X-ray spectrometry at external-beam IBA facilities for cultural heritage applications

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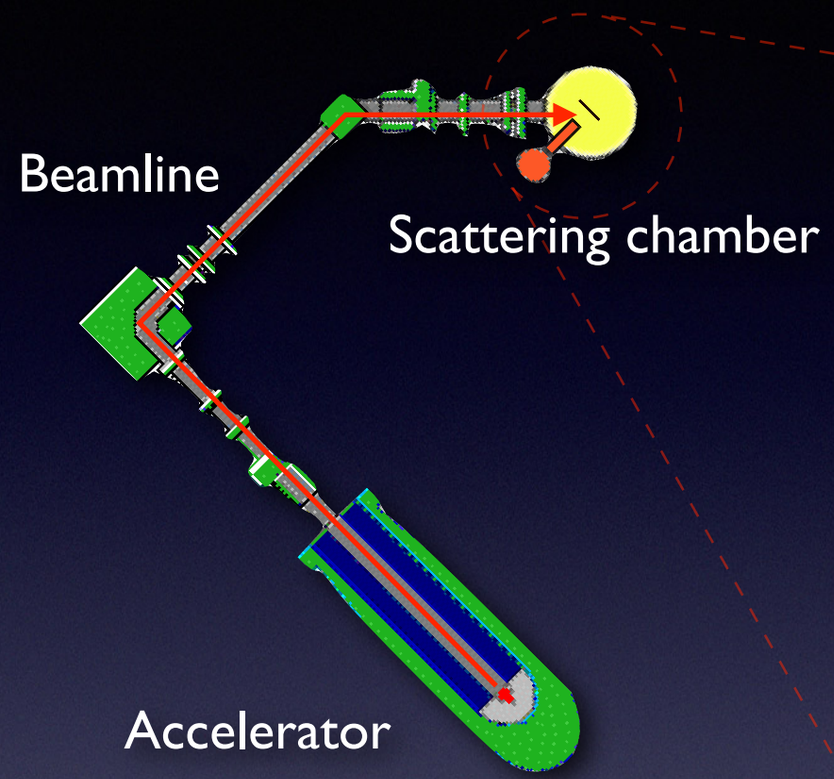
Joint ICTP-IAEA Workshop on "Advances in X-ray Instrumentation for Cultural Heritage Applications"
Trieste (Italy), 13 - 17 July, 2015

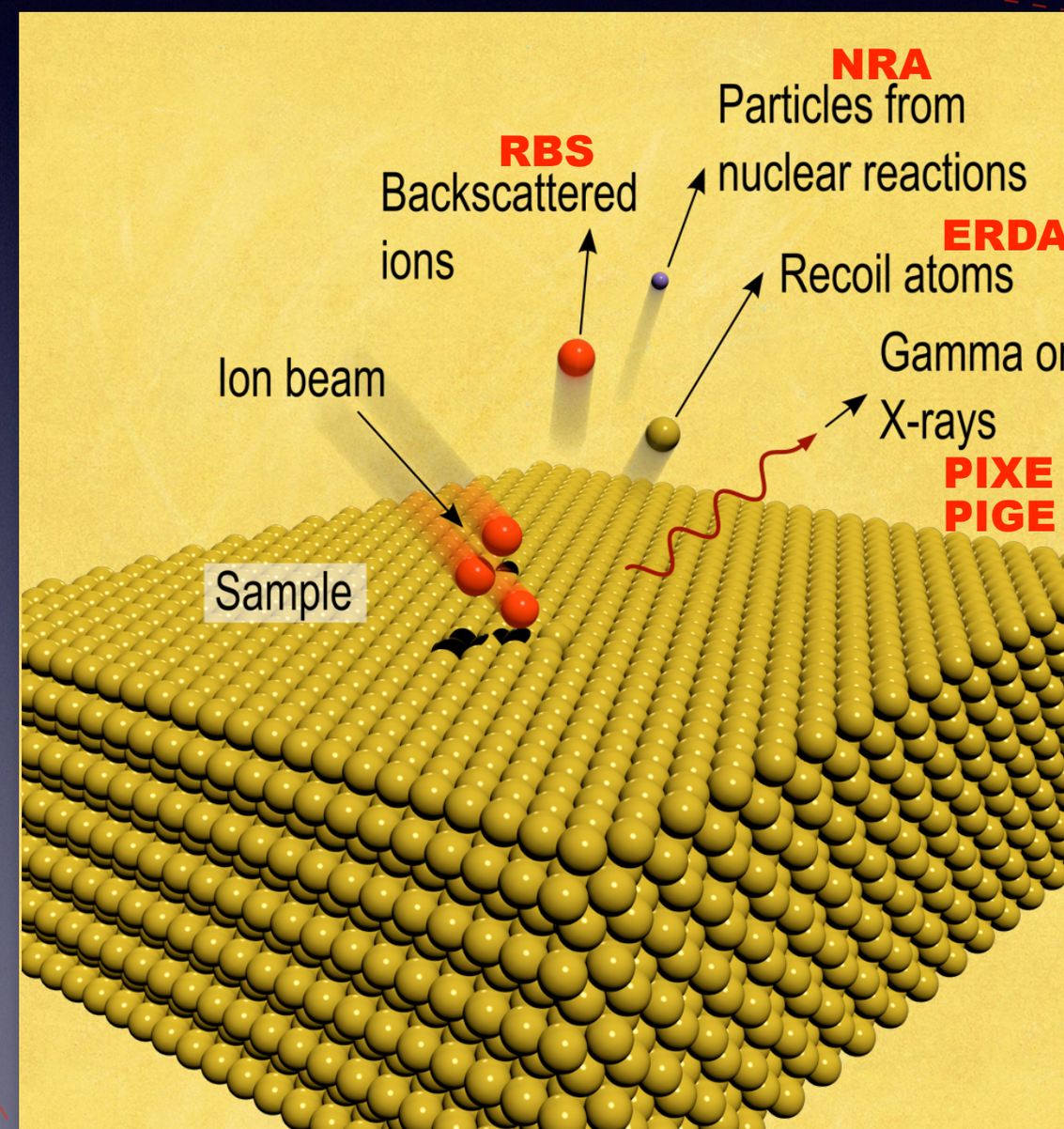
Outline

- Introduction to Ion Beam Analysis and to Particle Induced X-ray Emission technique
- External beams
- External-beam PIXE analysis of Cultural Heritage
- Synergy with other IBA techniques

Ion Beam Analysis techniques



Beam IN	Beam OUT	Analytical technique
ion	ion	RBS, NRA
ion	target	ERDA, SIMS, SNMS
ion	X-ray	PIXE
ion	Gamma-ray	PIGE, Activation Analysis
ion	hν	Ionoluminescence (IL)



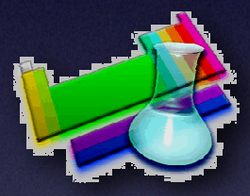
General features of IBA

- Multielemental
- Quantitative analysis ("traceability")
- High sensitivity (1-100 ppm in at/cm^3; 10^{11}-10^{12} in at/cm^2)
- Surface analysis (10 Å - 10 μm)
- Depth profiling
- Non-destructive
- No sample pre-treatment
- Microanalysis (lateral resolution <1 μm)
- 2D mapping

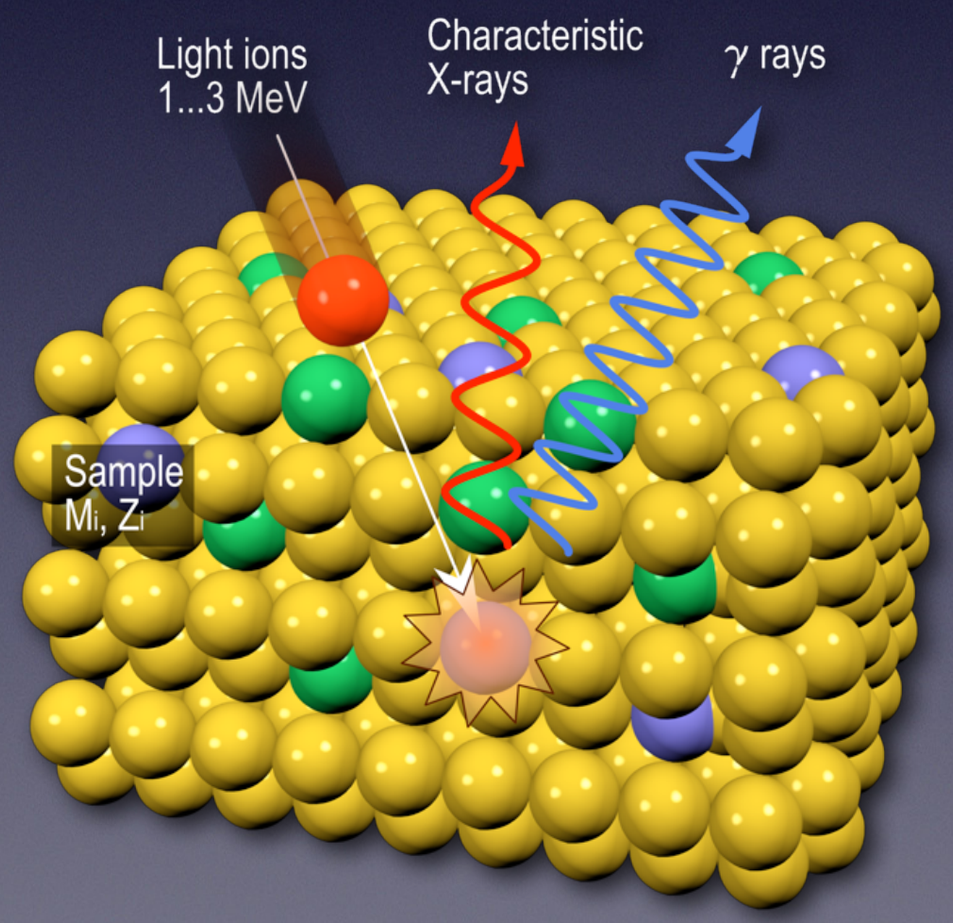
PIXE

Particle Induced X-ray Emission

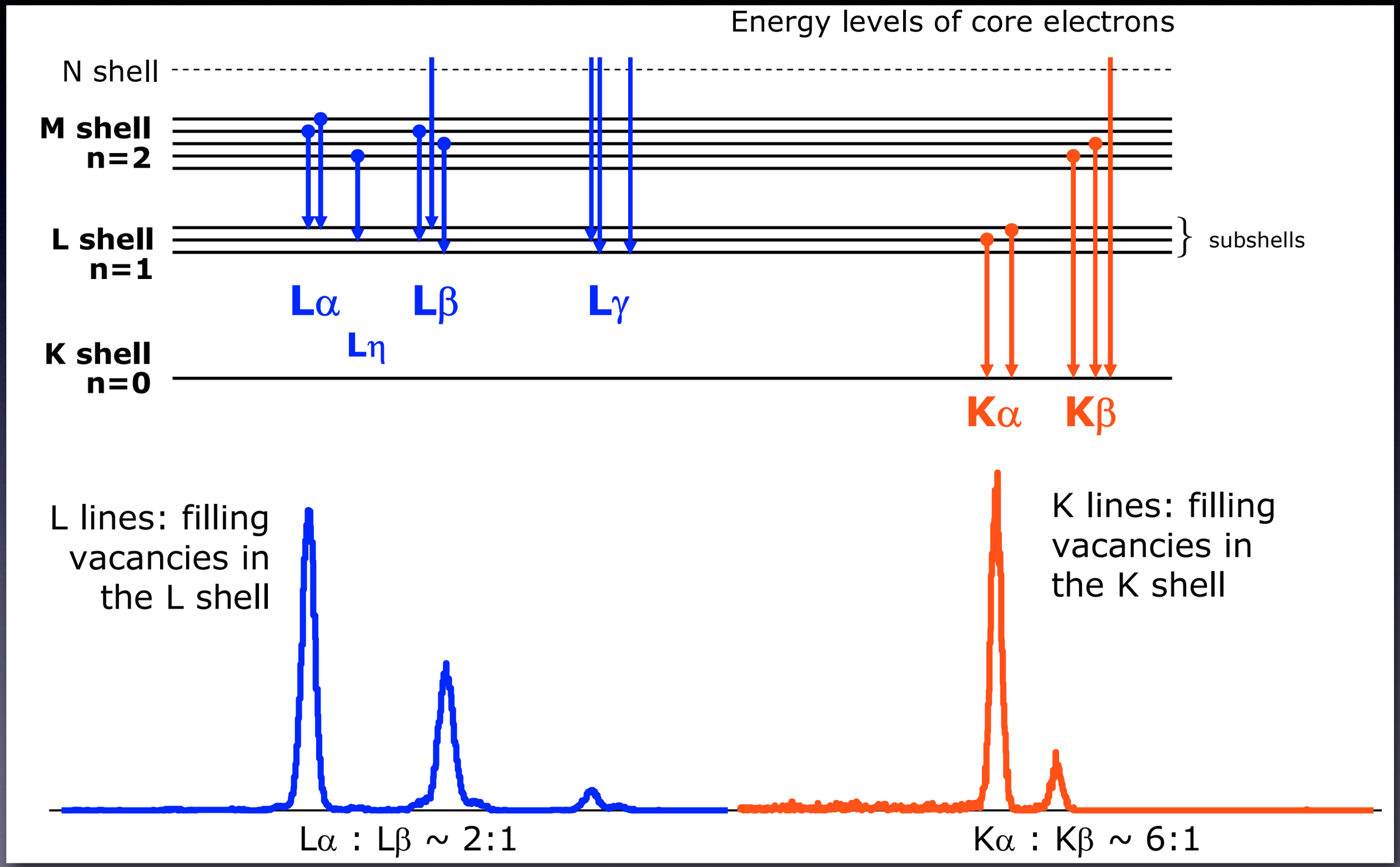
Emission of characterisic X-rays following ioniziation from incident ions



