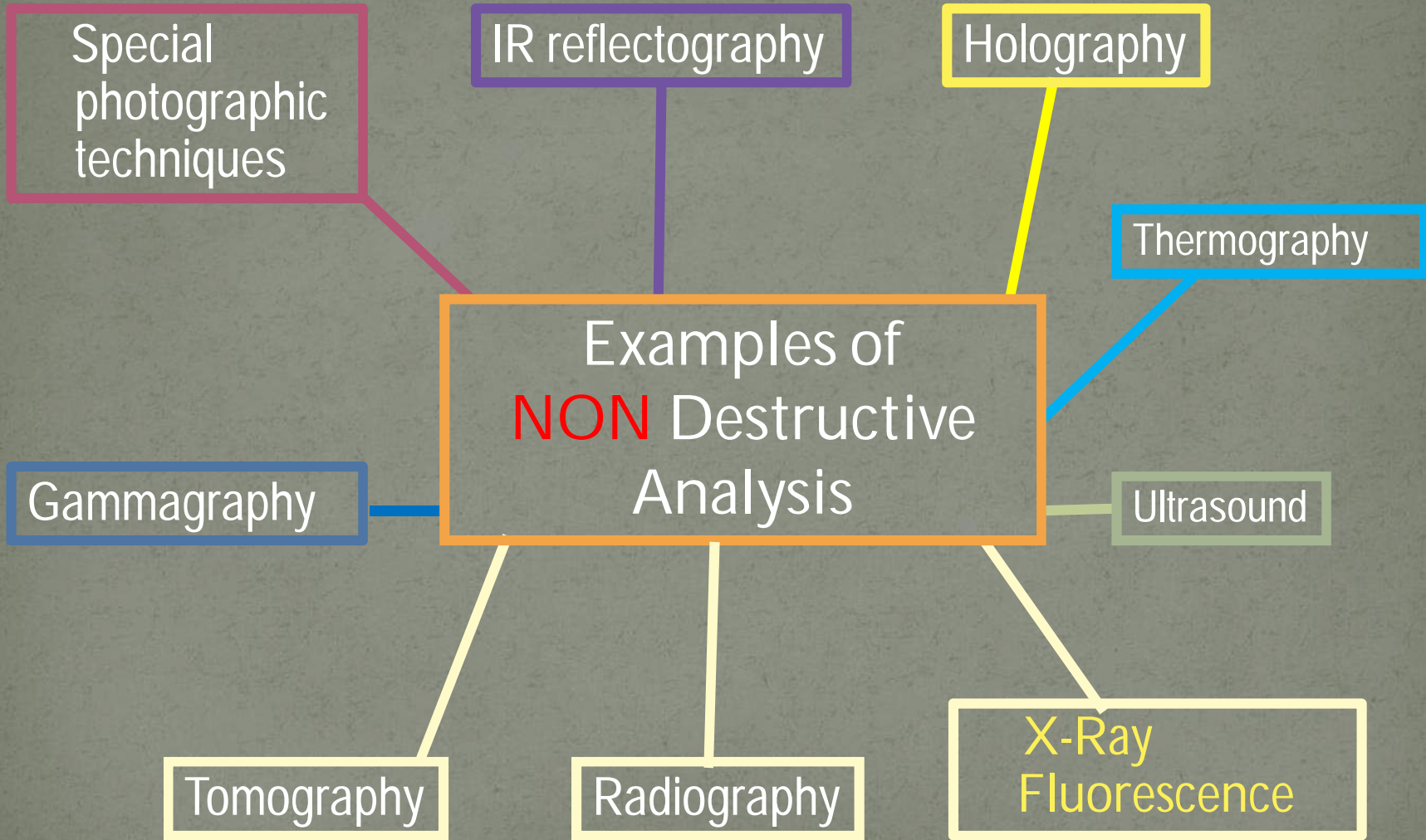
Diagnosics: inspection methods

➤ NON DESTRUCTIVE

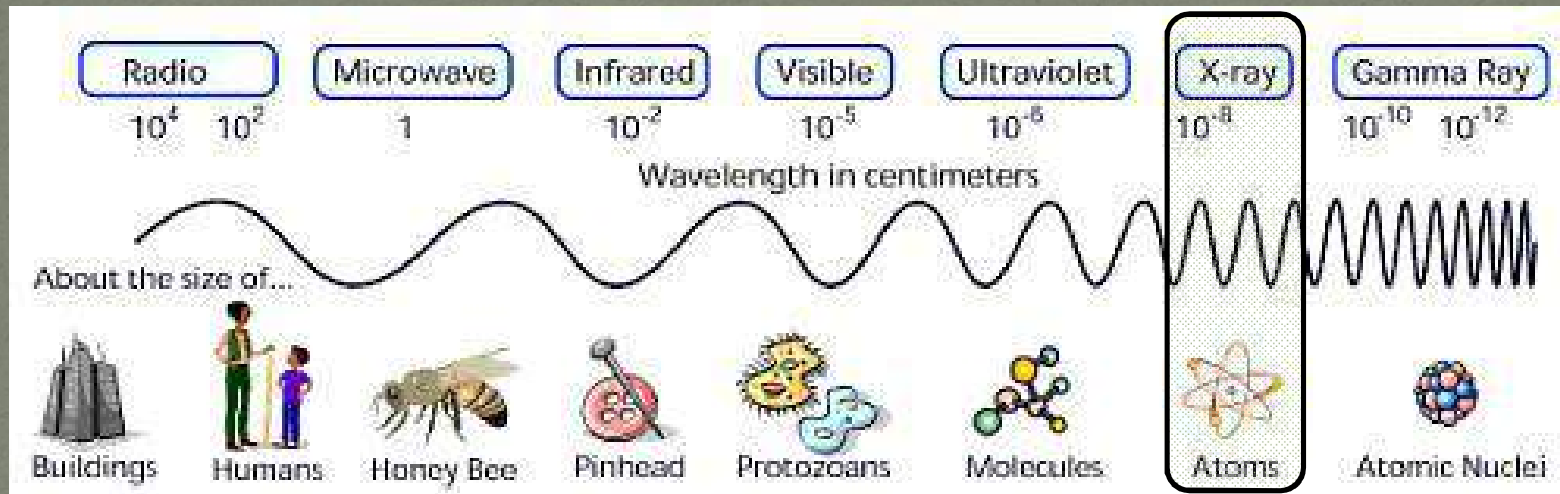
NO alteration on the object do occur during the analysis

➤ NON INVASIVE

The analysis is performed on representative samples, very small amount of sample taken from the artwork