Z>10



Energy of characteristic X-rays



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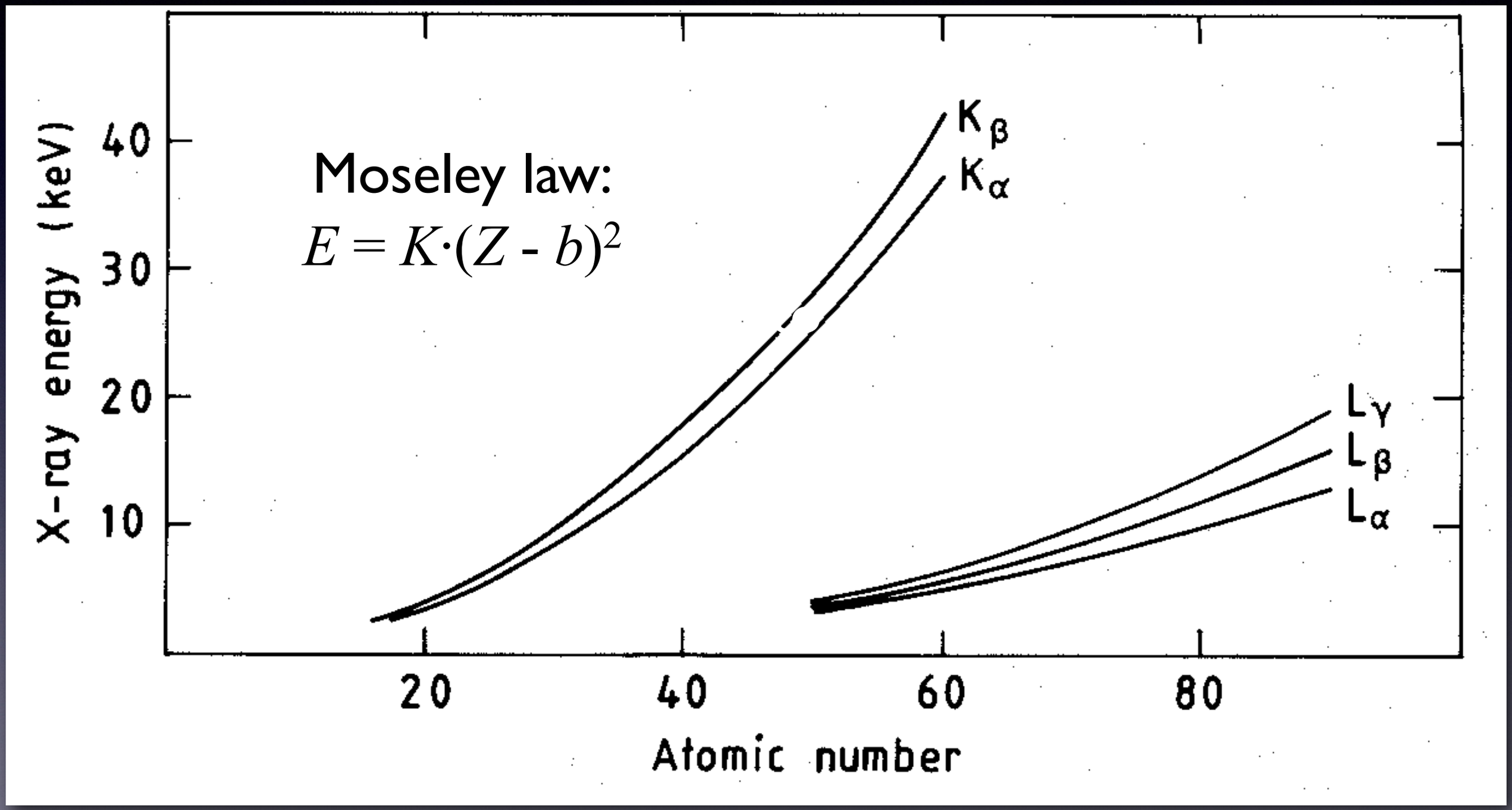
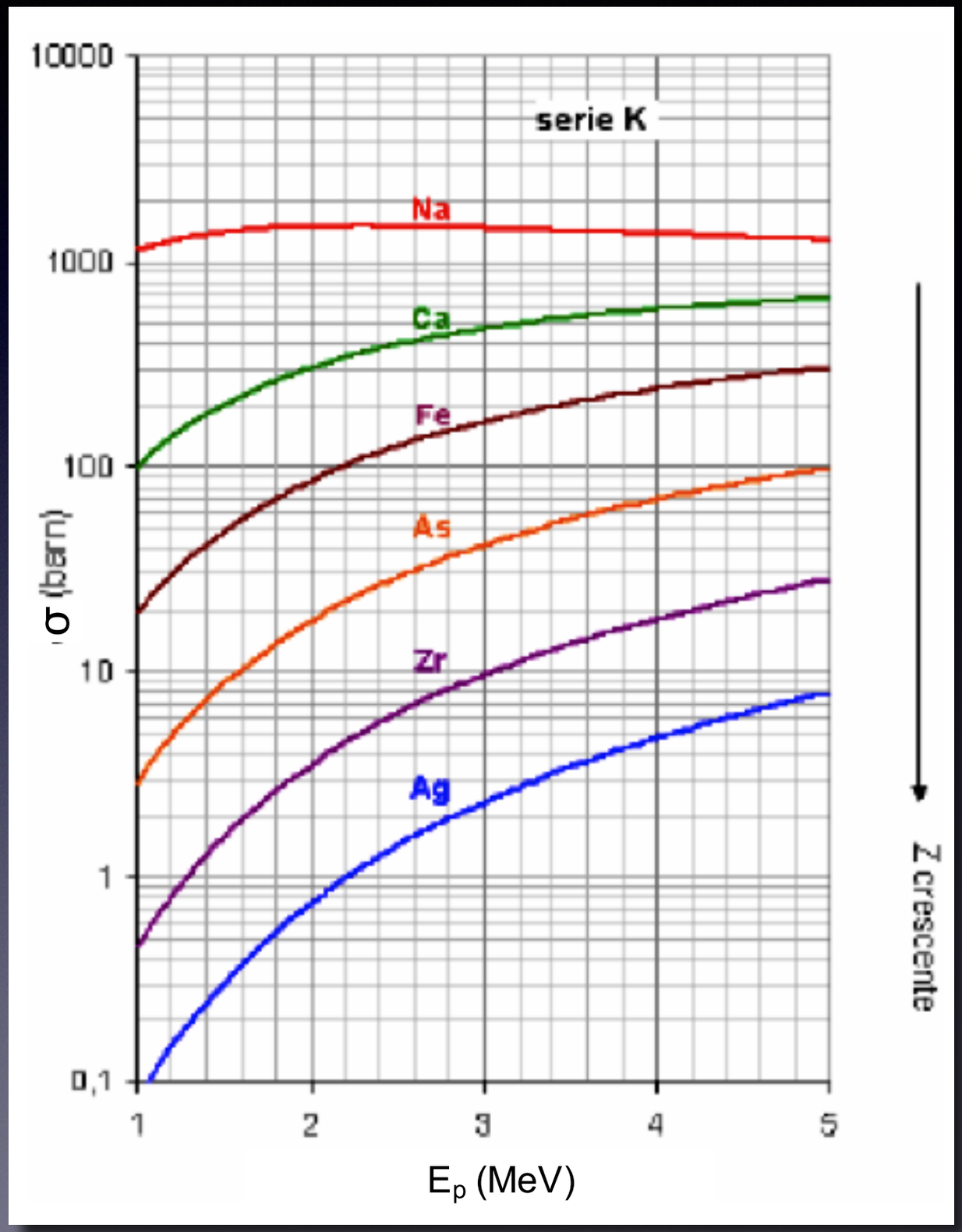
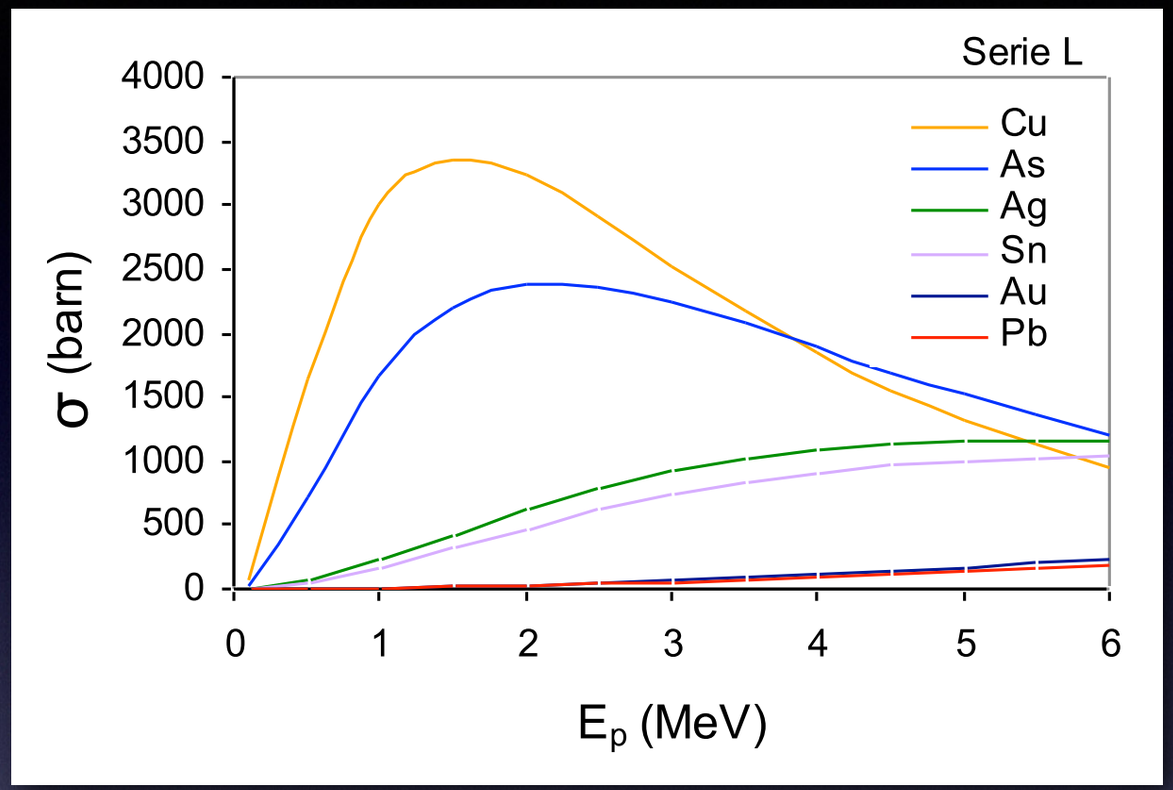
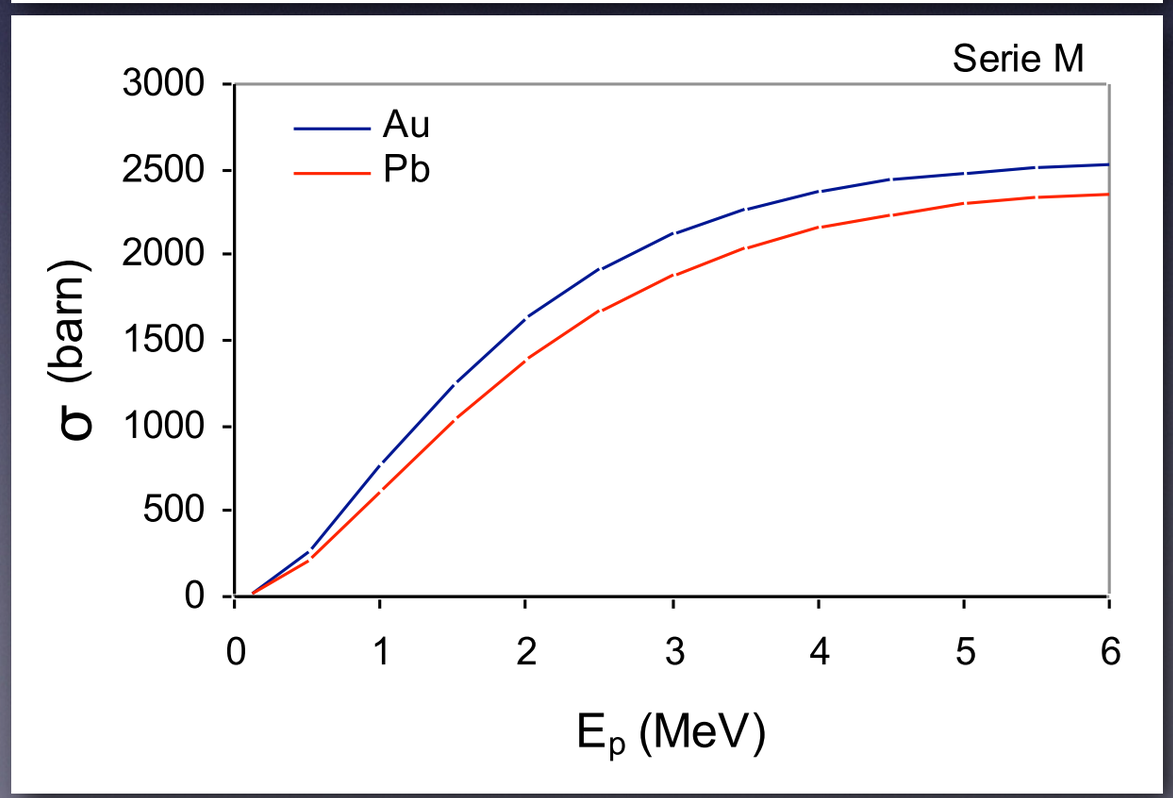


X-ray production cross sections







Adavantages of PIXE

Among IBA techniques, PIXE is a "killer application" for the non-destructive analysis of cultural heritage object since it is highly sensitive over a broad range of elements and it can be performed with external beams while maintaining the object in atmosphere, avoiding the need of picking up samples and greatly easing the object positioning, thus precious and big artefacts can be studied

- Very fast, high-sensitivity, **non-destructive** analysis
- **Quantitative** analysis
- Minimum energy of detected X-rays tipically ~1 keV

➡ *all the elements with $Z \geq 11$ are quantifiable simultaneously*

Limitations of PIXE

- No information on the organic components
- No information on chemical states
- No structural information
- Surface analysis (problems with altered objects)
- No direct information on the stratigrapgy and the depth distribution of the elements

What PIXE can do for cultural heritage?

- Materials identification

  ➡ *analysis of major elements by PIXE (and PIGE)*

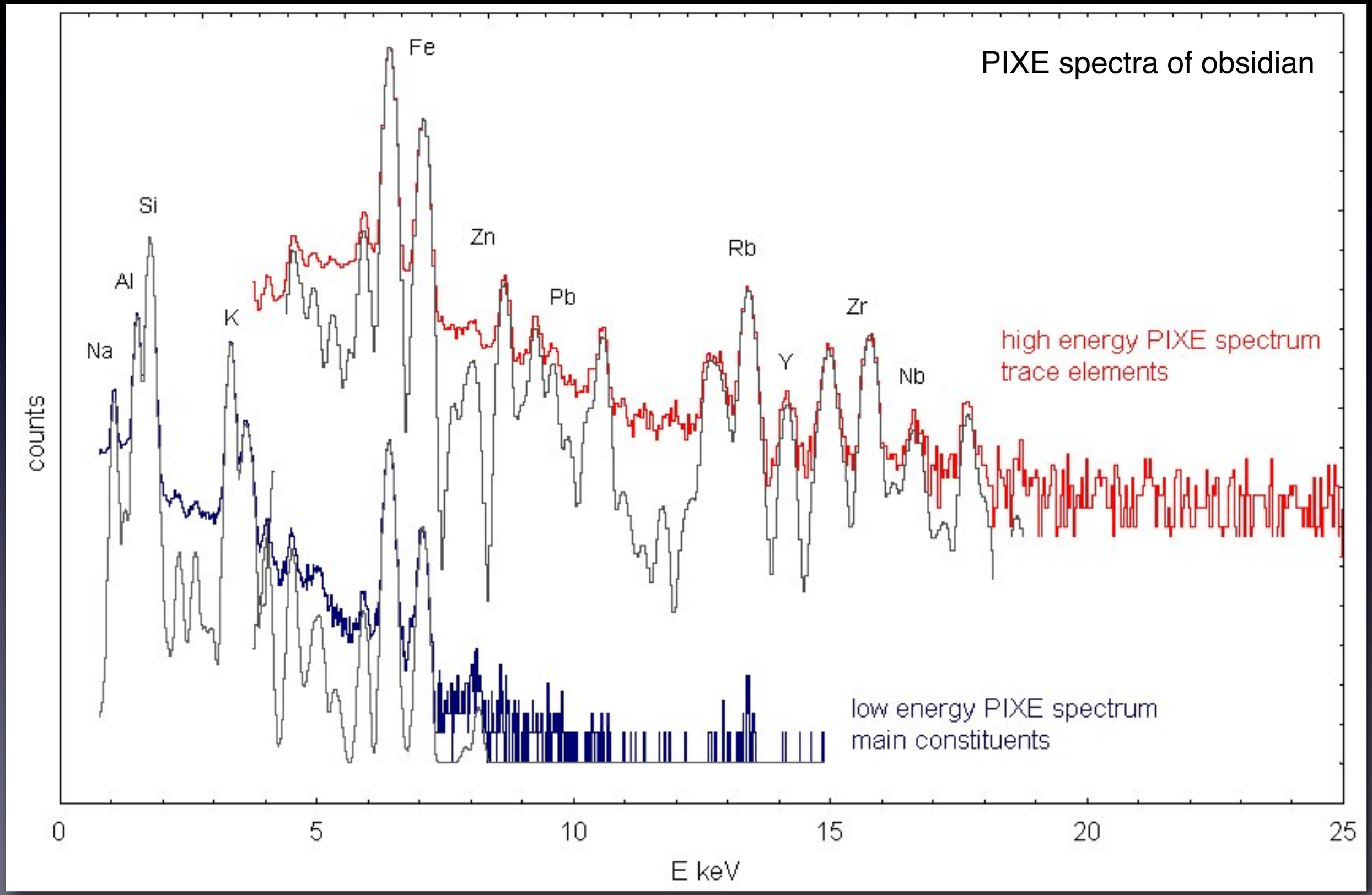
- Materials provenance
  (sources of raw materials and trade routes)

  ➡ *analysis of trace elements by PIXE*

- Manufacture technology

  ➡ *high spatial resolution: lateral by μ-PIXE (in-depth by RBS)*

Example of PIXE spectra



PIXE quantitative analysis (thin targets)

$$Y_0(Z) = N_P \cdot N_Z \cdot t \cdot \sigma_{Z,E0} \cdot (\alpha_Z \cdot \varepsilon_Z \cdot \Delta\Omega/4\pi)$$

$$Y_0(Z) = (Q/e)(N_A/A)(\rho_Z t) \cdot \sigma_{Z,E0} \cdot (\alpha_Z \cdot \varepsilon_Z \cdot \Delta\Omega/4\pi)$$

defining $\eta_Z = (1/e)(N_A/A) \cdot \sigma_{Z,E0} \cdot (\alpha_Z \cdot \varepsilon_Z \cdot \Delta\Omega/4\pi)$

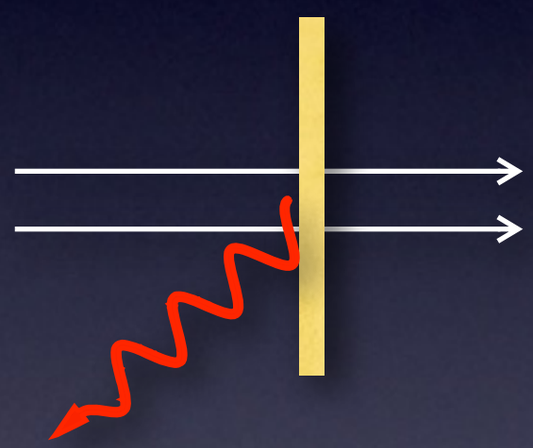
$$Y_0(Z) = \eta_Z \cdot Q \cdot (\rho_Z t)$$

Sensibility (counts/μC/(μg/cm²))

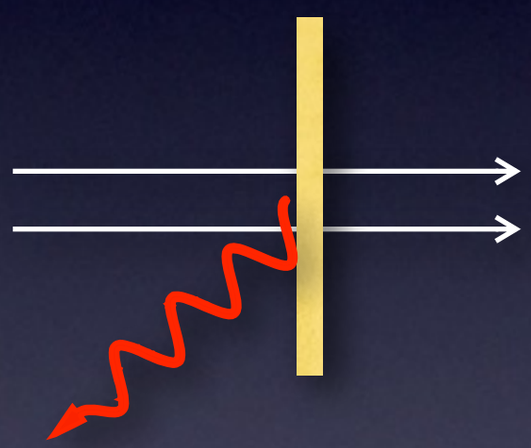
$$(\rho_Z t) = Y_0(Z) / (\eta_Z \cdot Q)$$