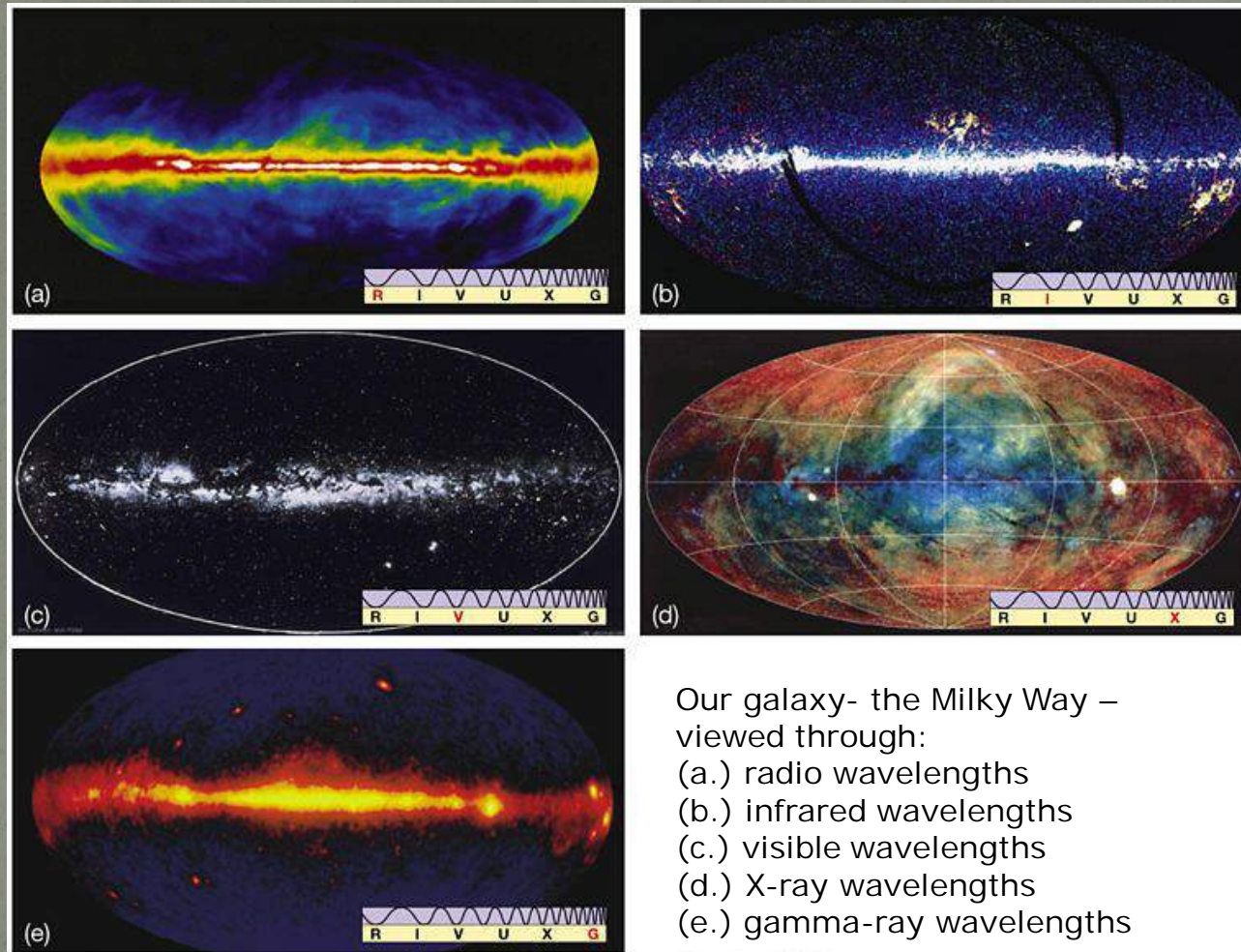
Electromagnetic Spectrum



Region	Wavelength (Angstroms)	Wavelength (centimeters)	Frequency (Hz)	Energy (eV)
Radio	$> 10^9$	> 10	$< 3 \times 10^9$	$< 10^{-5}$
Microwave	$10^9 - 10^6$	$10 - 0.01$	$3 \times 10^9 - 3 \times 10^{12}$	$10^{-5} - 0.01$
Infrared	$10^6 - 7000$	$0.01 - 7 \times 10^{-5}$	$3 \times 10^{12} - 4.3 \times 10^{14}$	$0.01 - 2$
Visible	$7000 - 4000$	$7 \times 10^{-5} - 4 \times 10^{-5}$	$4.3 \times 10^{14} - 7.5 \times 10^{14}$	$2 - 3$
Ultraviolet	$4000 - 10$	$4 \times 10^{-5} - 10^{-7}$	$7.5 \times 10^{14} - 3 \times 10^{17}$	$3 - 10^3$
X-Rays	$10 - 0.1$	$10^{-7} - 10^{-9}$	$3 \times 10^{17} - 3 \times 10^{19}$	$10^3 - 10^5$
Gamma Rays	< 0.1	$< 10^{-9}$	$> 3 \times 10^{19}$	$> 10^5$

Multiwavelength Milky Way

<https://kaiserscience.wordpress.com/physics/electromagnetism/light-is-an-em-field/>



- Our galaxy- the Milky Way – viewed through:
- (a.) radio wavelengths
 - (b.) infrared wavelengths
 - (c.) visible wavelengths
 - (d.) X-ray wavelengths
 - (e.) gamma-ray wavelengths

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X-Rays applied to Cultural Heritage Artworks