PIXE quantitative analysis by comparison with thin elemental standards

Sample



Standard

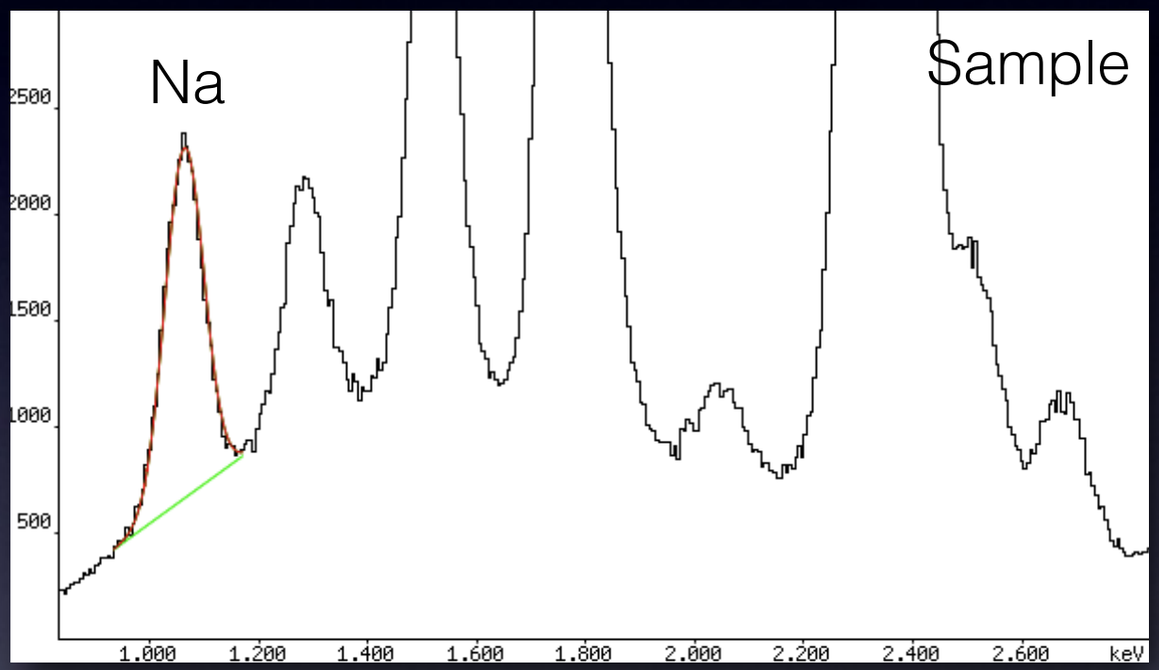


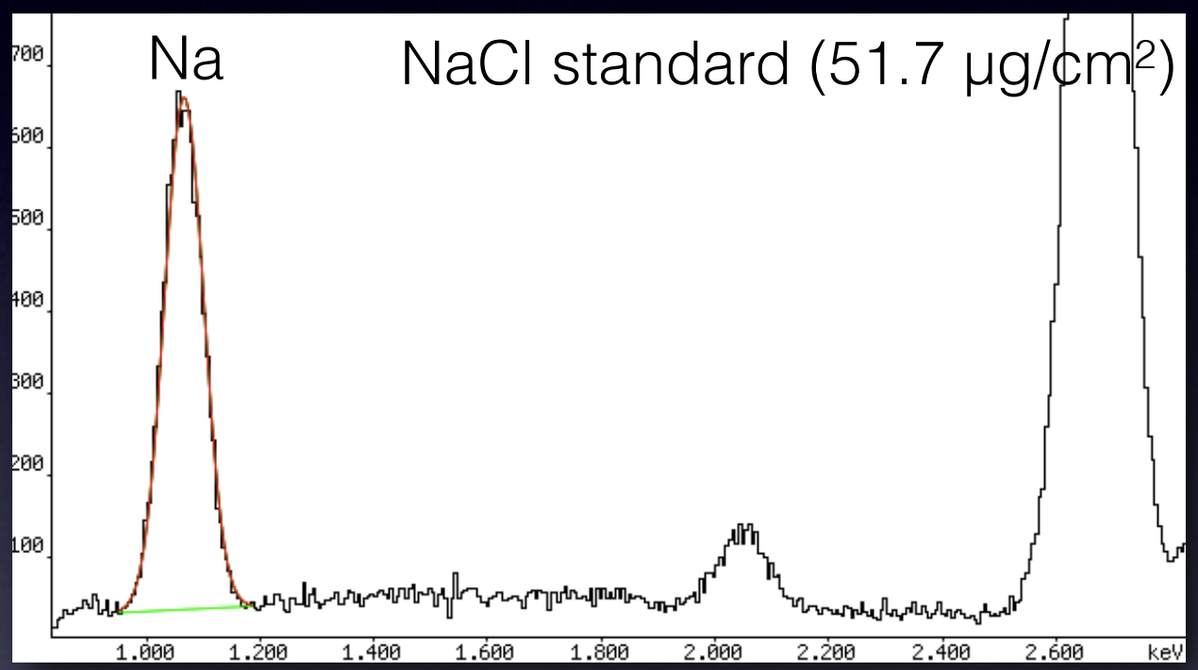
$$Y_0(Z)_{sample} = \eta_Z \cdot Q_{sample} \cdot (\rho_Z t)_{sample}$$

$$Y_0(Z)_{std} = \eta_Z \cdot Q_{std} \cdot (\rho_Z t)_{std}$$

$$(\rho_Z t)_{sample} = (\rho_Z t)_{std} \cdot [Y_0(Z)_{sample} / Y_0(Z)_{std}] \cdot (Q_{std} / Q_{sample})$$

Quantitative analysis by comparison with thin elemental standards





$$Y_0(Z)_{sample} = A_{Z,sample} \cdot 1/(1\text{-}DT_{sample}) \cdot 1/(1\text{-}PU_{sample})$$

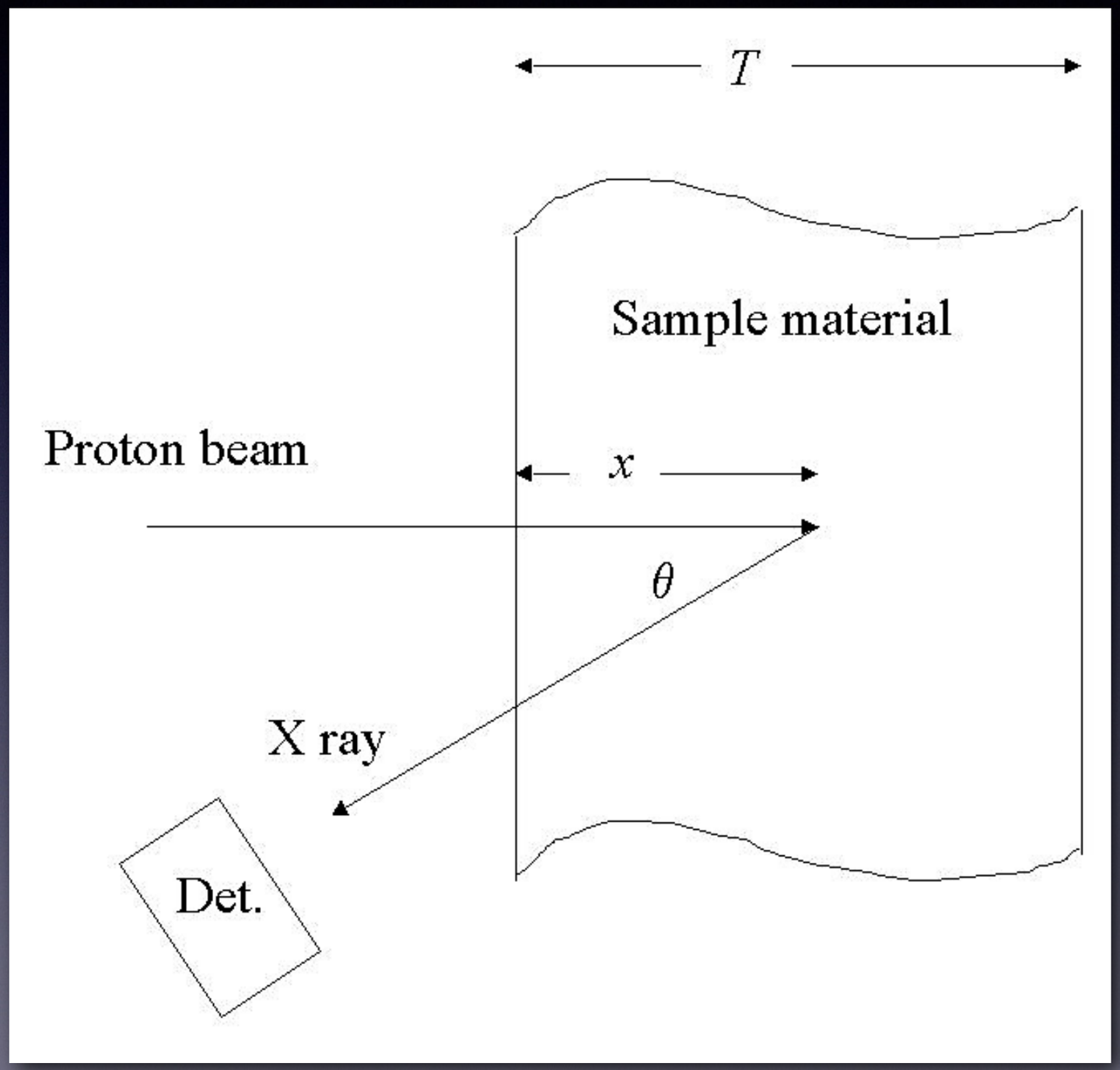
$$Y_0(Z)_{std} = A_{Z,std} \cdot 1/(1\text{-}DT_{std}) \cdot 1/(1\text{-}PU_{std})$$

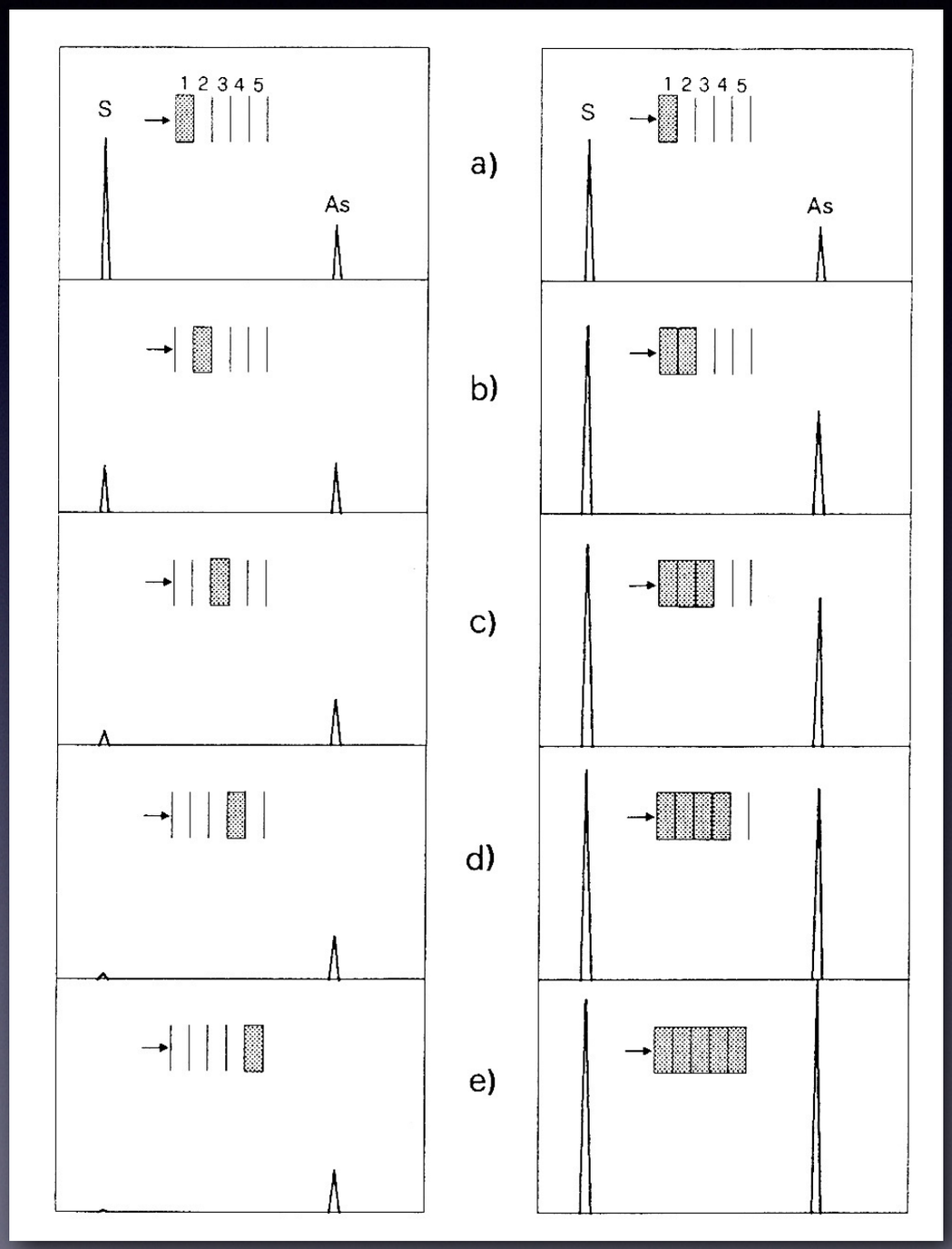
X-ray peak area

Dead time fraction

Pile-up fraction

Thick targets





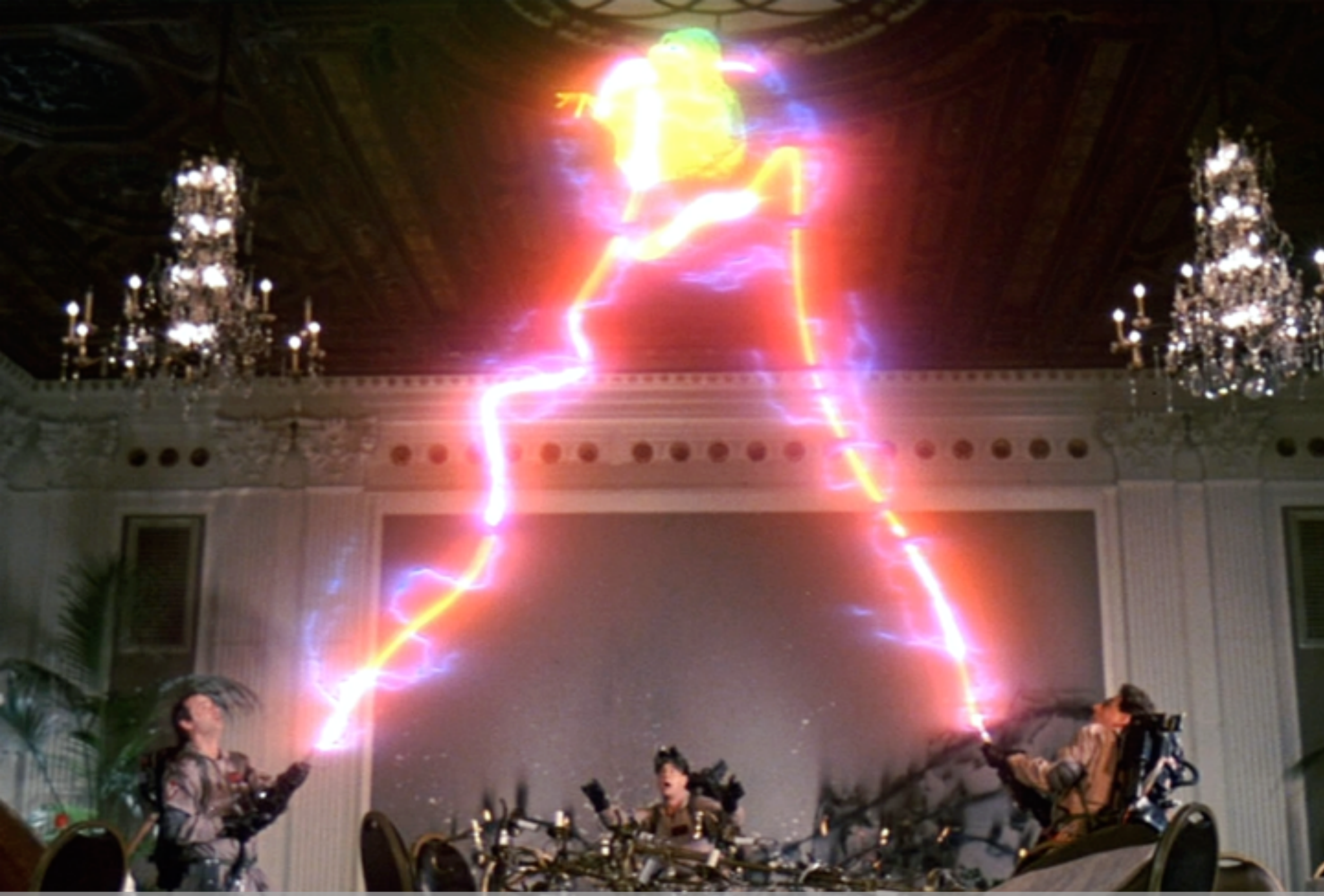
Quantitative analysis (thick targets)

$$Y(Z) = (Q/e)(N_A/A)(\alpha_Z \cdot \varepsilon_Z \cdot \Delta\Omega/4\pi) \cdot \rho_Z \int_0^T \sigma_{Z,E} \cdot \exp(-\mu \cdot x/\cos\theta) \cdot dx$$

$$Y(Z) = (Q/e)(N_A/A)(\alpha_Z \cdot \varepsilon_Z \cdot \Delta\Omega/4\pi)(\rho_Z/\rho) \int_{E_0}^{E_F} \sigma_{Z,E} \cdot \exp(-\mu \cdot x/\cos\theta) \cdot dE/S(E)$$

$$F(Z) = Y_0(Z)/Y(Z) = \frac{\rho \cdot T \cdot \sigma_{Z,E0}}{\int_{E_0}^{E_F} \sigma_{Z,E} \cdot \exp(-\mu \cdot x/\cos\theta) \cdot dE/S(E)}$$

$$\boxed{(\rho_Z t) = F(Z) \cdot Y(Z) / (\eta_Z \cdot Q)}$$

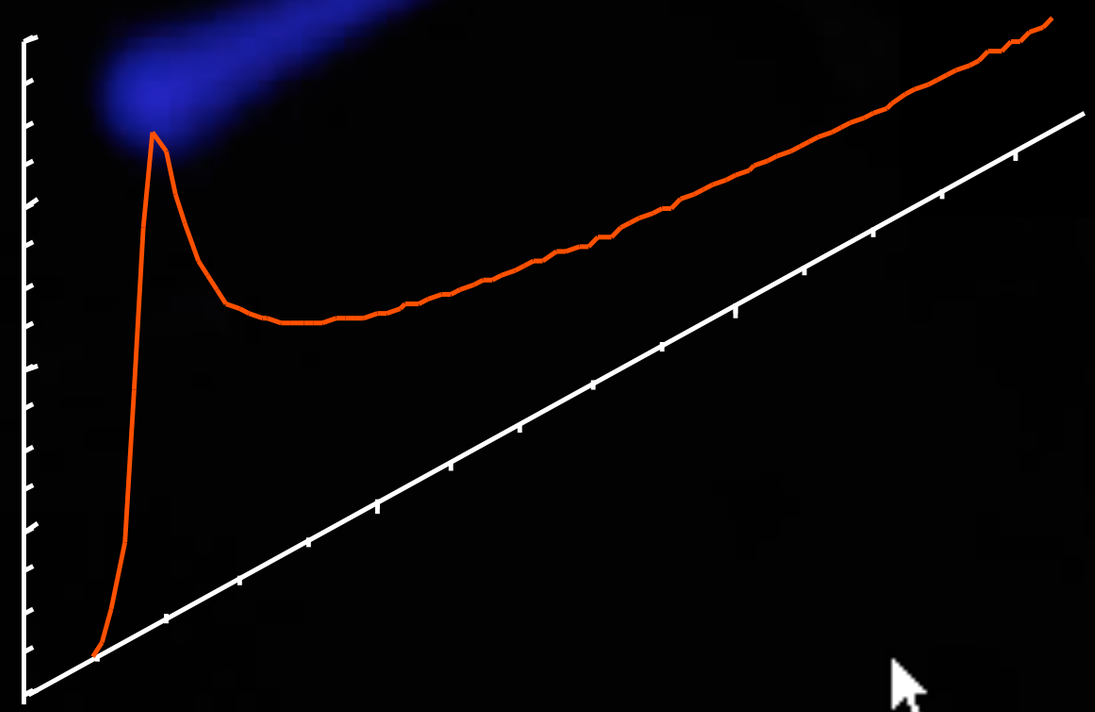


Do extracted ion beams look like these?