NON Destructive Diagnostics

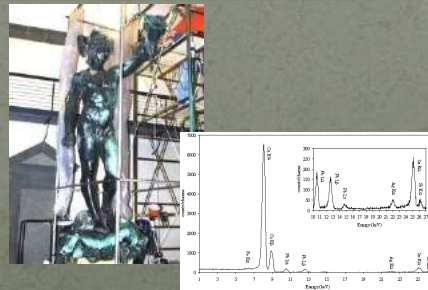
Radiography



Tomography

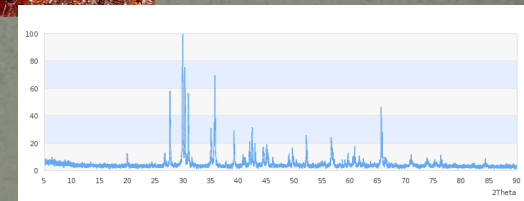


X-Ray Fluorescence

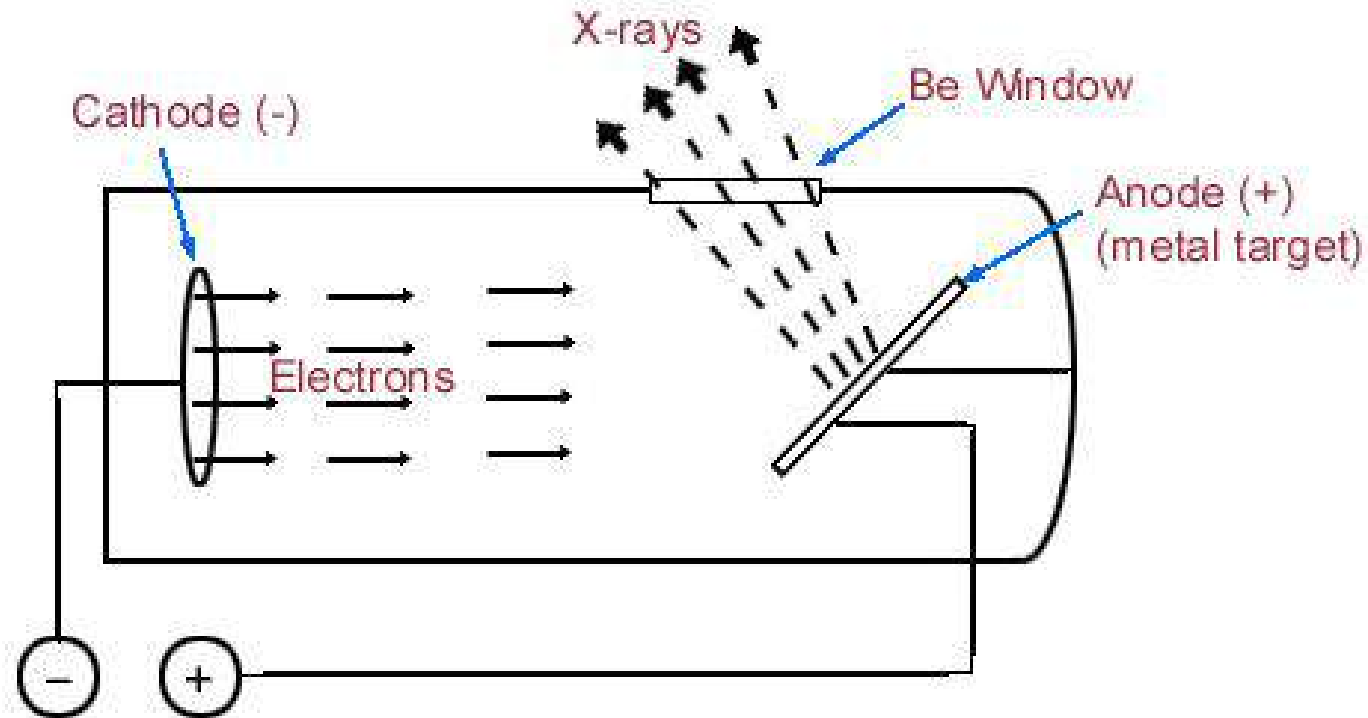


NON Invasive Diagnostics

Diffraction



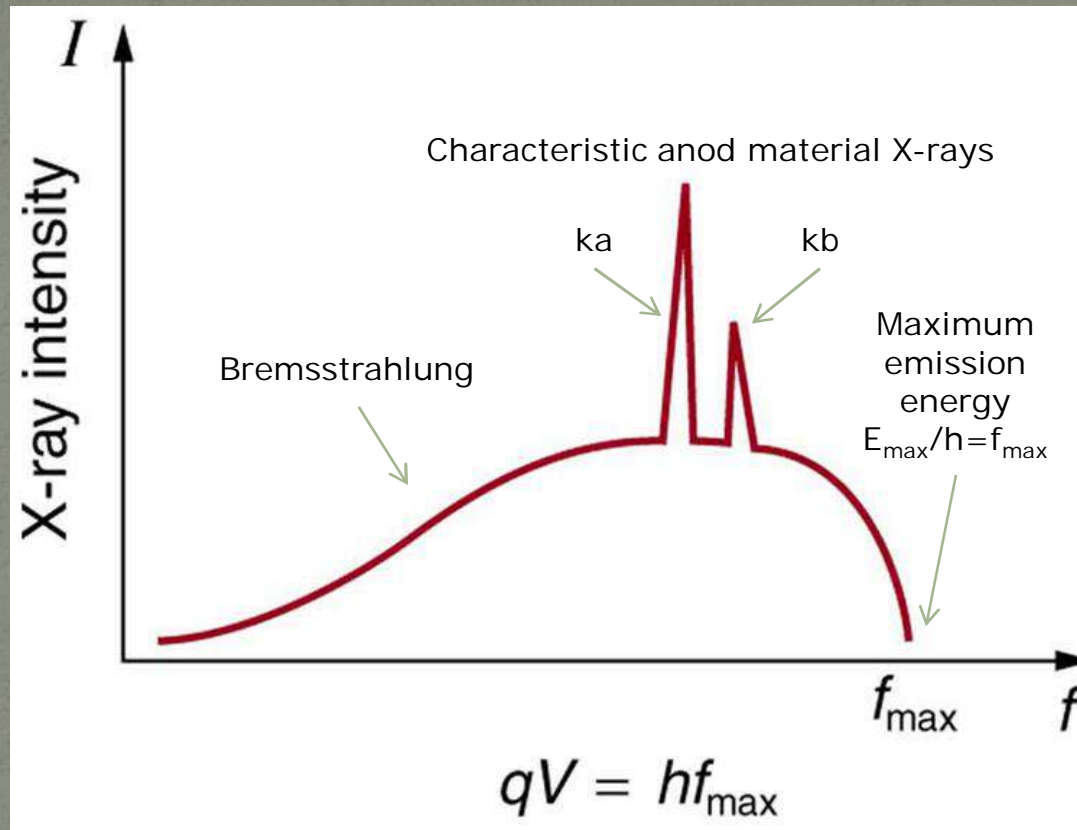
Scheme of an X-Ray tube



voltage 1-60 kV

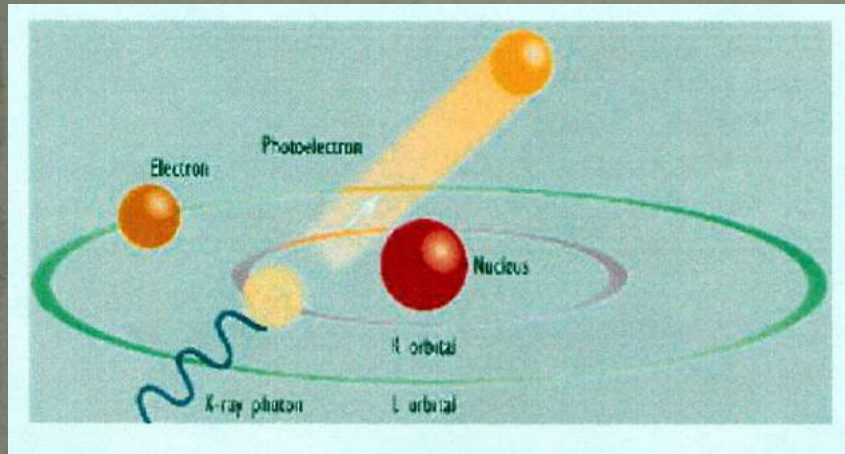
Current: some hundreds of mA

X-Ray tube spectrum

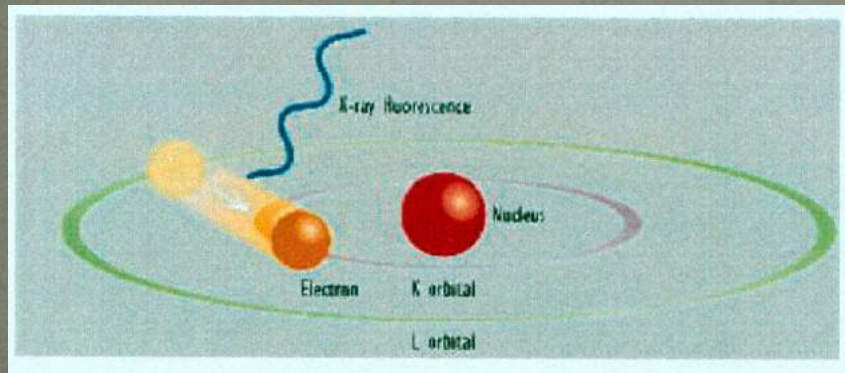


X-ray spectrum obtained when energetic electrons strike a material. The smooth part of the spectrum is bremsstrahlung, while the peaks are characteristic of the anode material. Both are atomic processes that produce energetic photons known as x-ray photons.

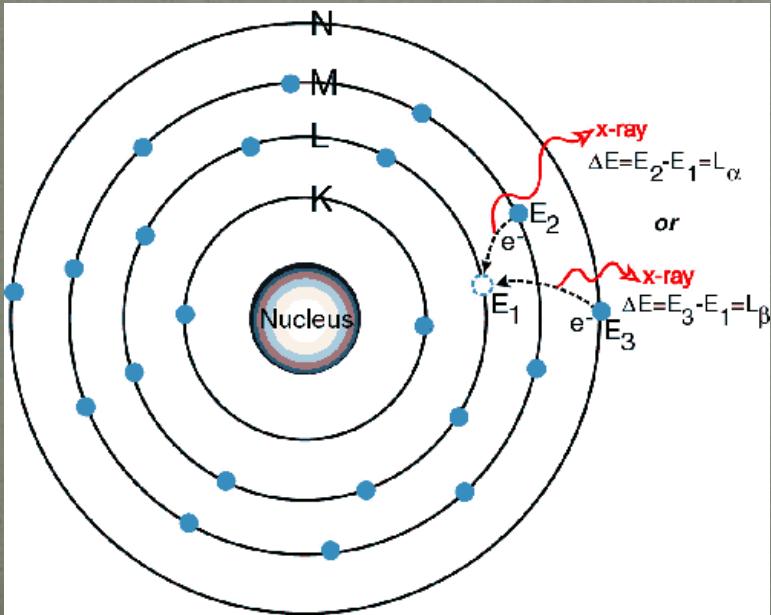
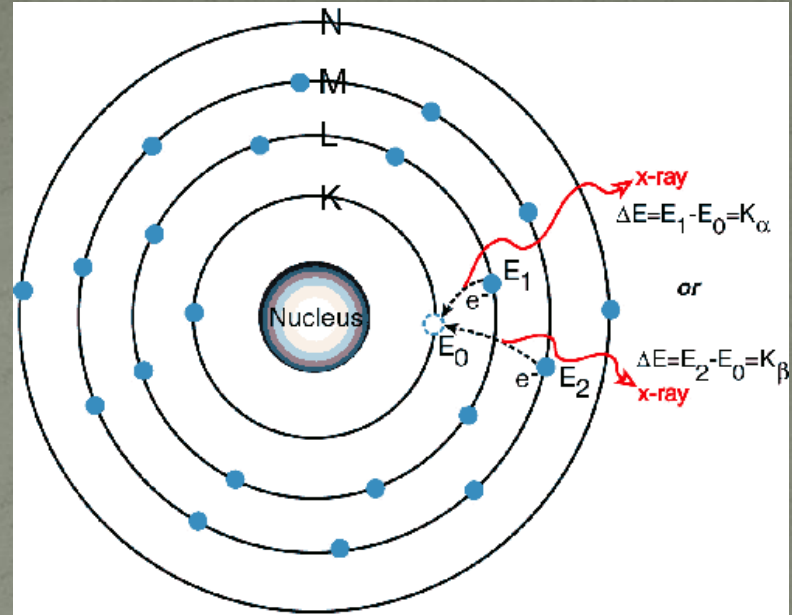
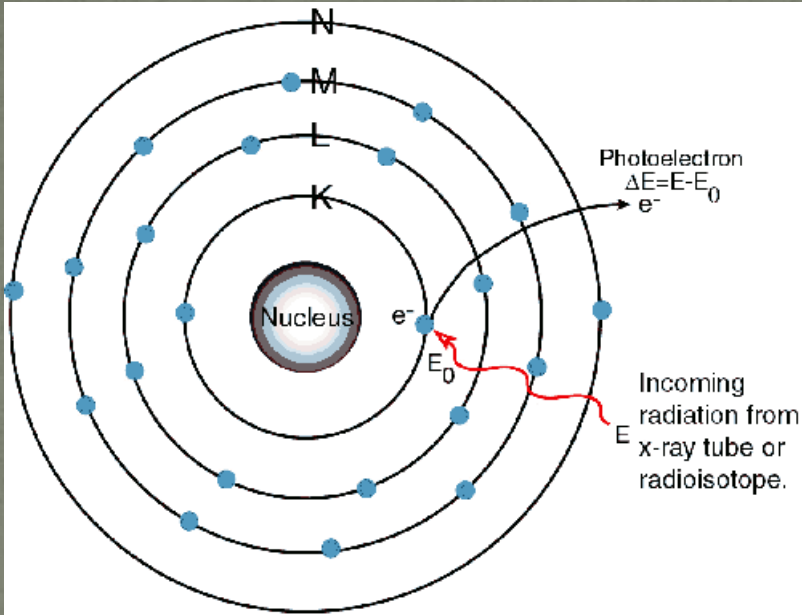
X-Ray FLUORESCENCE (XRF)



An X-Ray beam strikes a specimen and transfers part of its energy, in known quantities characteristic of the absorbing atom, to the bound electrons e^- of the inner shells producing the ejection of the e^- (photoelectric effect)



In the excited atom a transition is induced with consequent X-Ray emission. The emitted radiation has an energy and intensity related to the **type** and **abundance** of the **element** present in the involved sample.



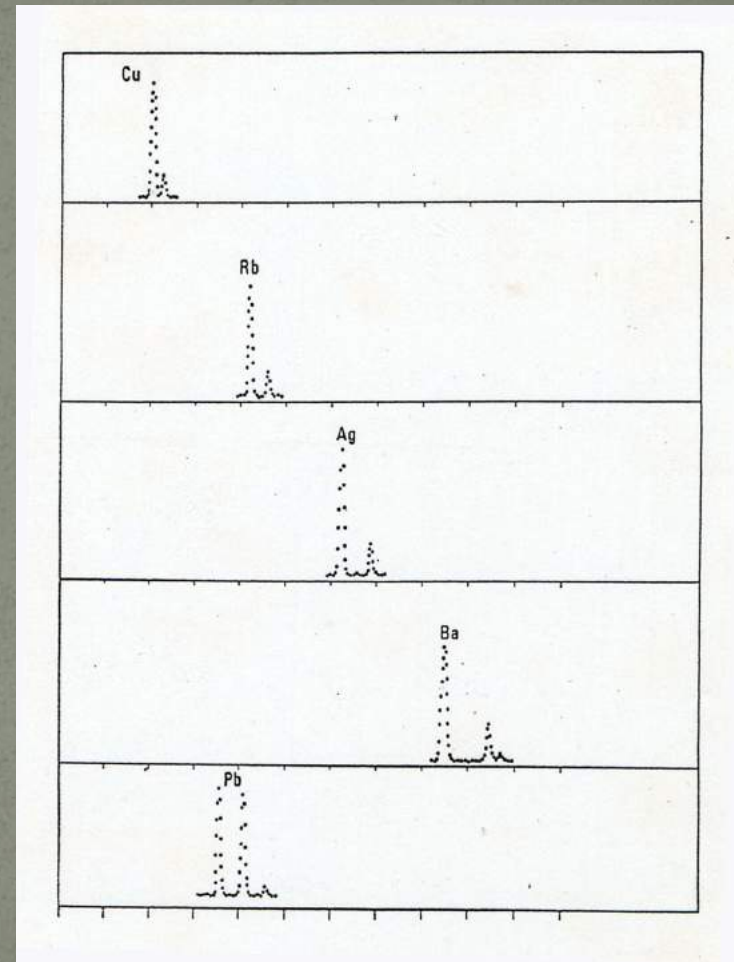
Z	ka keV	kb keV	La keV	Lb keV
Cu	8.04	8.90	0.93	0.95
Ag	22.01	24.94	2.98	3.15
Pb	74.22	84.92	10.55	12.61

XRF Spectrum

The result of the investigation is a plot named **XRF Spectrum** : in this diagram the **number** of characteristic X-Ray photons emitted by an element is plotted versus its **energy**.