External ion beam

Advantages

- direct analysis of artefacts having any shape and any size
- no sampling
- no charging, no preparation (conductive coating etc.)
- no heating, reduced damage risk
- easy sample positioning
- fast and efficient



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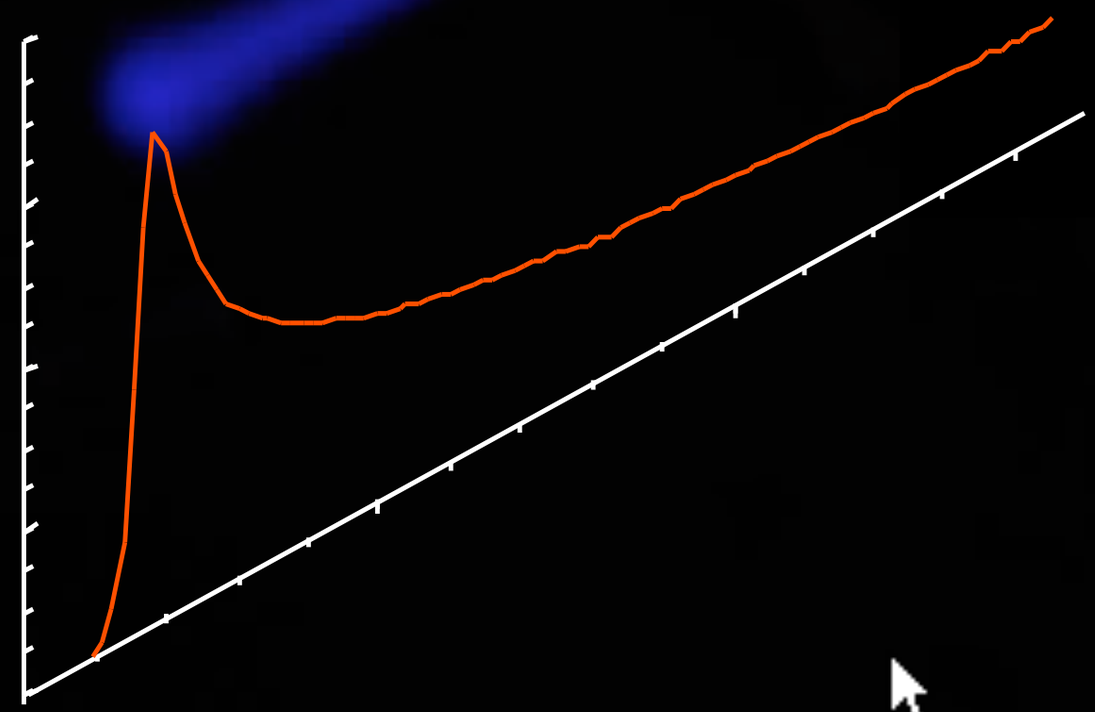
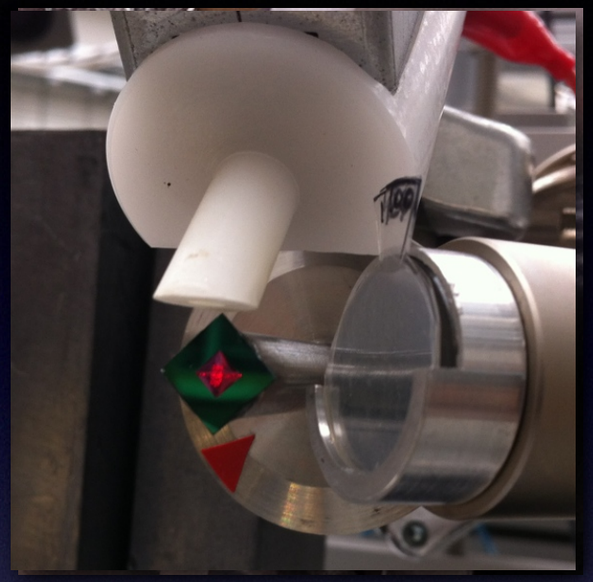


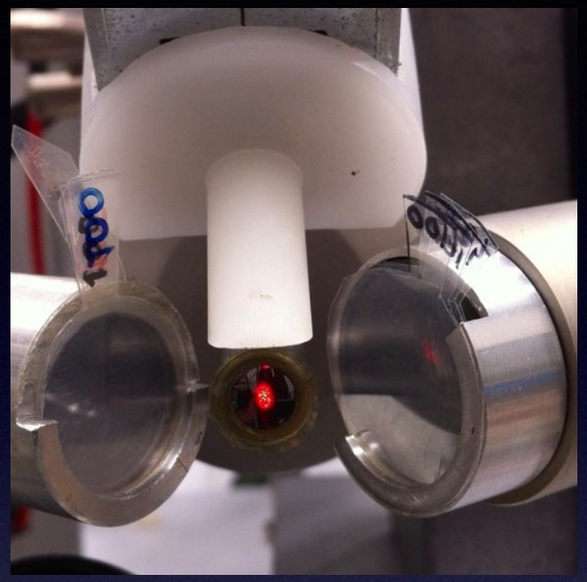
Disadvantages

- energy loss
- energy straggling
- beam lateral spread
- x-ray attenuation

Typical extraction windows



0.5 μm Si_3N_4

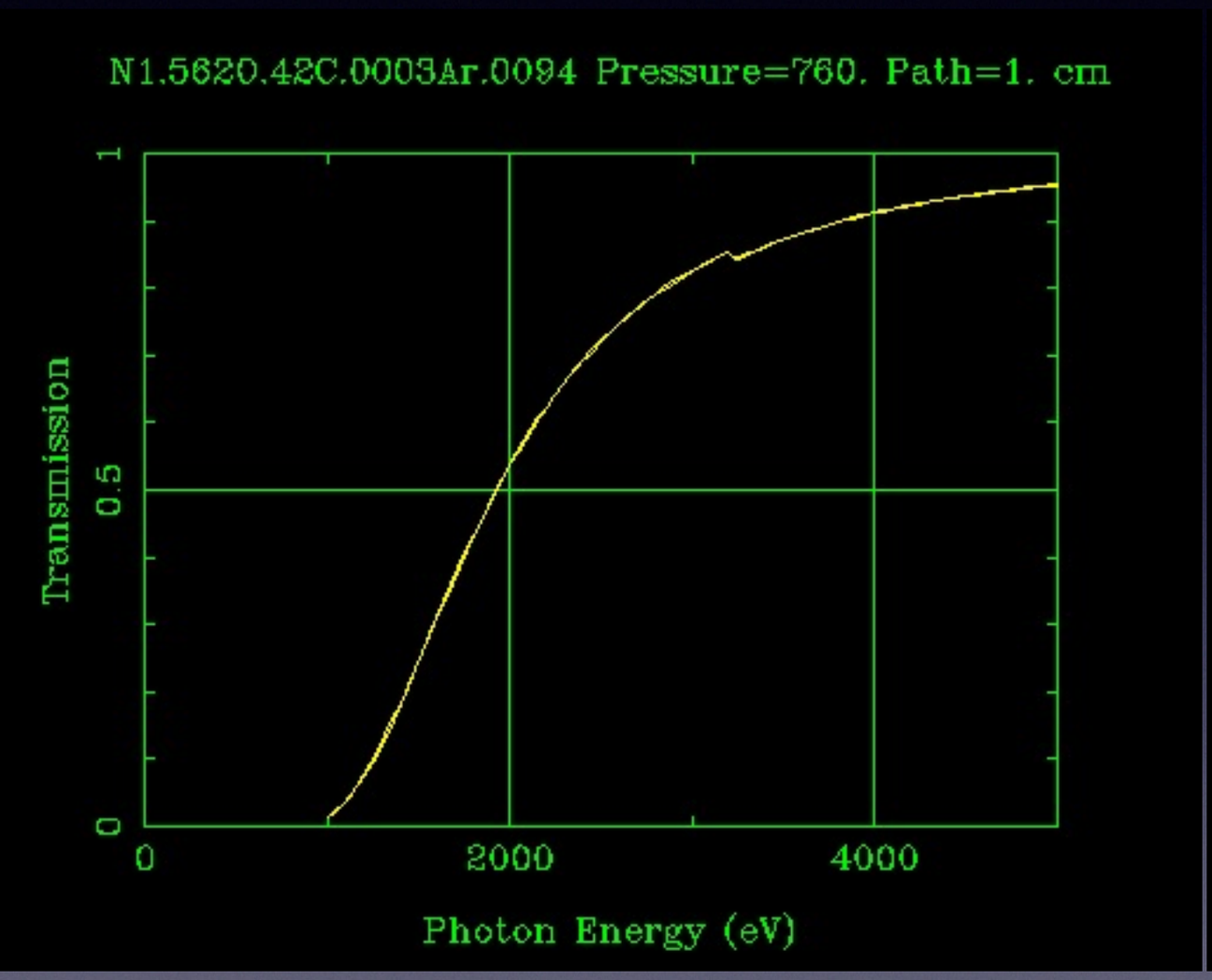


7.5 μm Upilex

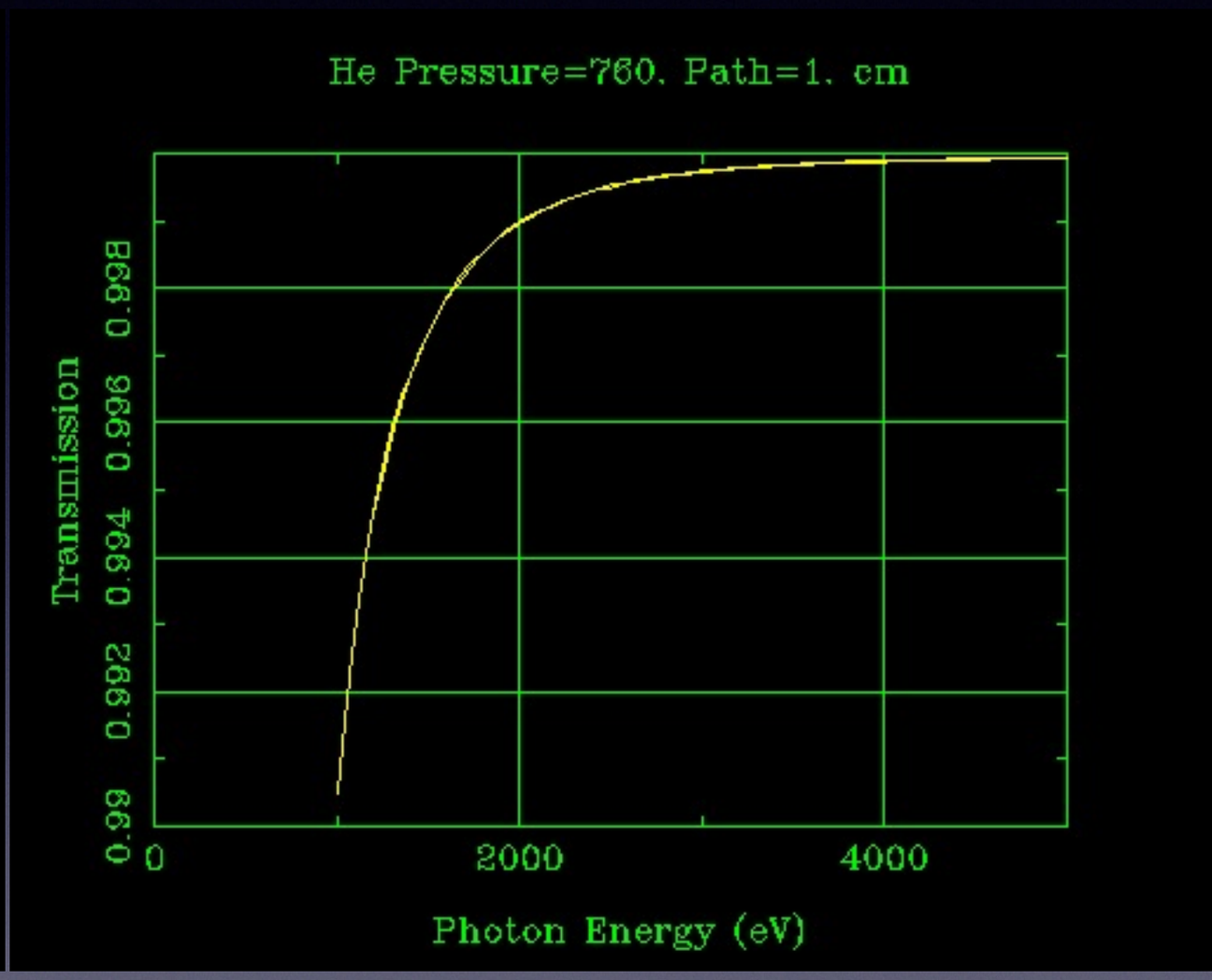
Material	Thickness (μm)	ΔE (keV)	σ_E (keV)	σ_θ (μm/mm)
Al	10	235	16	14
Kapton	8	130	9	6
Zr	2	75	7,3	15
Si	0.1	8	5	<1
	0.5	40	9	<2

Choice of external atmosphere

Air

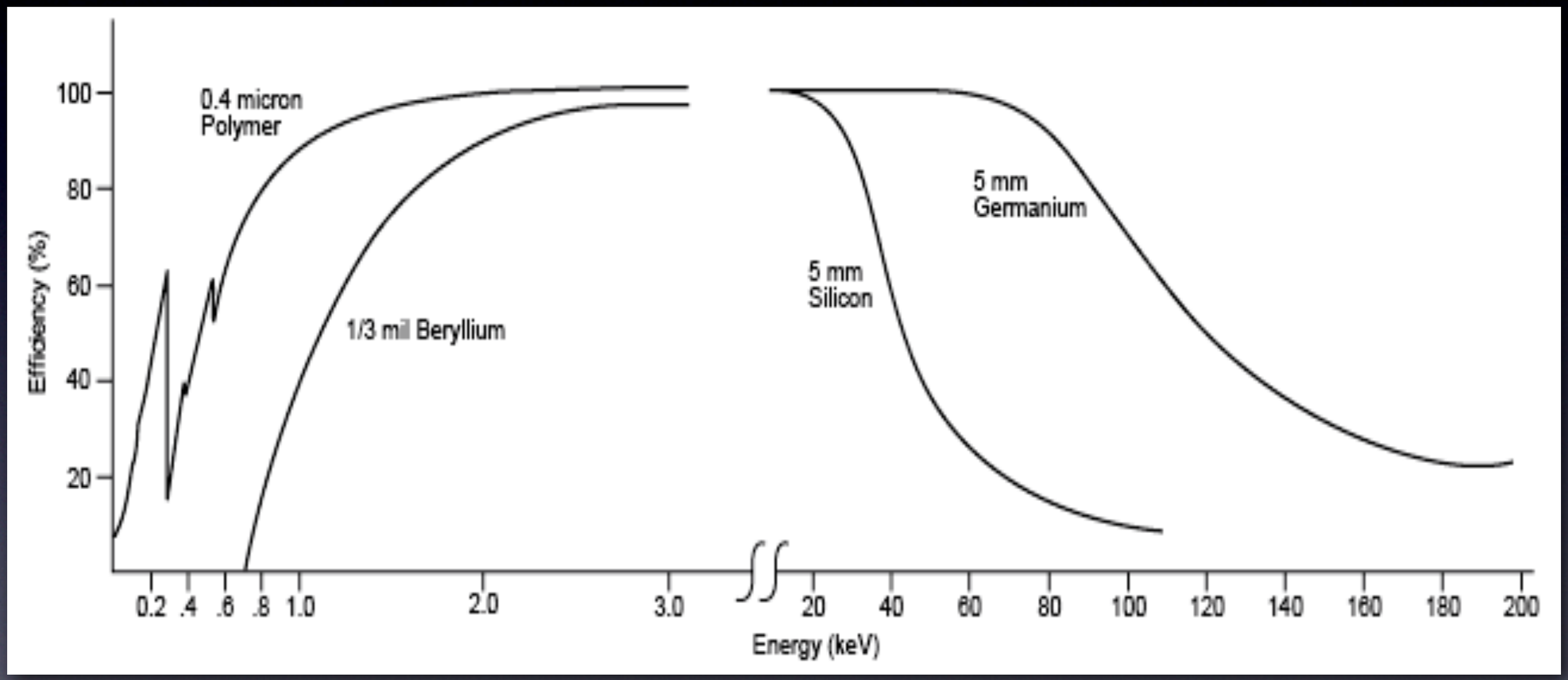


Helium



The use of an helium-saturated atmosphere in front of the X-ray detector is mandatory