Z	ka keV	kb keV	La keV	Lb keV
Cu	8.04	8.90	0.93	0.95
Ag	22.01	24.94	2.98	3.15
Pb	74.22	84.92	10.55	12.61

Emitted photons (Counts)

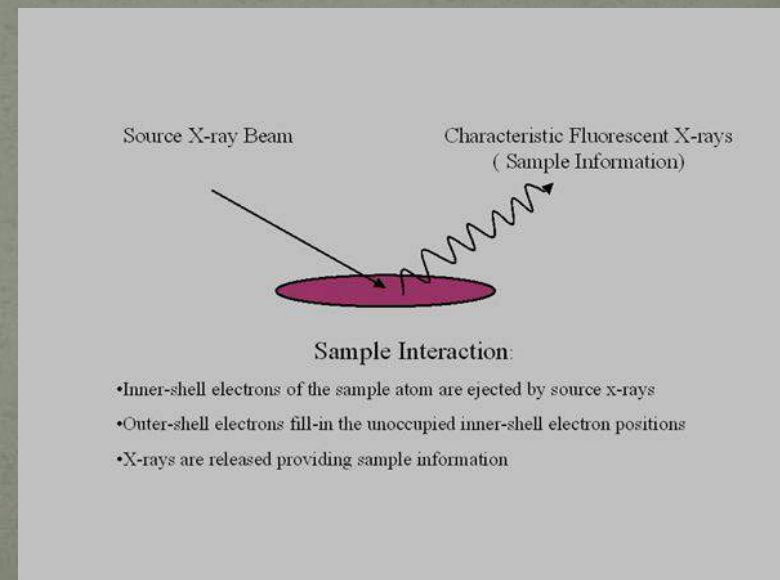


XRF

Photon's Energy (keV)

XRF Measurement

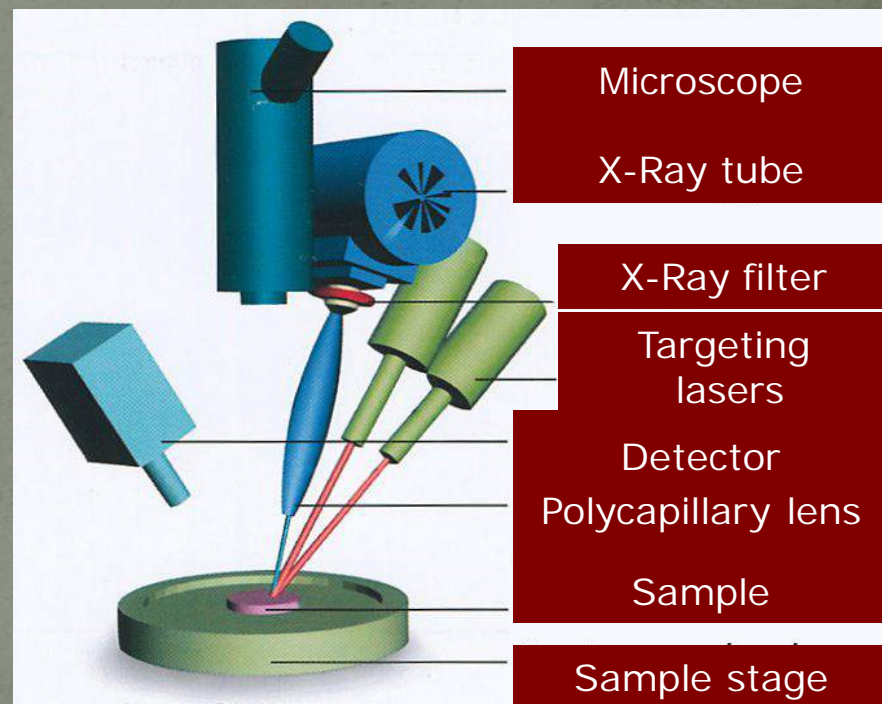
- Measurements are performed in short time (some hundreds of seconds)
- The information is related to a **superficial layer** of the specimen (fractions of some mm for metals to some cm for woods)
- The investigated **area** has the same dimension of the beam spot : depending on needs, this parameter can be reduced from **some cm²** to **mm² fractions**.



XRF spectrometer at LNF



Unisantis XMF 104



Measurement Geometry

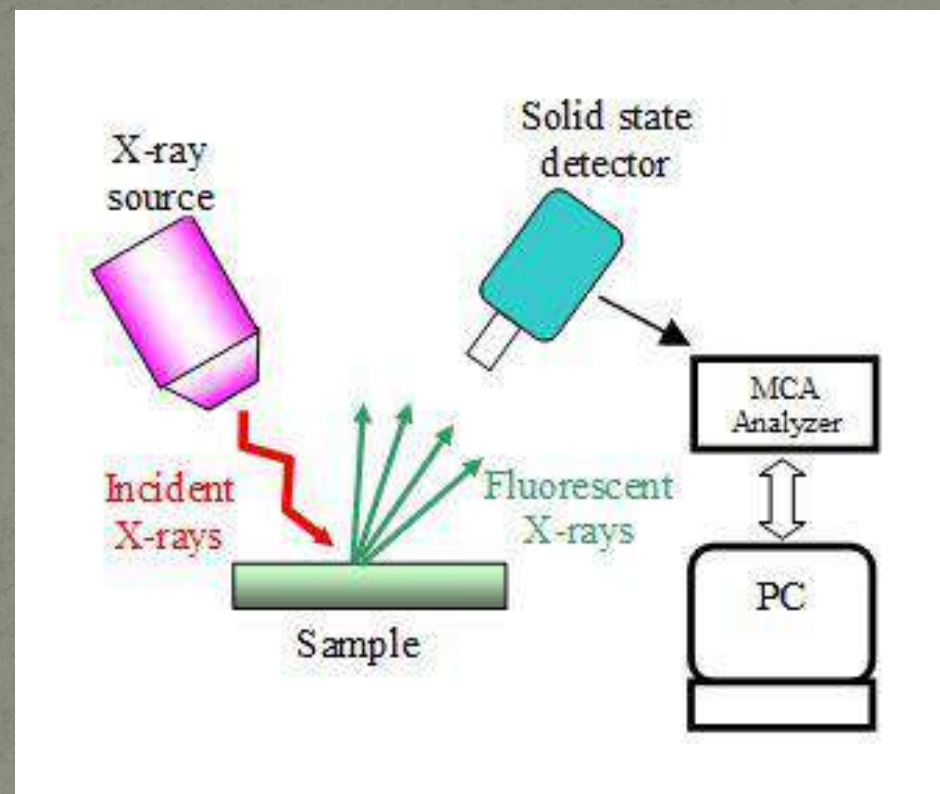
Information (XRF)

- Qualitative identification of the chemical elements present in the sample with weight percentage < some percentage
- Quantitative determination of the chemical elements \pm some percentage error in a specimen

Experimental Set-Up

- X-Ray tube (energy ≤ 60 keV)
- Sample
- Semiconductor detector Si(Pin) Peltier cooled
- Signal Amplifier
- Multichannel analyzer MCA (analog/digital converter)
- Acquisition and data processing system

Experimental Set-Up





Paintings



Metal artworks



Earthenware & pottery

XRF Applications

Stones & gems



Enamel & glass

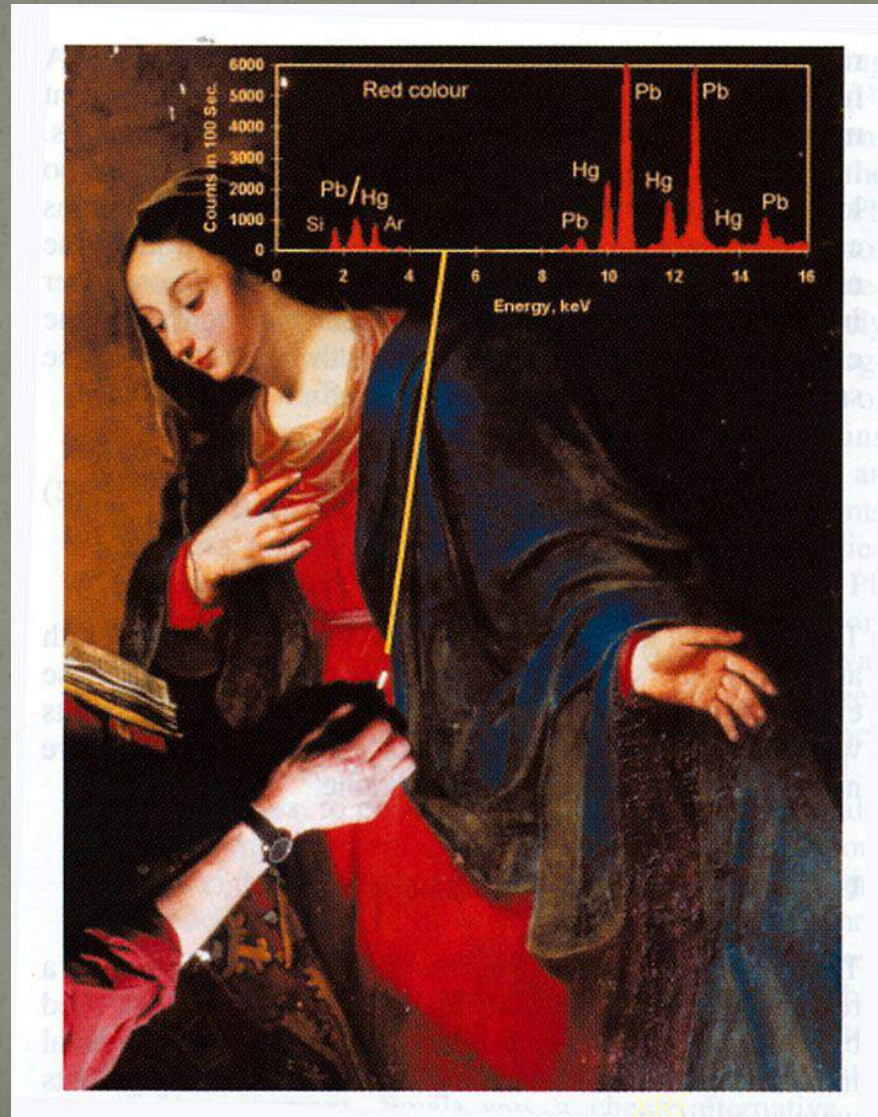


XRF painting

*qualitative
analysis*

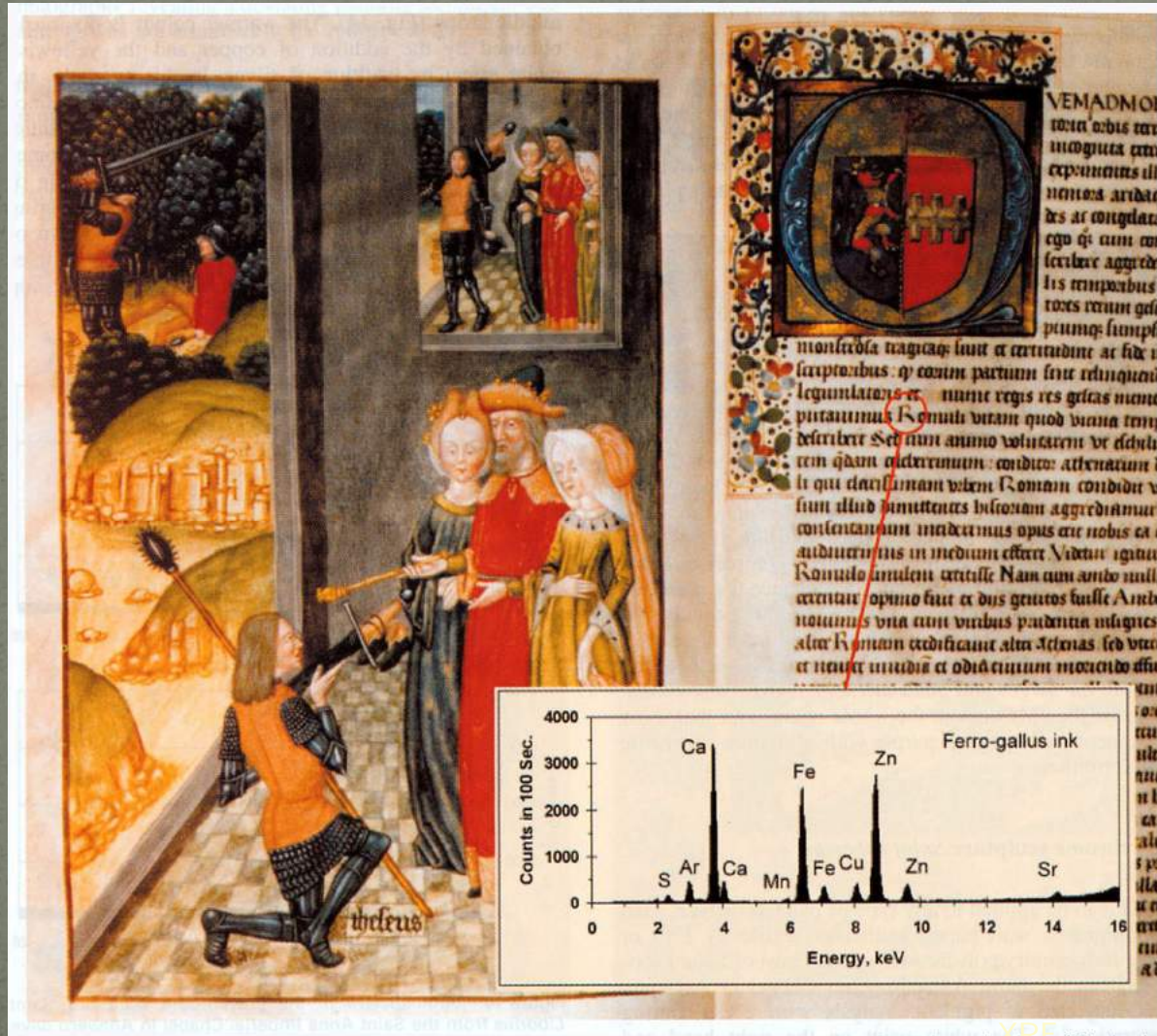
Vermilion:
grounded
Cinnabar HgS

White lead:
primer



Van den Heuvel
Annunciation
Saint Nicholas
Church , Ghent

XRF ink



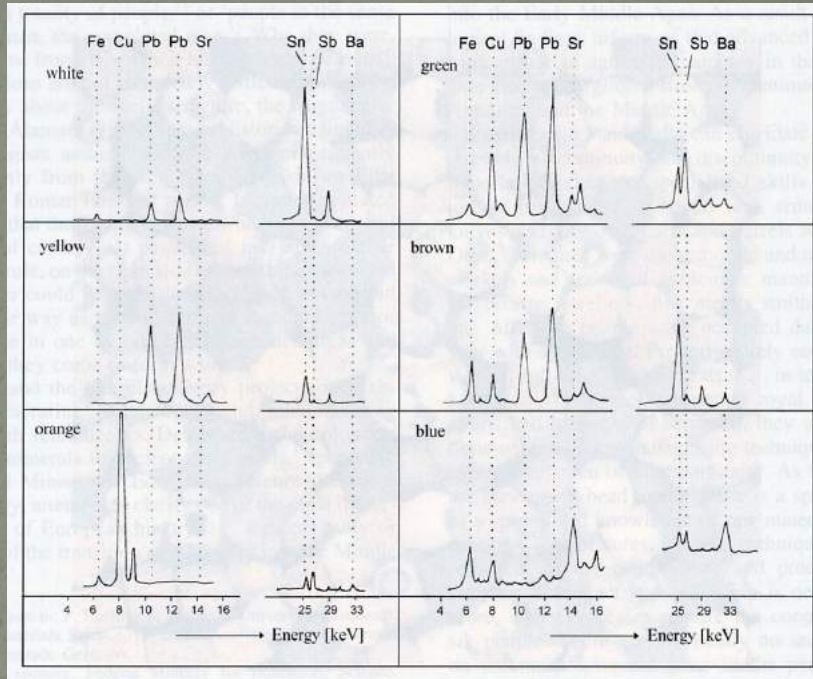
Raffaello de
Mercatellis
collection
Manuscript n.109
University Library,
Ghent