X-ray detector efficiency



Low energy:

$$\varepsilon \approx \exp[-\mu(Z,E_X)\cdot t_{\text{window}}]$$

High energy:

$$\varepsilon \approx 1 - \exp[-\mu(Z,E_X)\cdot L_{\text{detector}}]$$

Typical PIXE detectors

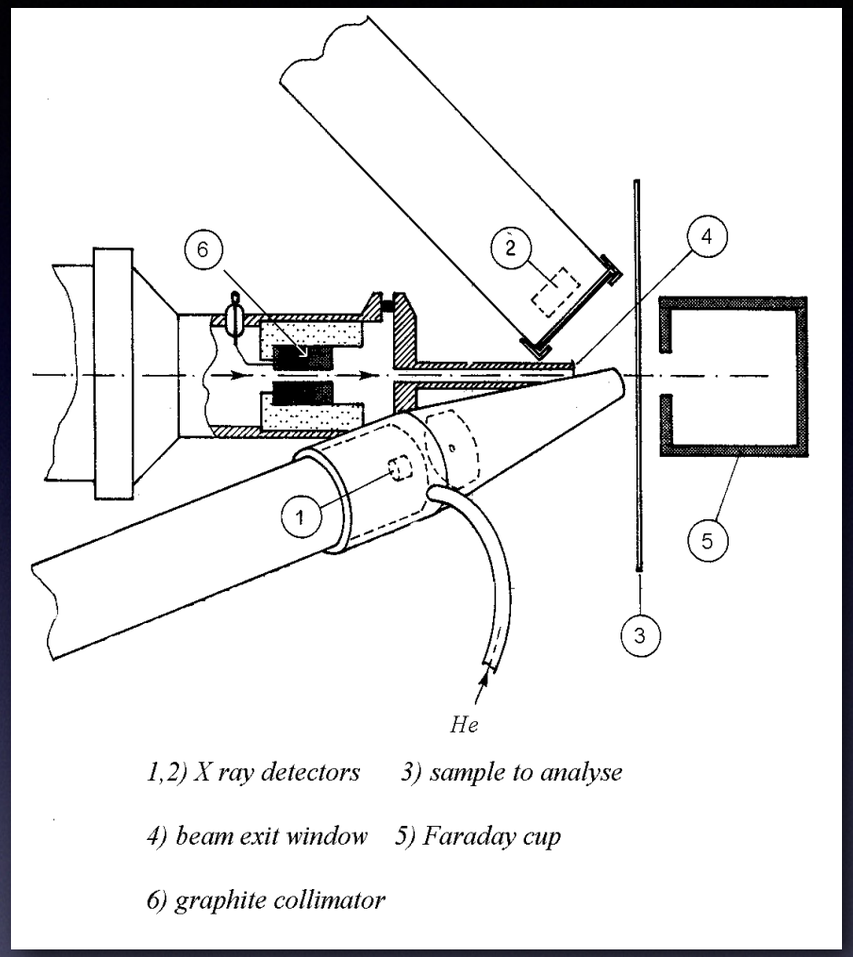
Silicon Drift Detector (SDD)

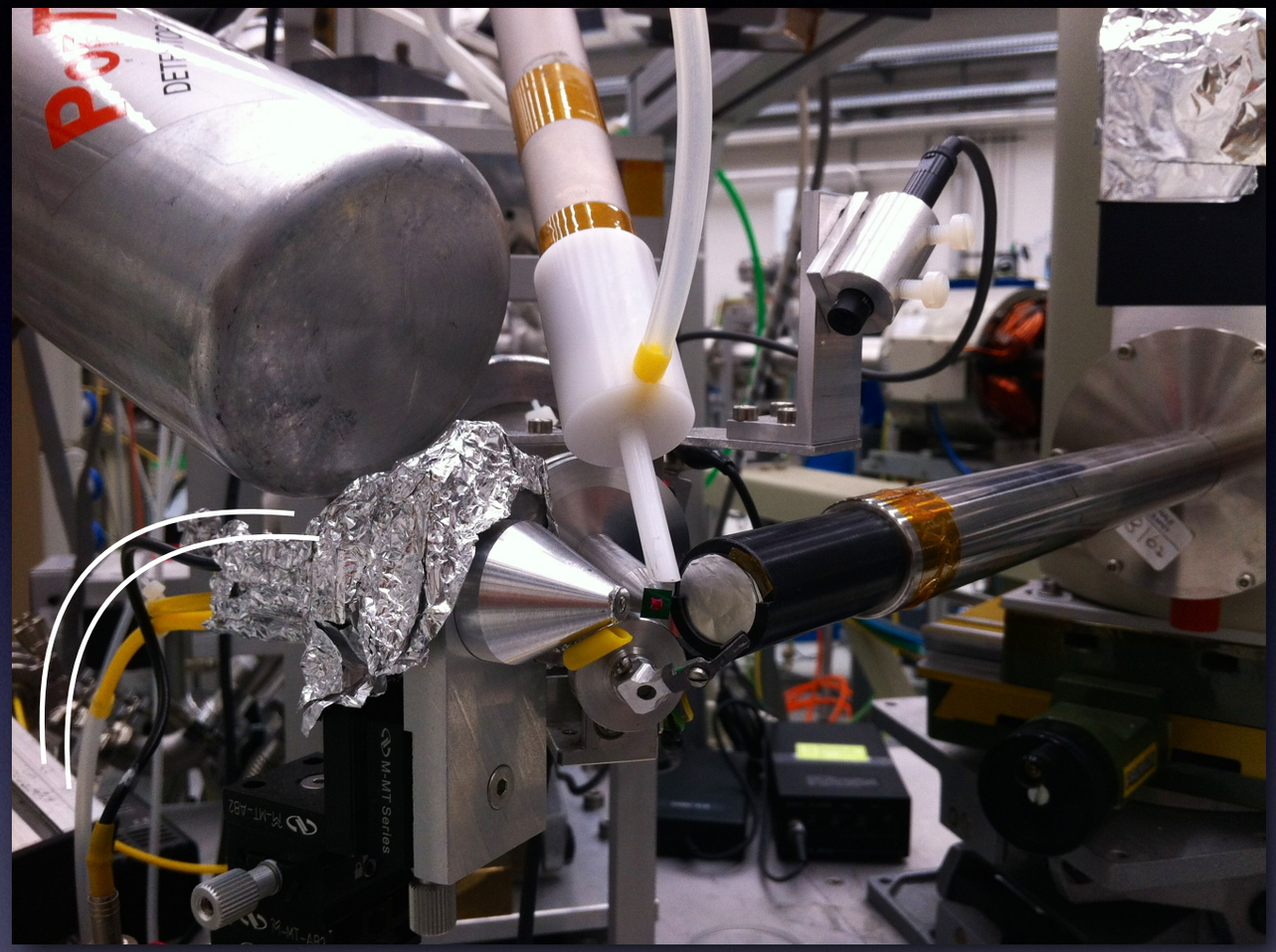
- Active area: 7 - 100 mm^2
- Thickness: 300 - 450 μm
- Energy resolution <140 eV
- High count-rate (100 kHz)
- Peltier cooling (-10, -20 °C)

Lithium-drifted Si / Ge, Si(Li) / Ge(Li)

- Active area: 10 - 100 mm^2
- Thickness: 3 - 5 mm
- Energy resolution <180 eV
- Liquid N2 cooling (77 K)
- Ge(Li): high-Z material, but "escape peak"

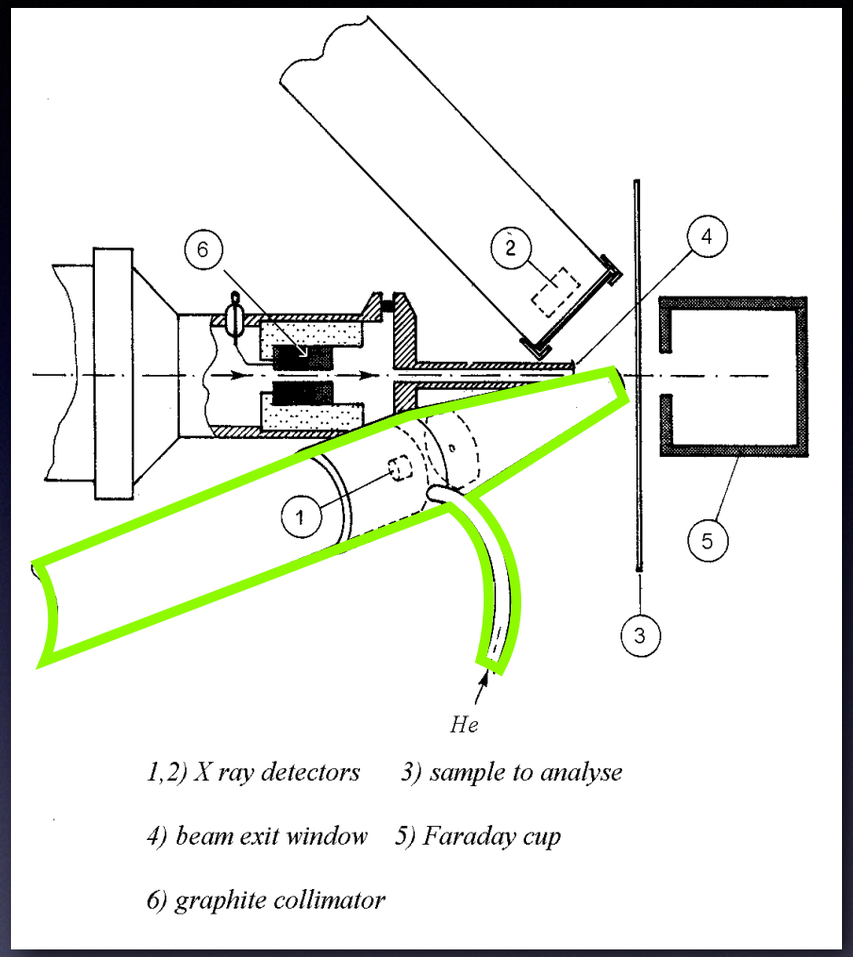
2-detectors PIXE set-up

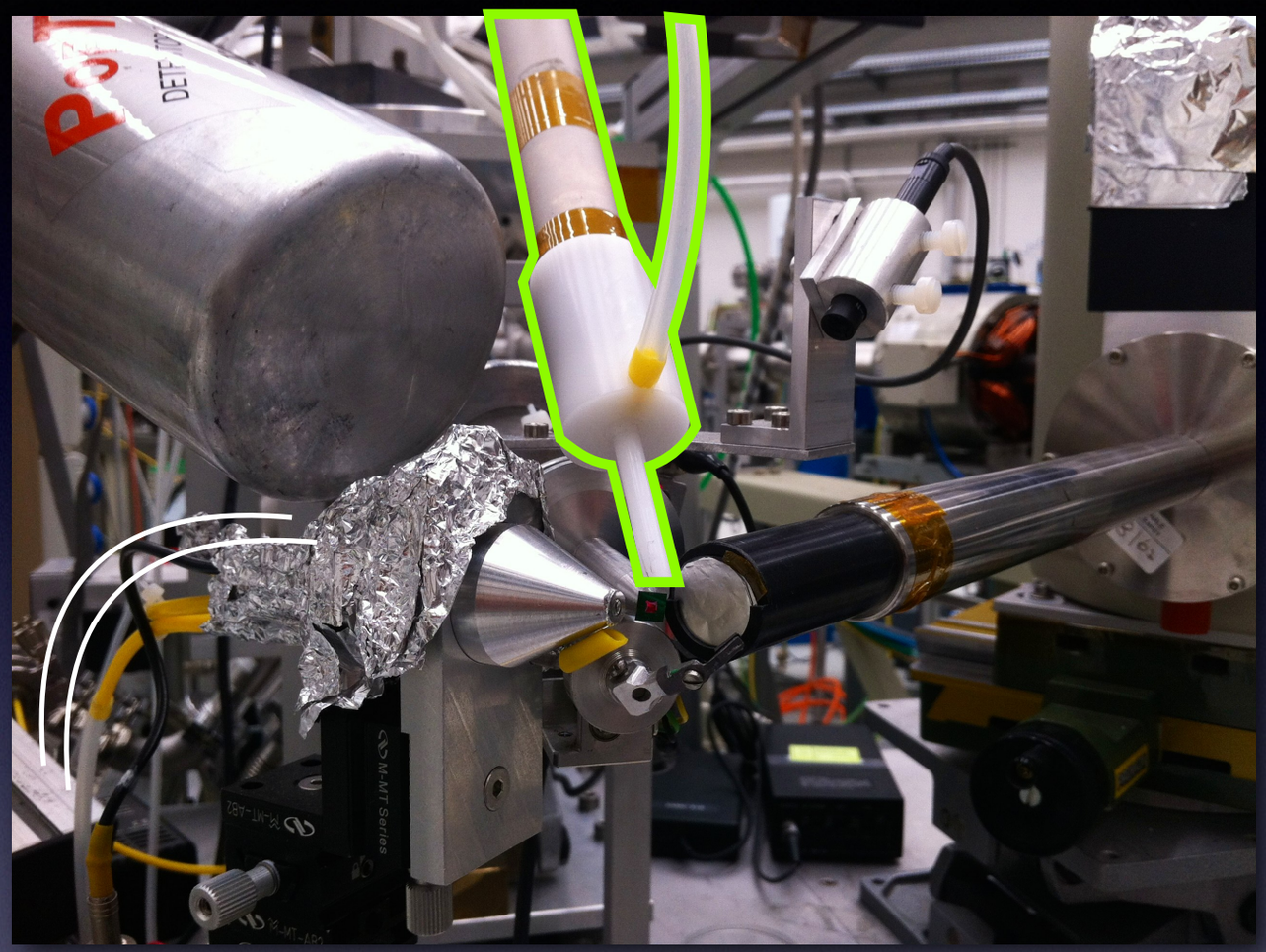




Target	X-rays	What is needed	Detector features
Low-Z elements	Low energy High cross sections	Minimum dead layers Small solid angles	Thin entrance window Small active area
Medium-high-Z elements	High energy Low cross sections	Large solid angles Efficiency	Large active area Large active thickness

2-detectors PIXE set-up





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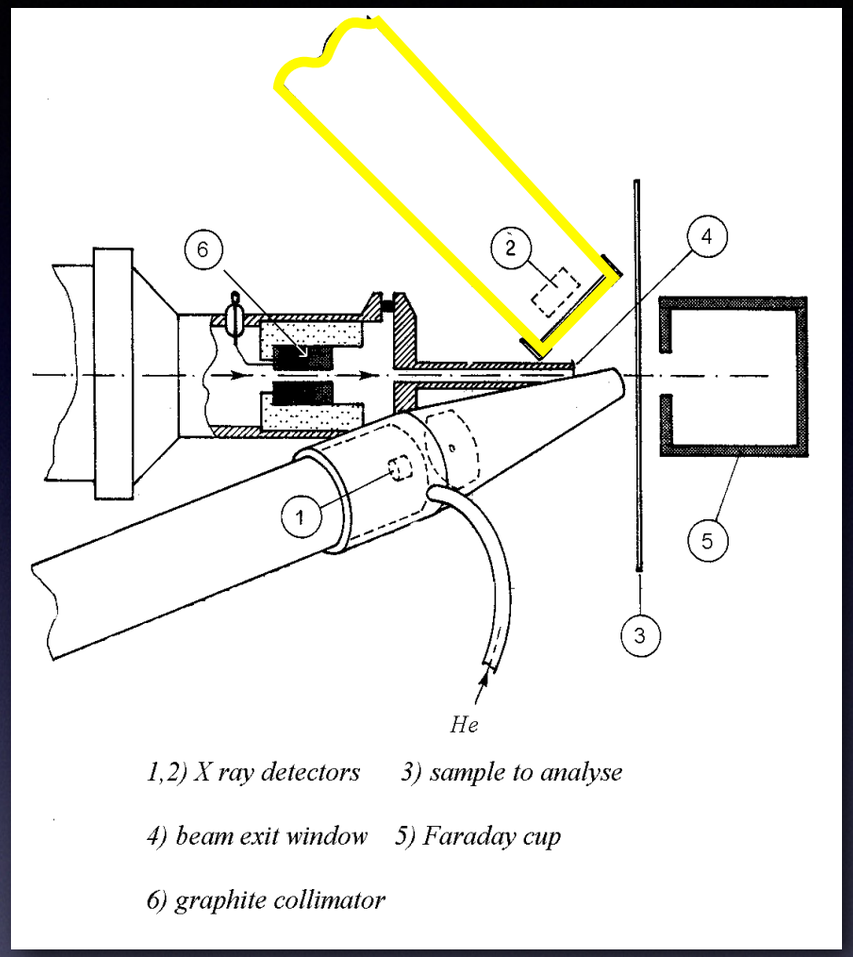