Qualitative analysis
Ferro-gallus ink
Fe+Zn salt in gallus
acid

XRF glass



Beads
Merovingian graveyards

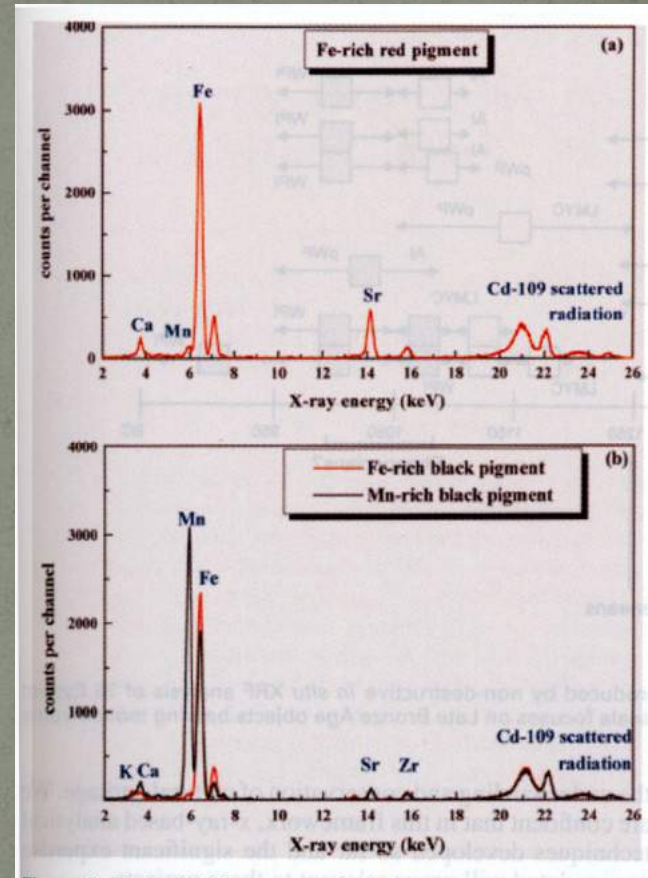


qualitative analysis
Colouring elements

XRF terracotta



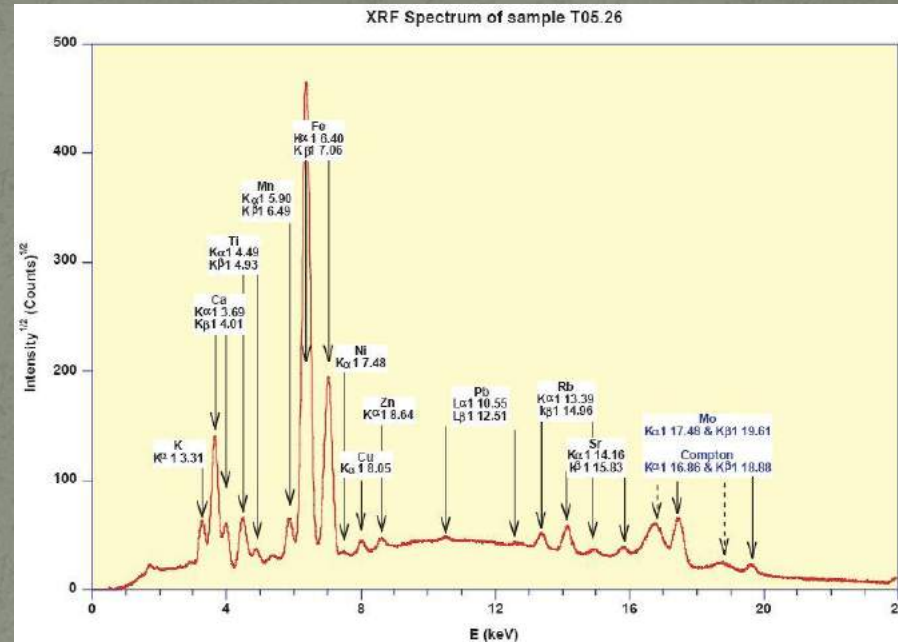
Chyroarchaic terracotta
Nicosia Museum



XRF pottery



Black glaze pottery
Lavinium (Pratica di Mare)

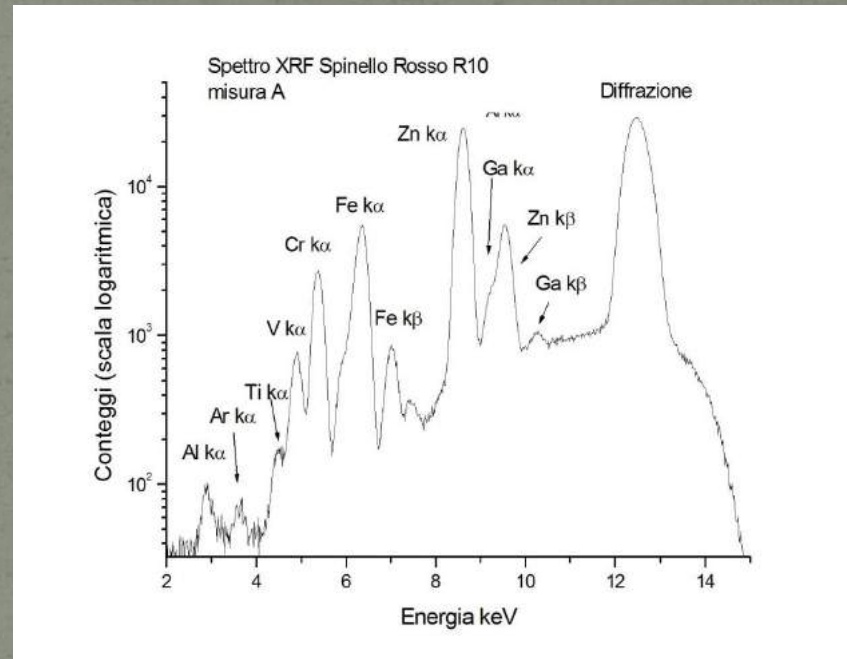


Quantitative analysis
Elements concentration determination

XRF gemstones



Red Spinel
 MgAl_2O_4



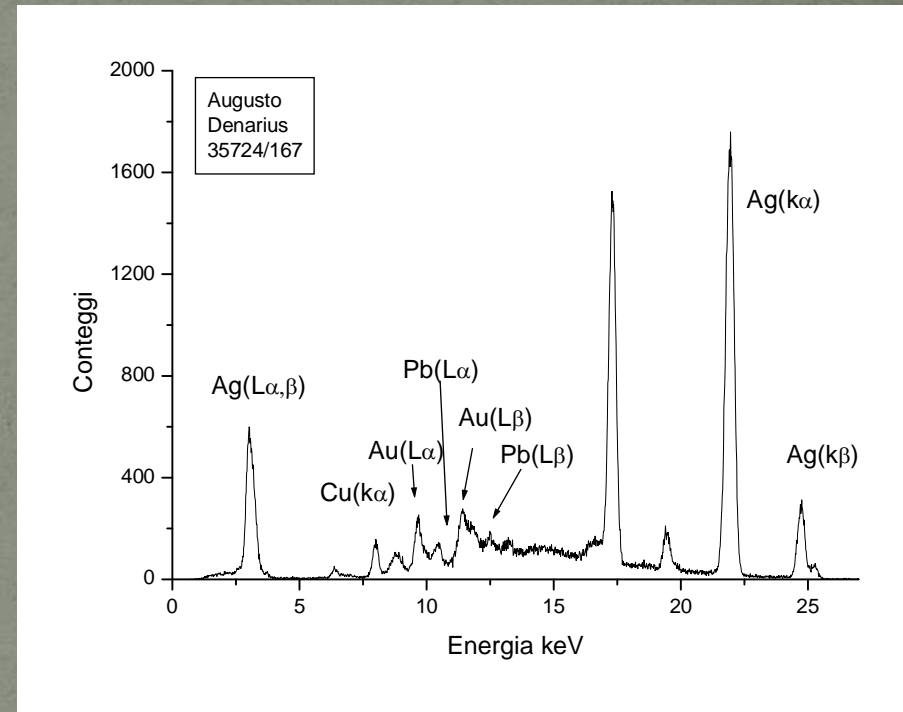
Quantitative analysis
determination of trace elements

XRF metals : coins

Denarius
Brundisium/Roma
29-27 BC
35724/167 – 3.67 g



National Archaeological Museum of Florence
Coin Cabinet

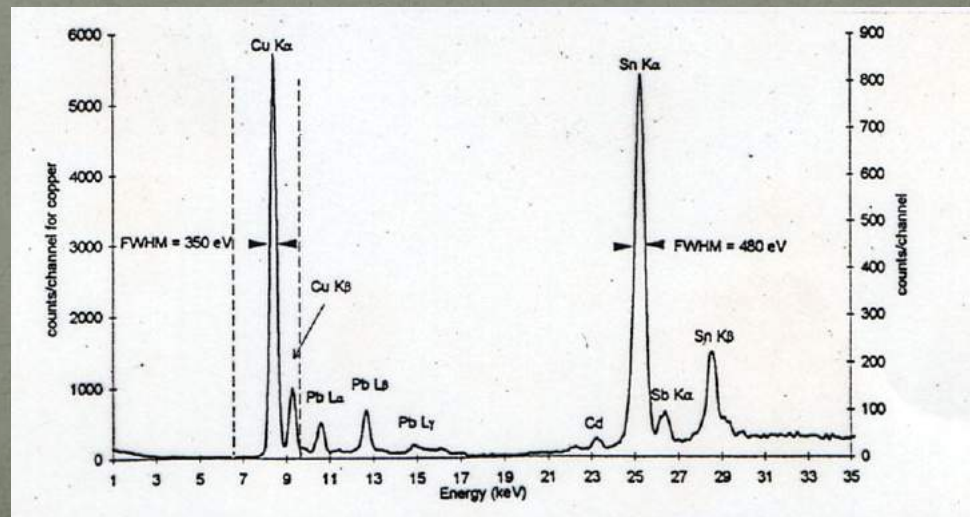
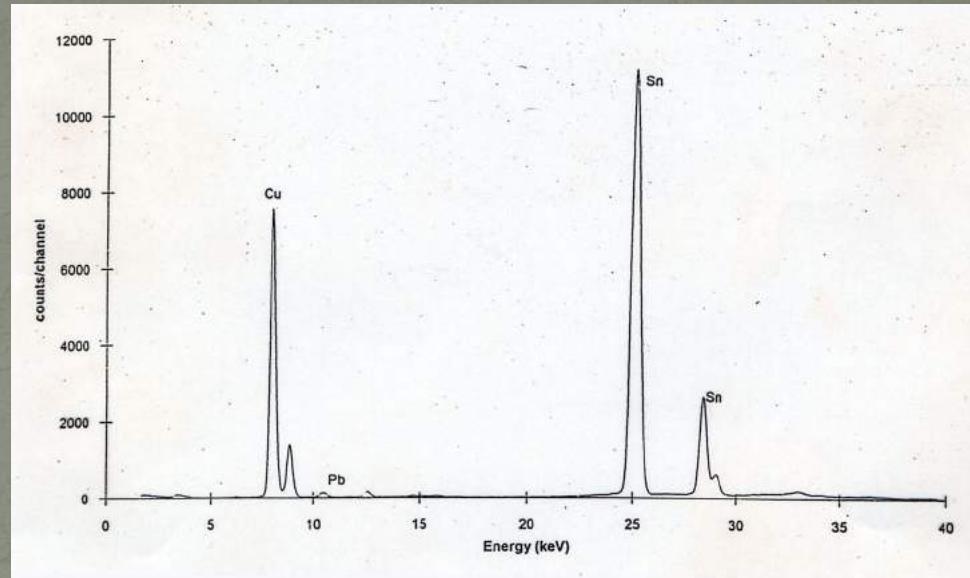


*Quantitative analysis
of the alloy*

XRF metals: statues

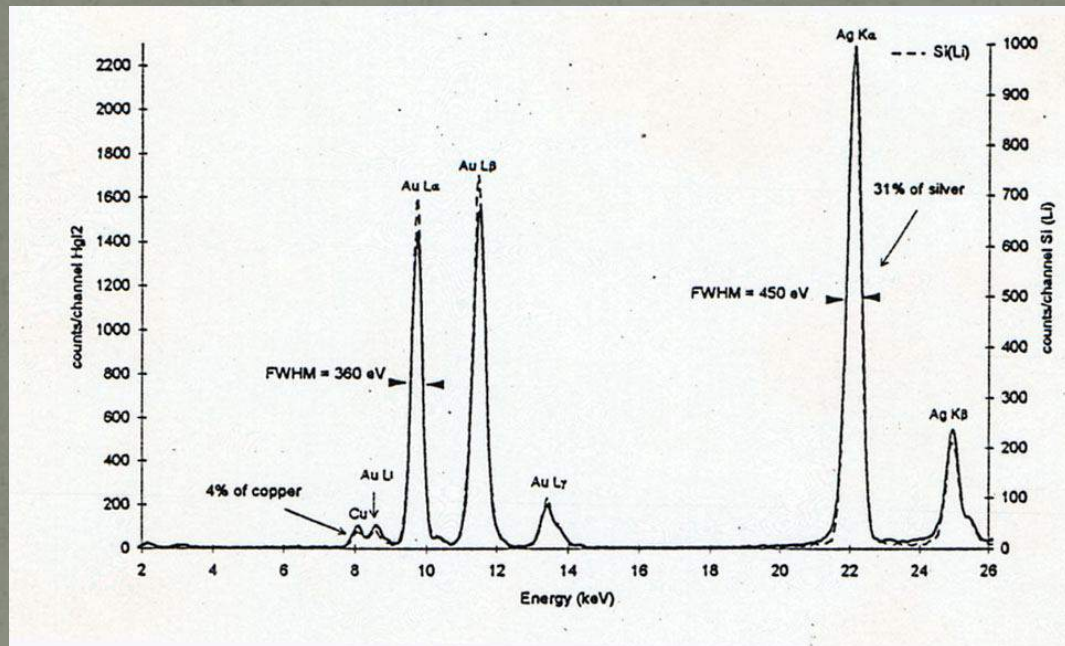
Alloy Different composition
Quantitative analysis
of the alloy

Typical spectrum of
a Nuragic bronze
(Pb < 1%)



Bronze object found
at Vivara Island (Na)

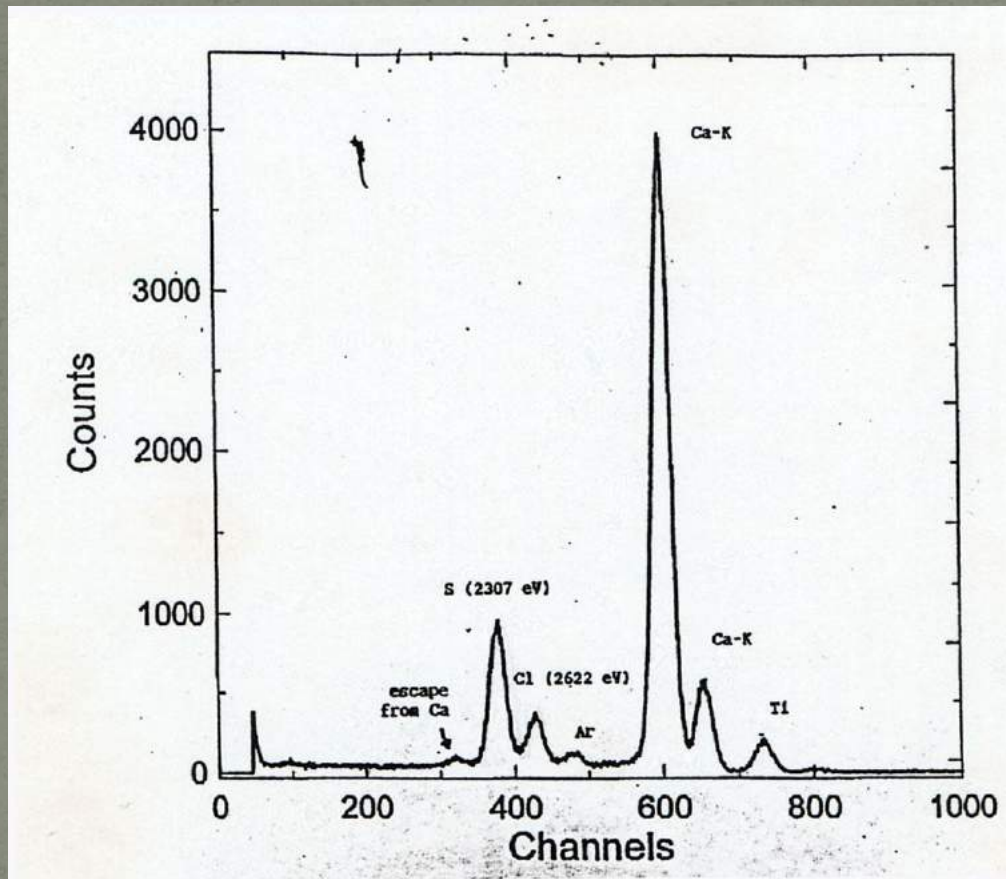
XRF metals: Jewellery



*Quantitative
analysis
of the alloy*

Etruscan **jewel** (Castellani Collection)
National museum of Villa Giulia

XRF pollution: frescoes



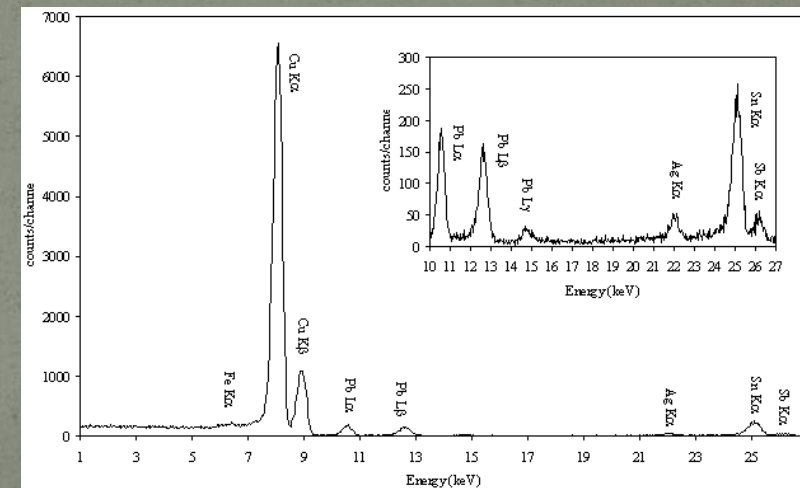
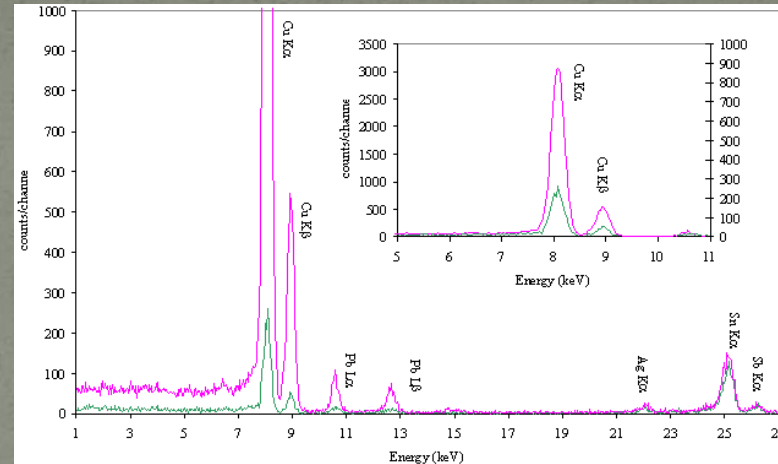
Qualitative analysis

Case study of S & Cl depositions on frescos, caused by air pollution
Detection down to 0.1% of S or Cl

XRF corrosion and patina: bronze



Cellini – **Perseus**
Signoria Circus, Florence

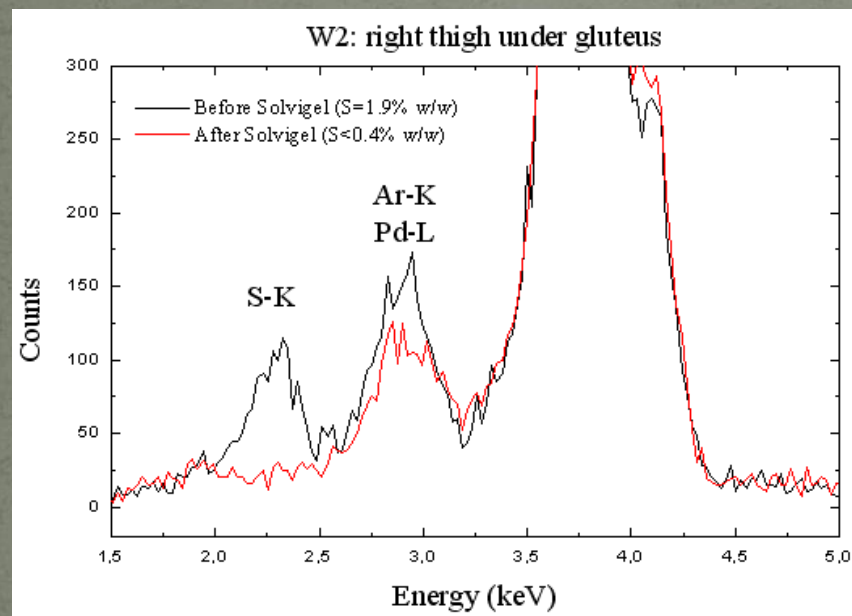


Qualitative analysis
Patina studies

XRF

XRF restore/preserve: marble

Solvent efficiency to remove sulfur



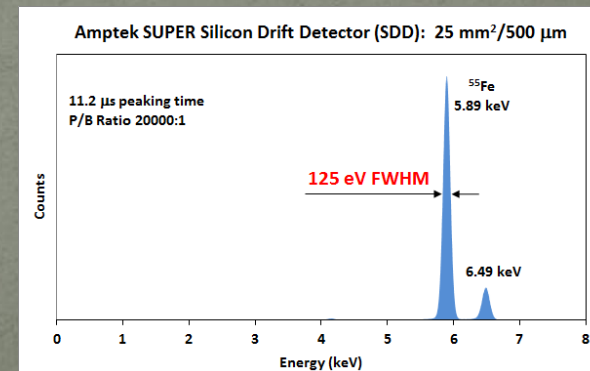
Qualitative analysis
Surface Cleaning studies