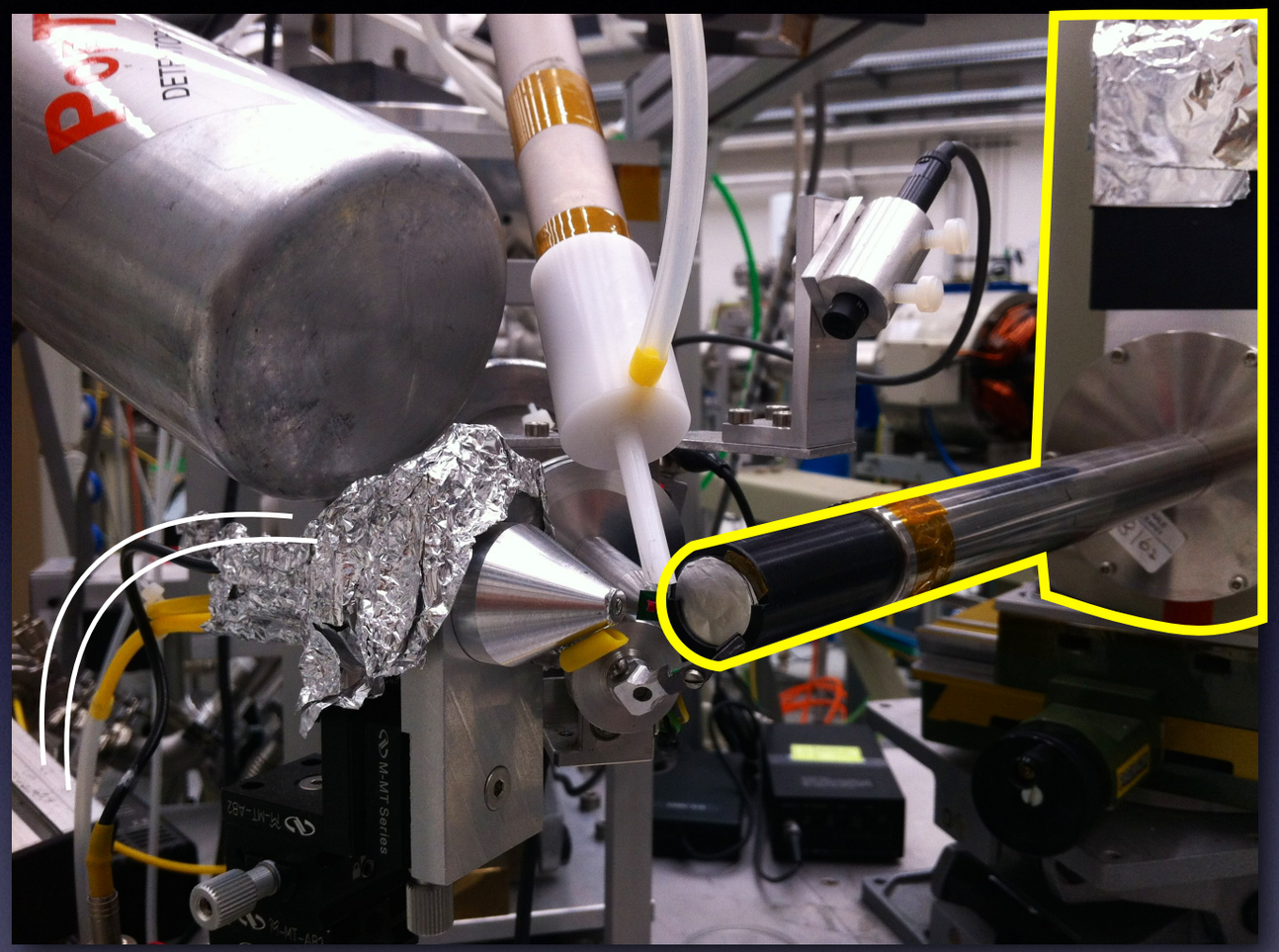

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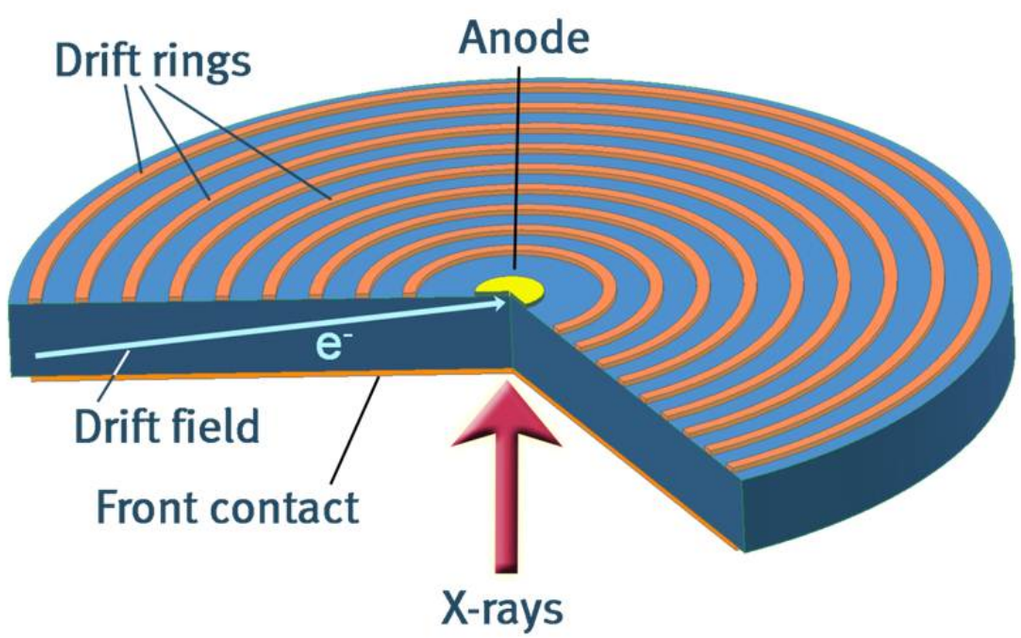
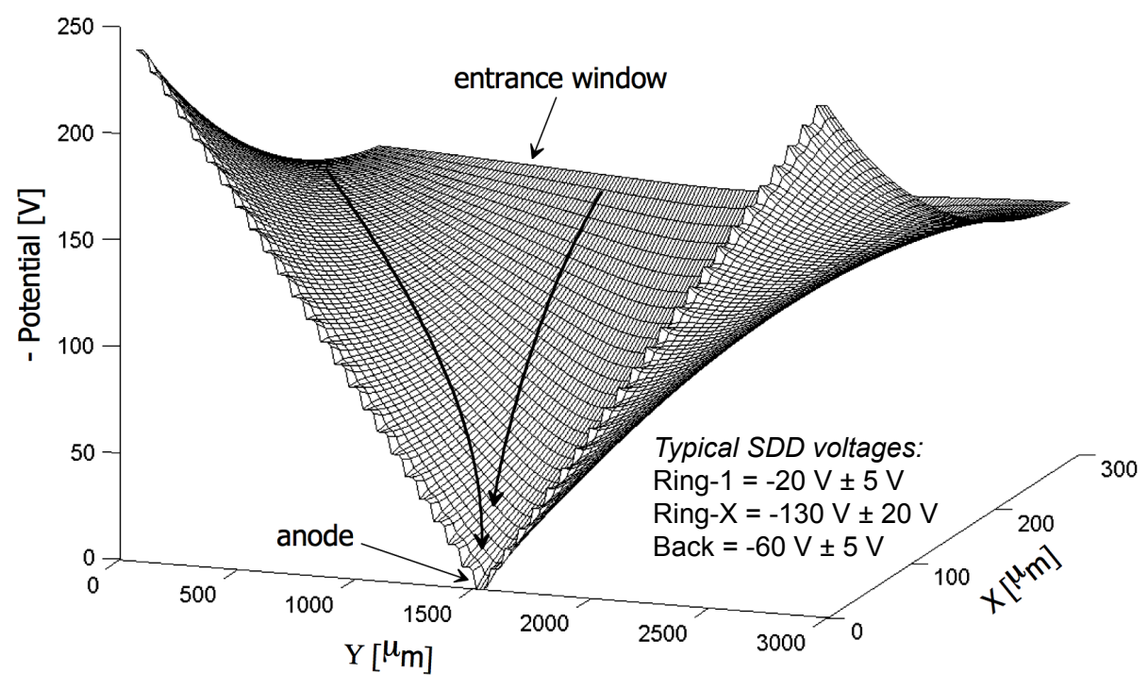
The working principle of Silicon Drift Detectors

- The Silicon Drift Detector (SDD) was first proposed in the early '80s by Emilio Gatti and Pavel Rehak [Gatti & Rehak, NIM 225 (1983) 608] as a position sensitive semiconductor detector for high energy charged particles, based on a novel charge transport scheme where the field responsible for the charge transport is independent of the depletion field



Schematic diagram of the Silicon Drift Detector for X-ray spectroscopy with radiation entrance window of the detector consisting of a continuous shallow p+ implant

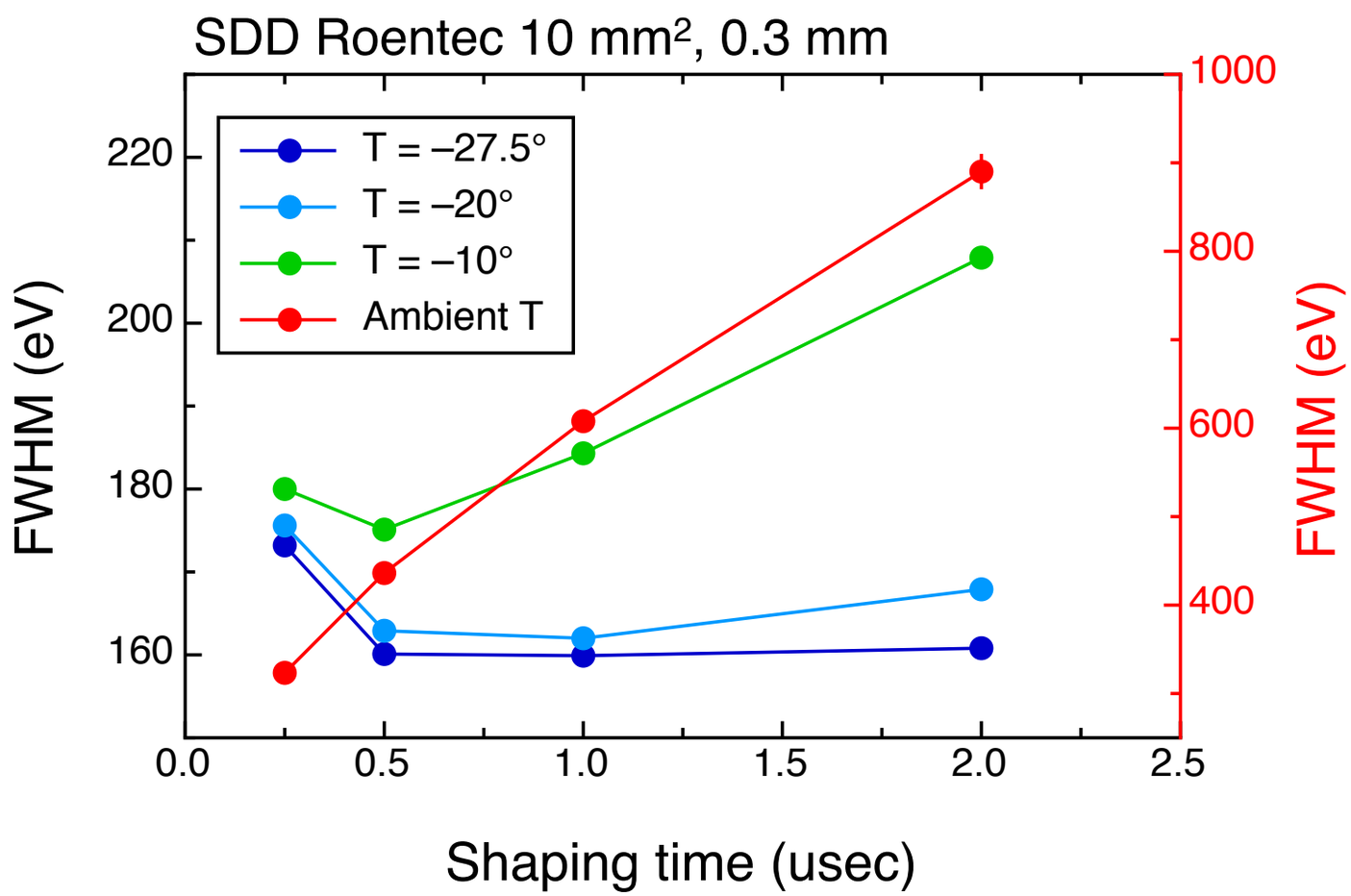


Energy potential for electrons inside a SDD with homogeneous entrance window.

The SSD for X-ray spectroscopy

- The SDD is employed in high-resolution X-ray spectroscopy because of the low capacitance of the collecting electrode (0.5-1 pF/cm^2) and the low leakage current (1-2 nA/cm^2 at room temperature) resulting in improved energy resolution

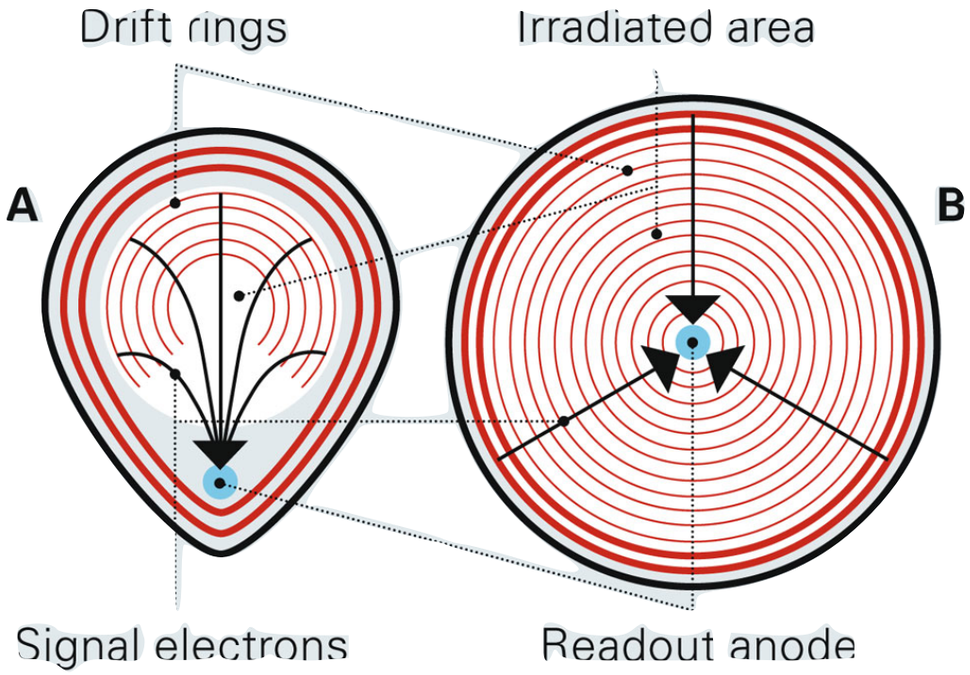
$$\mathtt{ENC} = \left[\frac{k_1 \cdot \langle e_w^2 \rangle \cdot (C_d + C_i + C_p)^2}{\tau} + k_3 A_{1/f}(C_d + C_i + C_p)^2 + 2k_2 q I_l \tau\right]^{1/2}$$



	SDD	Si(Li)
Energy resolution	140-160 eV	180-200 eV
Shaping time	1 μs	6 μs
Sustainable count-rate	50 kHz	5 kHz
Cooling	-10/-20 °C	-195 °C

Commercial SDD

- Starting from the first SDDs, 5 or 10 mm^2 area, 0.3 mm thick, now several companies are selling SDDs with a wide range of characteristics and designs, and competitive prices



SDD "Droplet" design (SD^3)

Classic cylindrical SDD design

KETEK Creative Detector Solutions

PNDetector

PNSensor

SGX SENSORTECH

AMP TEK

BRUKER

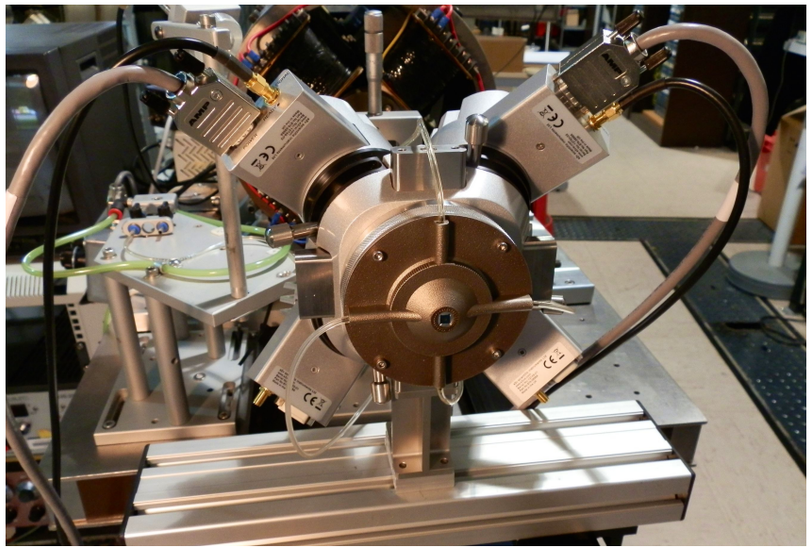
XGLAB X and Gamma Ray Electronics

Hitachi High-Technologies Science America, Inc.

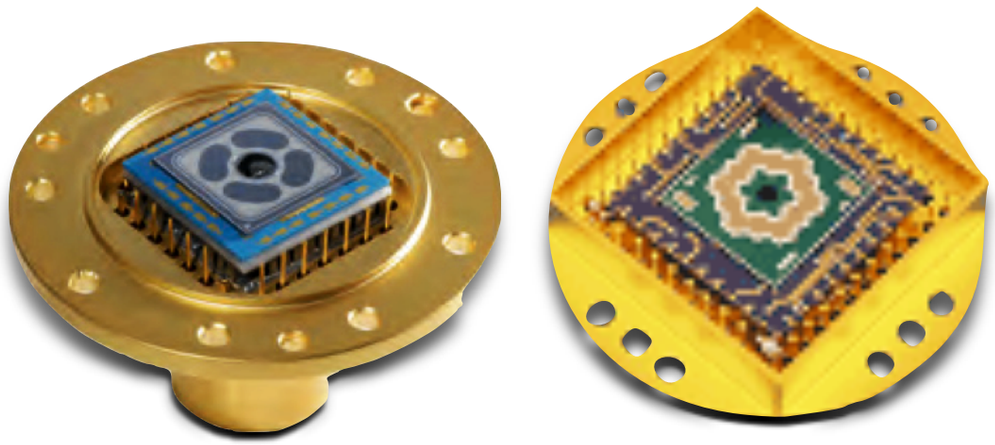
Large area SDD

- A single SDD with active area up to 150 mm^2 is now commercially available (Ketek Gmbh)

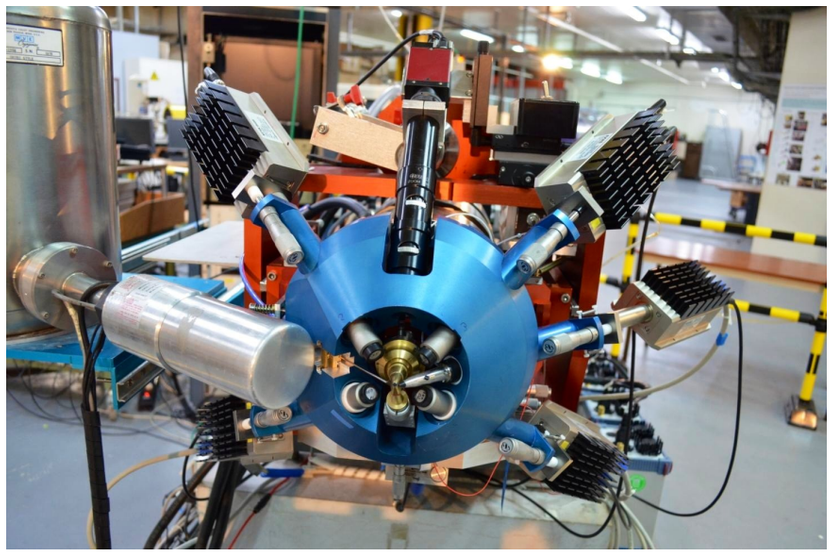
- Larger areas can be obtained using arrays of individual systems or integrated multi-channel SDDs



4-channel SDD (30 mm^2 each) PIXE system at Surrey Ion Beam Centre(SGX Sensortech, UK)



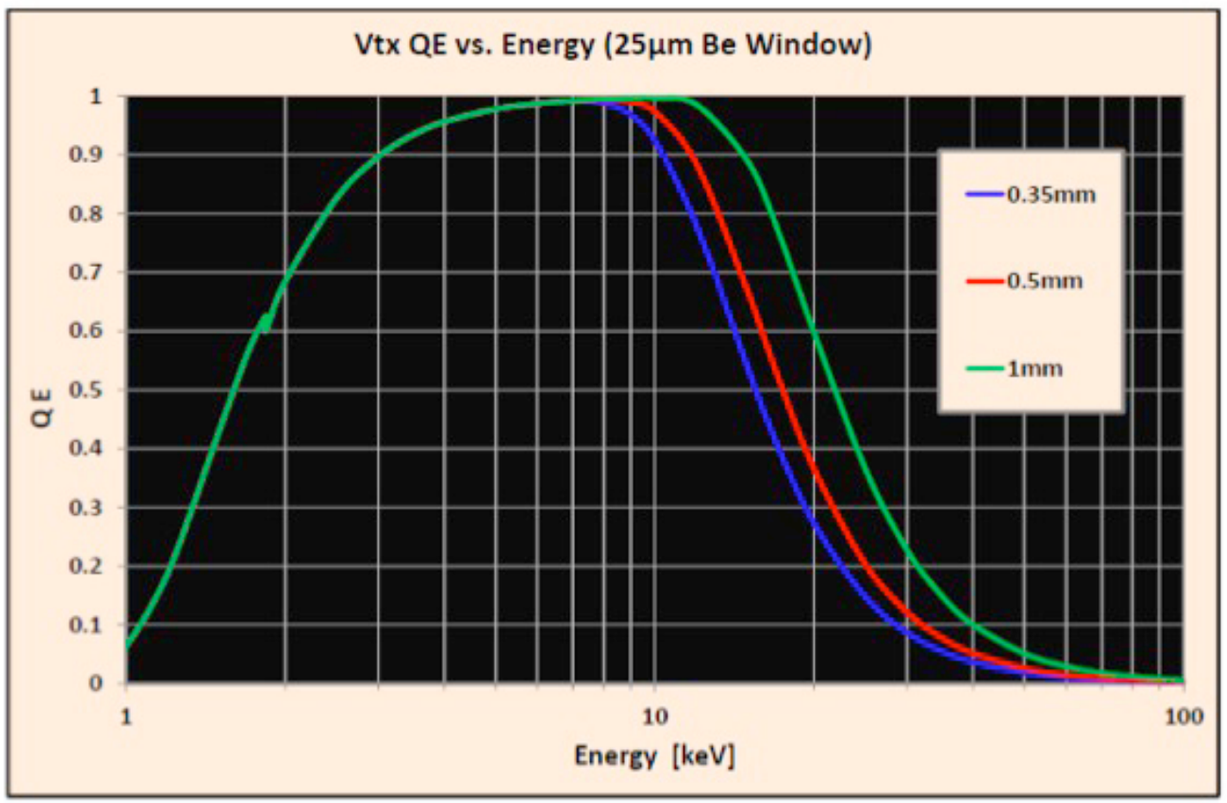
Ring-shaped multi cell SDD with 12 x 5 mm^2 hexagonal cells (PN Detectors, Germany)

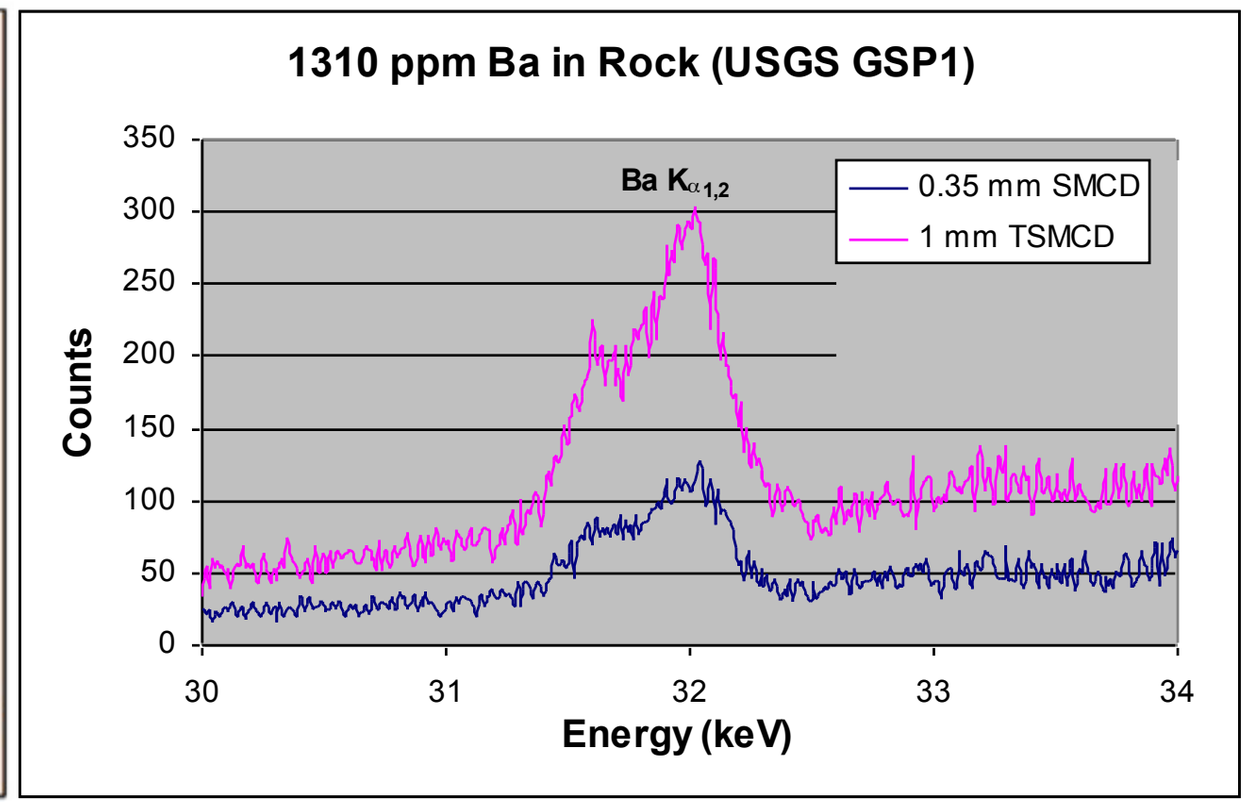


Multi SDD PIXE system (1 low and 4 high energy), total solid angle 500 msr, at AGLAE, Paris (Ketek Gmbh, Germany)

Increased thickness SDD

- Single SDD with active thickness of 0.7 mm (Ketek Gmbh) or 1 mm (Hitachi High-Technologies Science America, Inc) are now commercially available

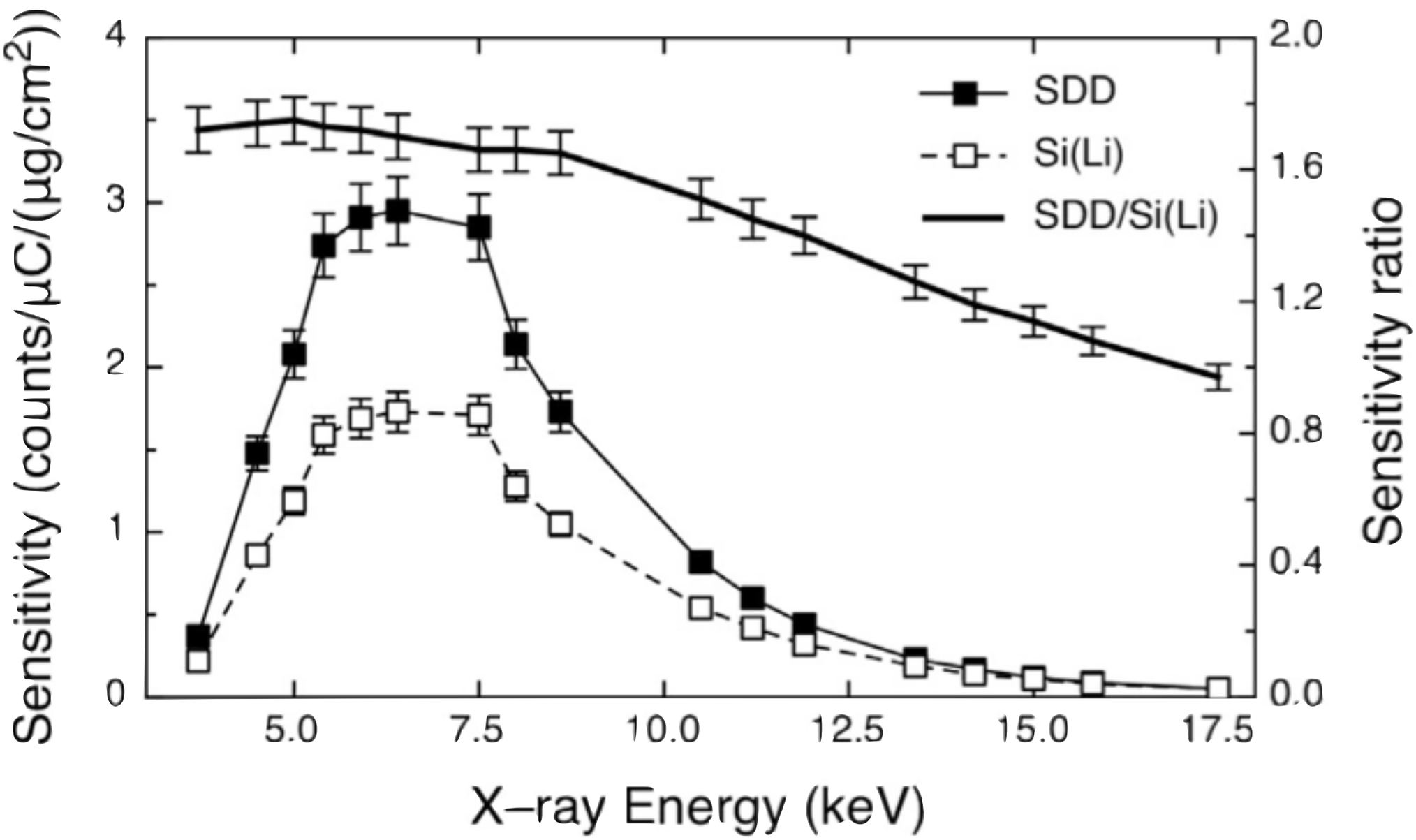




QE (0.3 mm) = 90% @10 keV; 25% @20 keV
QE (0.5 mm) = 100% @10 keV; 40% @20 keV
QE (1.0 mm) = 100% @10 keV; 60% @20 keV

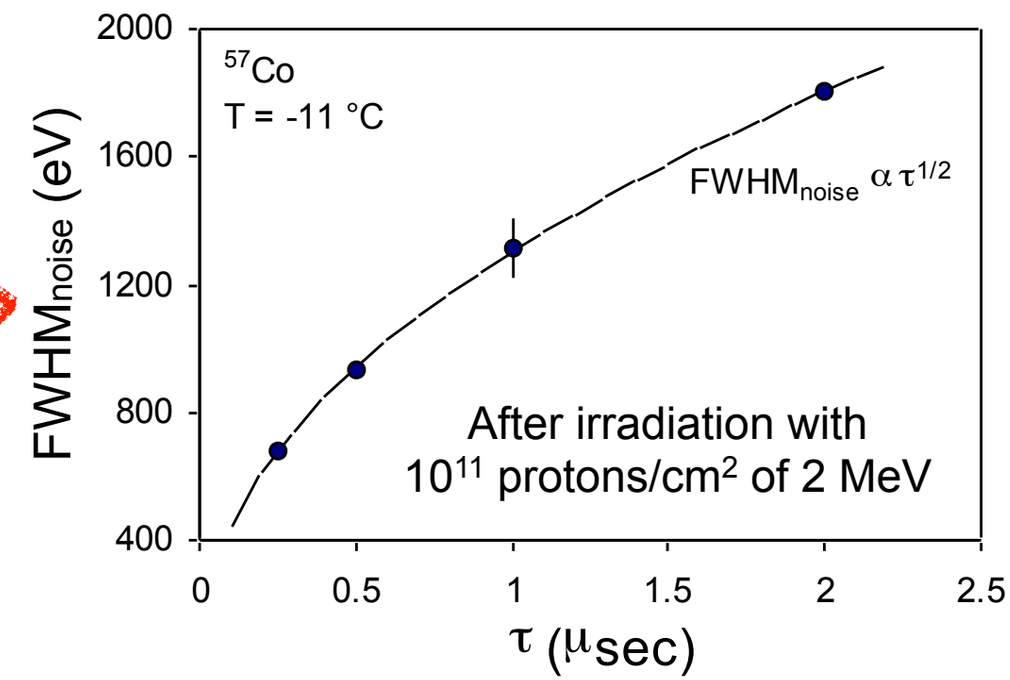
32 keV Ba spectra from USGS GSP1 – Rh tube, 50 kV, 1 mA, 0.5 mm Cu + 6 mm Al Filter, 0.5 µs peaking time, 300 sec. livetime. (Gordon Myers, Hitachi High-Technologies Science America, Inc.)

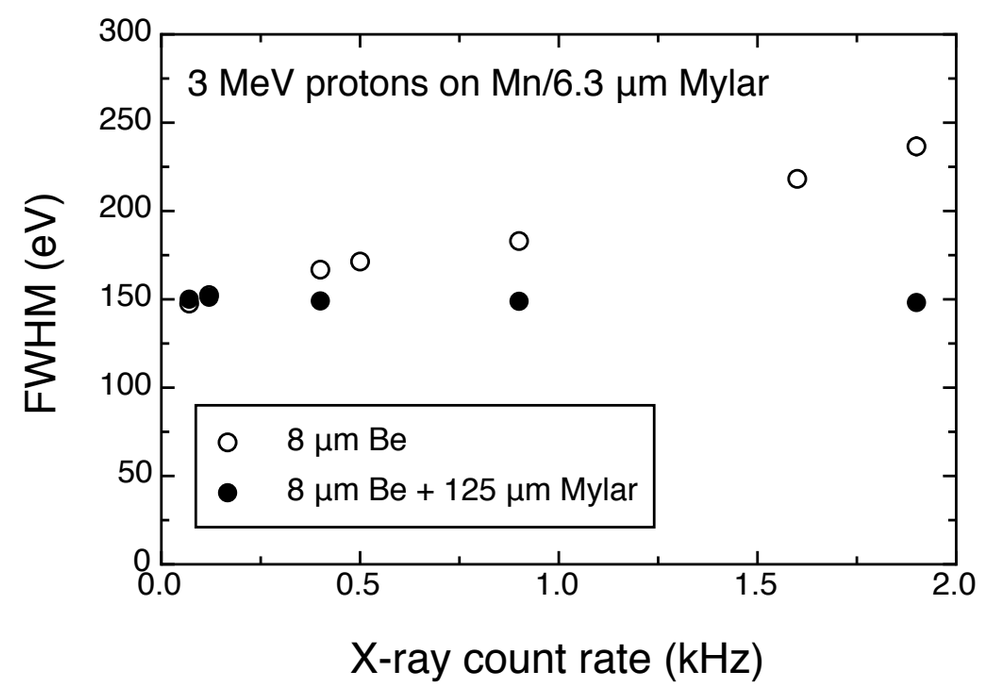
Sensitivity curve for large area SDD and Si(Li)



Backscattered protons effects on SDD

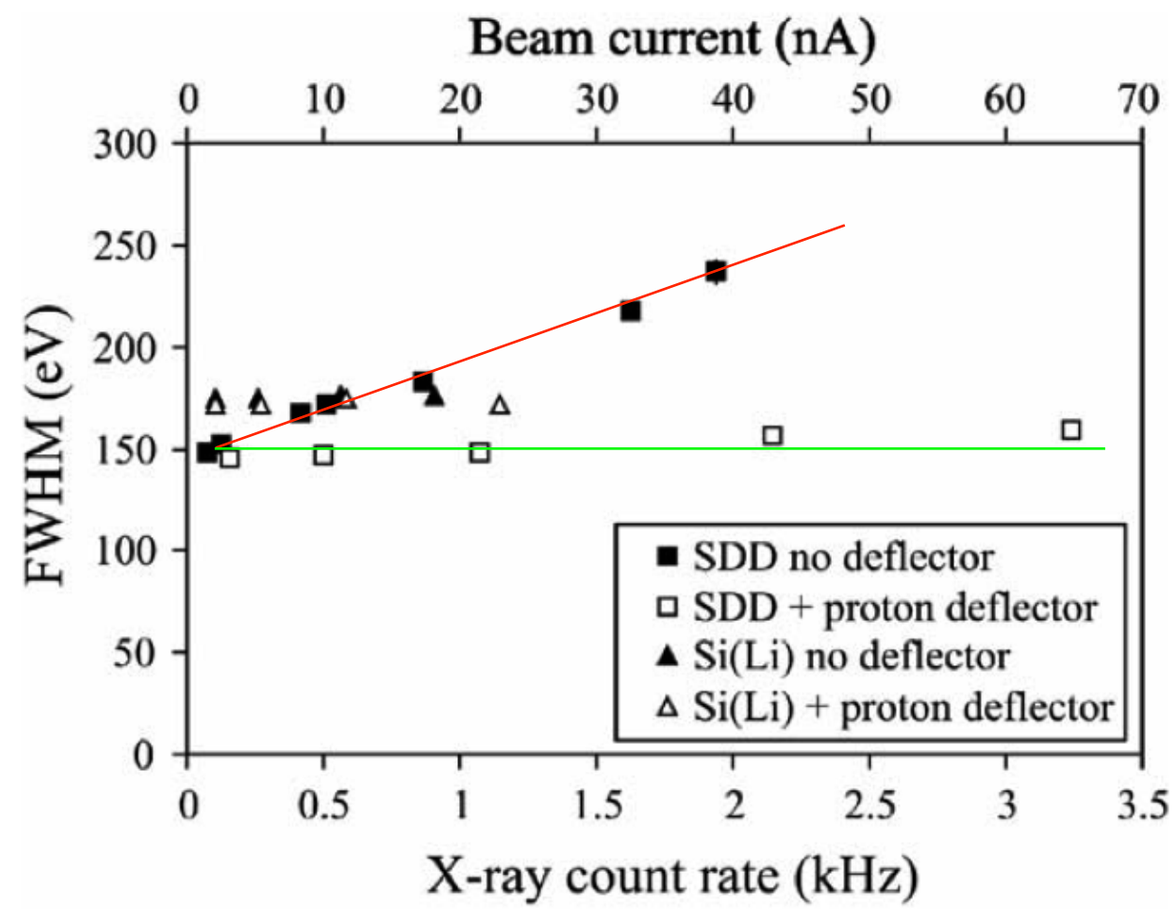
- PIXE detectors with thin entrance window used in presence of a large backscattered protons flux from the sample can suffer unrecoverable damages (long-term effects) and worsening of the energy resolution under beam irradiation (short-term effects)