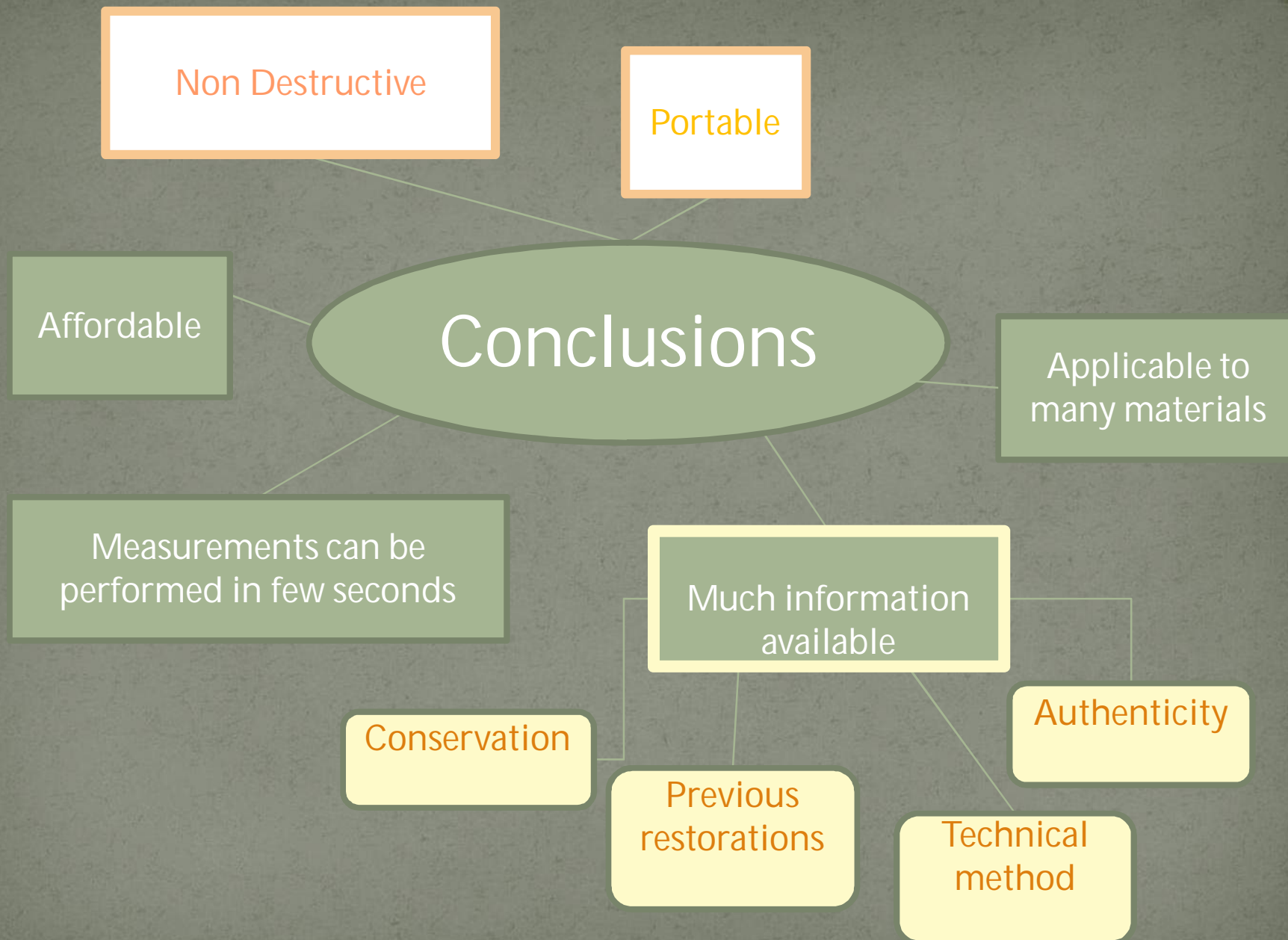


Michelangelo
Davide
Galleria dell'Accademia, Florence

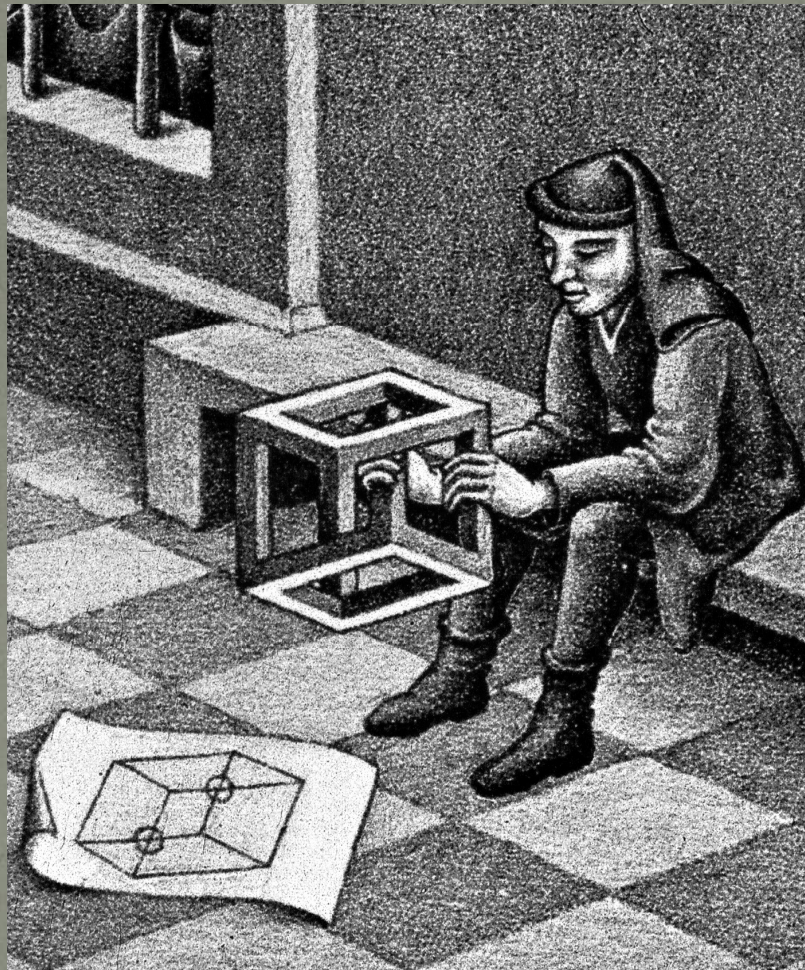
XRF Limits

- Light Chemical Elements (organic substances) not detectable
- Surface analysis: to study the bulk other techniques must be used
- Detector's resolution (>100 eV)





Thank you for your **attention**



http://padlet.com/astrikgorghinian/XRF_en

http://padlet.com/astrikgorghinian/XRF_it

M.C. Escher
Impossible Cube
(Necker's Cube)

Glossary

term	definition
atomic spectra	the electromagnetic emission from atoms and molecules
binding energy	also called the <i>work function</i> ; the amount of energy necessary to eject an electron from a material
bremsstrahlung	German for <i>braking radiation</i> ; produced when electrons are decelerated
Compton effect	the phenomenon whereby x rays scattered from materials have decreased energy
characteristic x rays	x rays whose energy depends on the material they were produced in
ionizing radiation	radiation that ionizes materials that absorb it
photoelectric effect	the phenomenon whereby some materials eject electrons when light is shined on them
photon energy	the amount of energy a photon has
photon	a quantum, or particle, of electromagnetic radiation
x ray	EM photon between γ -ray and UV in energy

Copies or alterations made with fraudulent intent fall into 4 main categories:

- **Forgery**= a whole new work in imitation of something else
- **Fake**=an object that has been altered such that it appears to be something else, usually more valuable
- **Pastiche**=something made up of unrelated pieces
- **Genuine**=object that has been deceptively restored, such that serious damage is hidden or disguised

Bibliography

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- <https://courses.candelalearning.com/colphysics/chapter/29-3-photon-energies-and-the-electromagnetic-spectrum/>
- P. Craddock, Science Investigation of copies, fakes and forgeries, 2009 Elsevier
- <http://xdb.lbl.gov/>
- <http://quest.nasa.gov/aero/planetary/archimedes>

Mach-up

Alloy	Earthenware	Pollution
Analog	Electron ejection	Preservation
Artwork	Fresco	Qualitative analysis
Bead	Gemstone	Quantitative analysis
Coin	Glaze	Radiation source
Conservation	Imprimatur	Sample
Conservative science	Investigation	Semiconductor
Cultural Heritage	Layer	Specimen
Detector	Non Invasive	Spectrum
Diagnostic	Non Destructive	