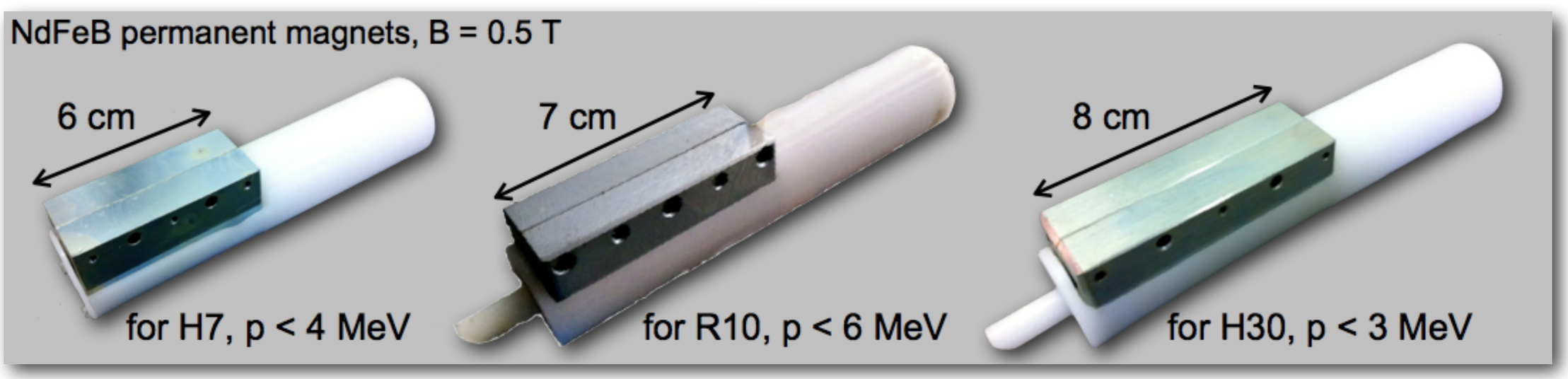




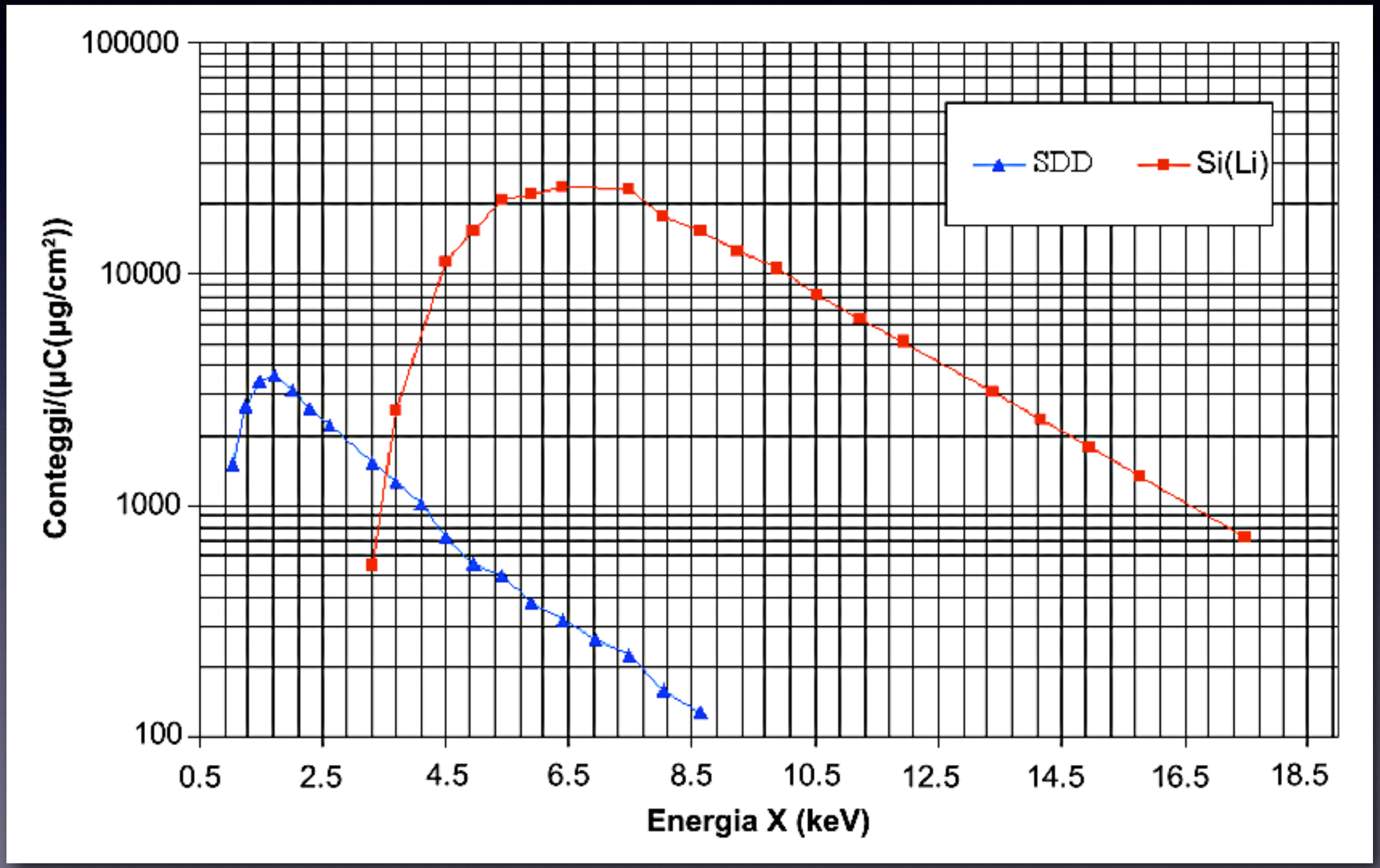
Magnetic proton deflector

- The use of a properly designed magnetic deflector to filter out the backscattered protons without substantial limitations to the SDD intrinsic efficiency at low X-ray energies is mandatory to prevent any long-term damages and to avoid the worsening of the energy resolution



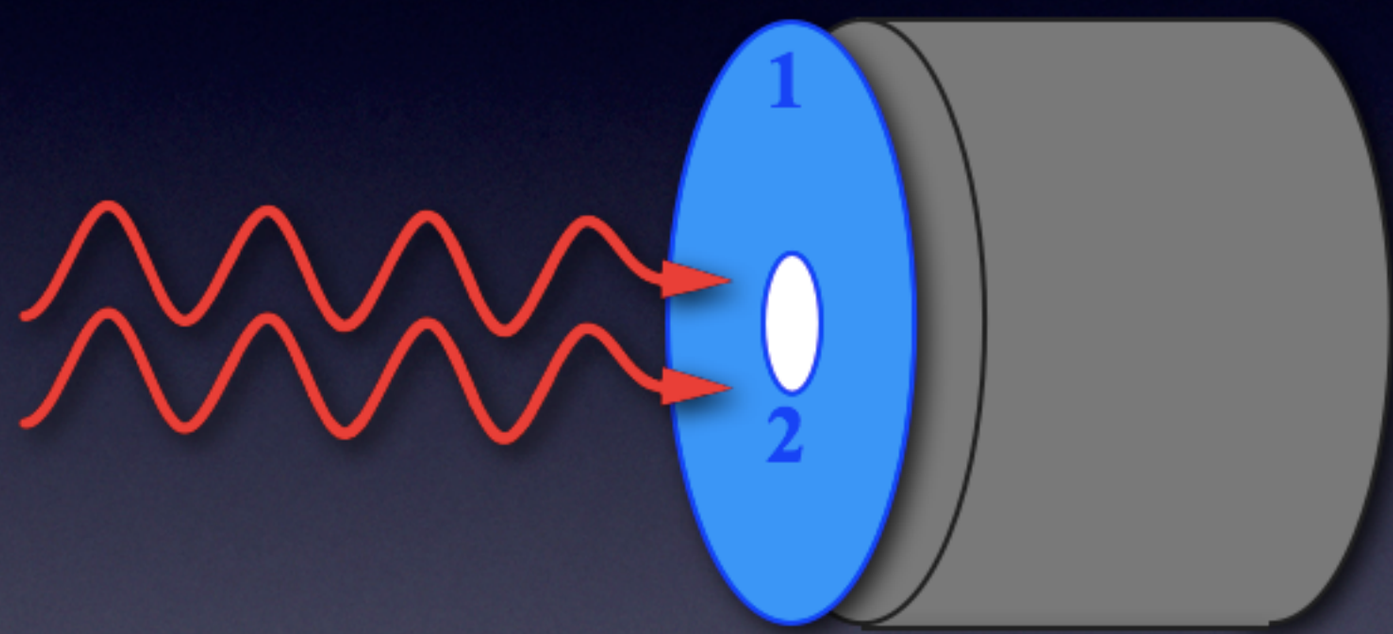


Detection efficiency for a 2-detectors PIXE set-up



“Funny filter”

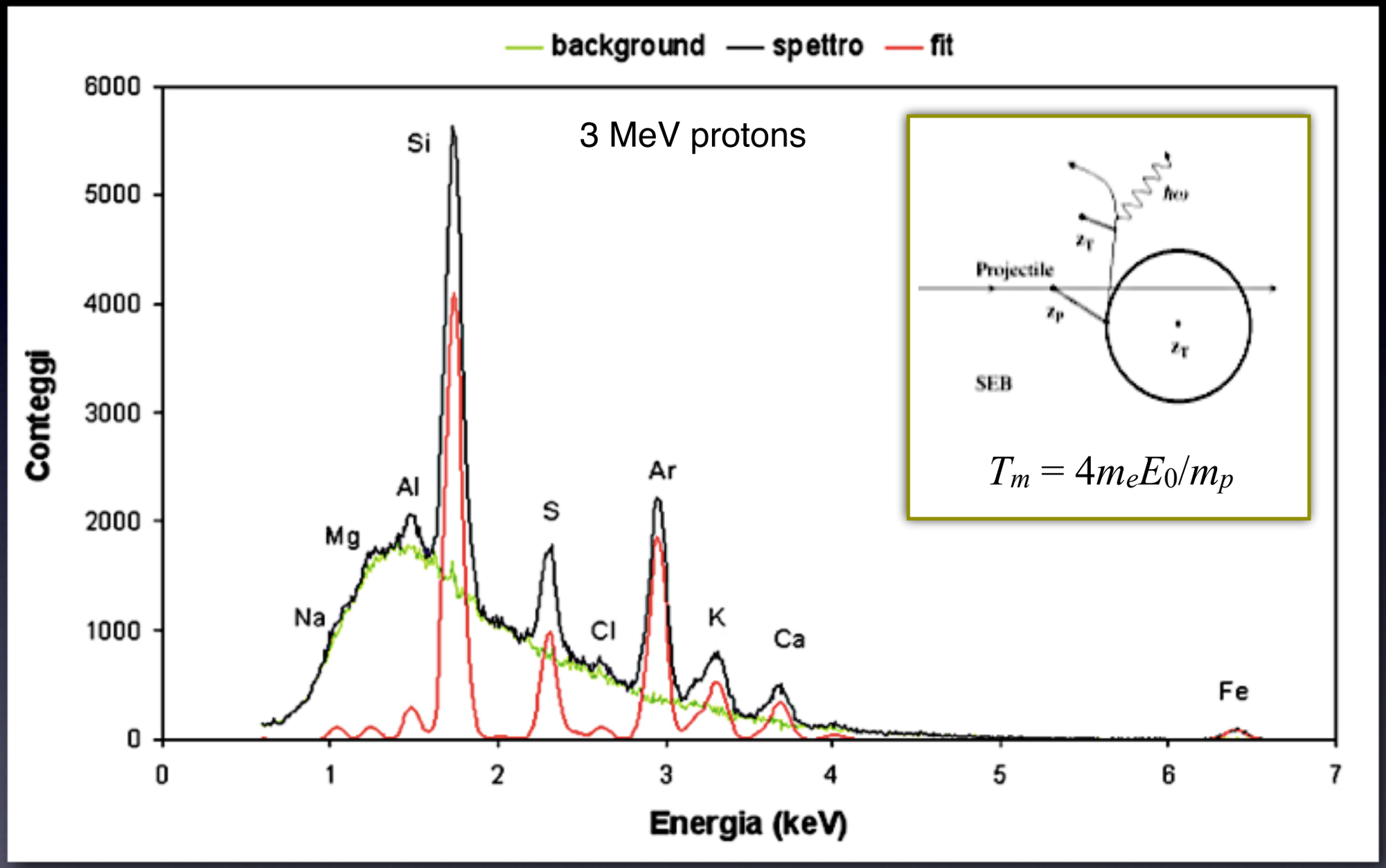
The “funny filter” concept was introduced by Harrison and Eldred in 1973, when PIXE was starting to develop as an analytyal technique



$\alpha_1(Z)$, transmission coefficient of absorber 1
$\alpha_2(Z)$, transmission coefficient of absorber 2
R, ration between absorber 2 area and detector area

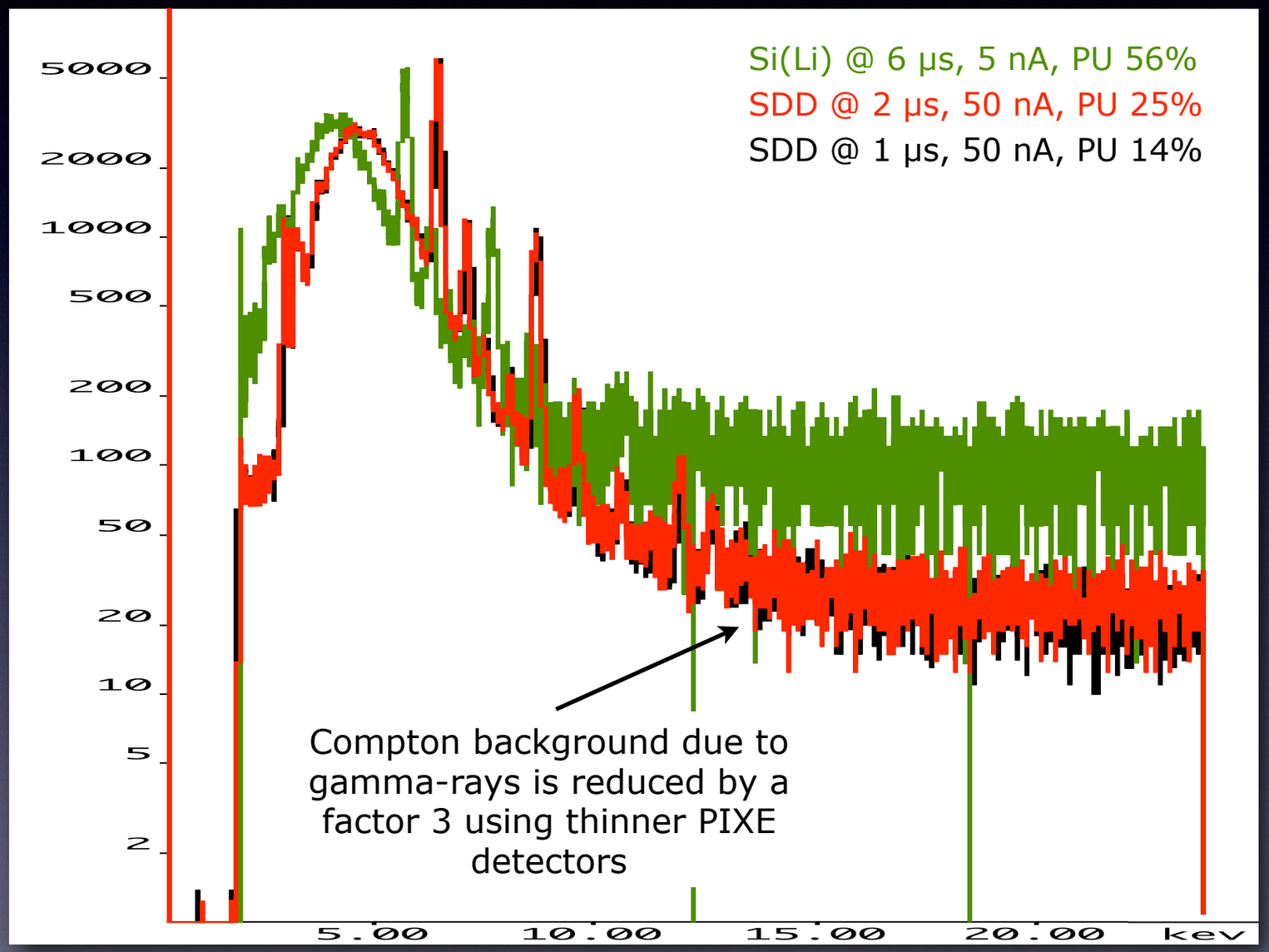
$$\alpha_Z = \alpha(Z) = \alpha_1(Z)\cdot[R + (1 - R)\cdot\alpha_2(Z)]$$

PIXE spectrum background



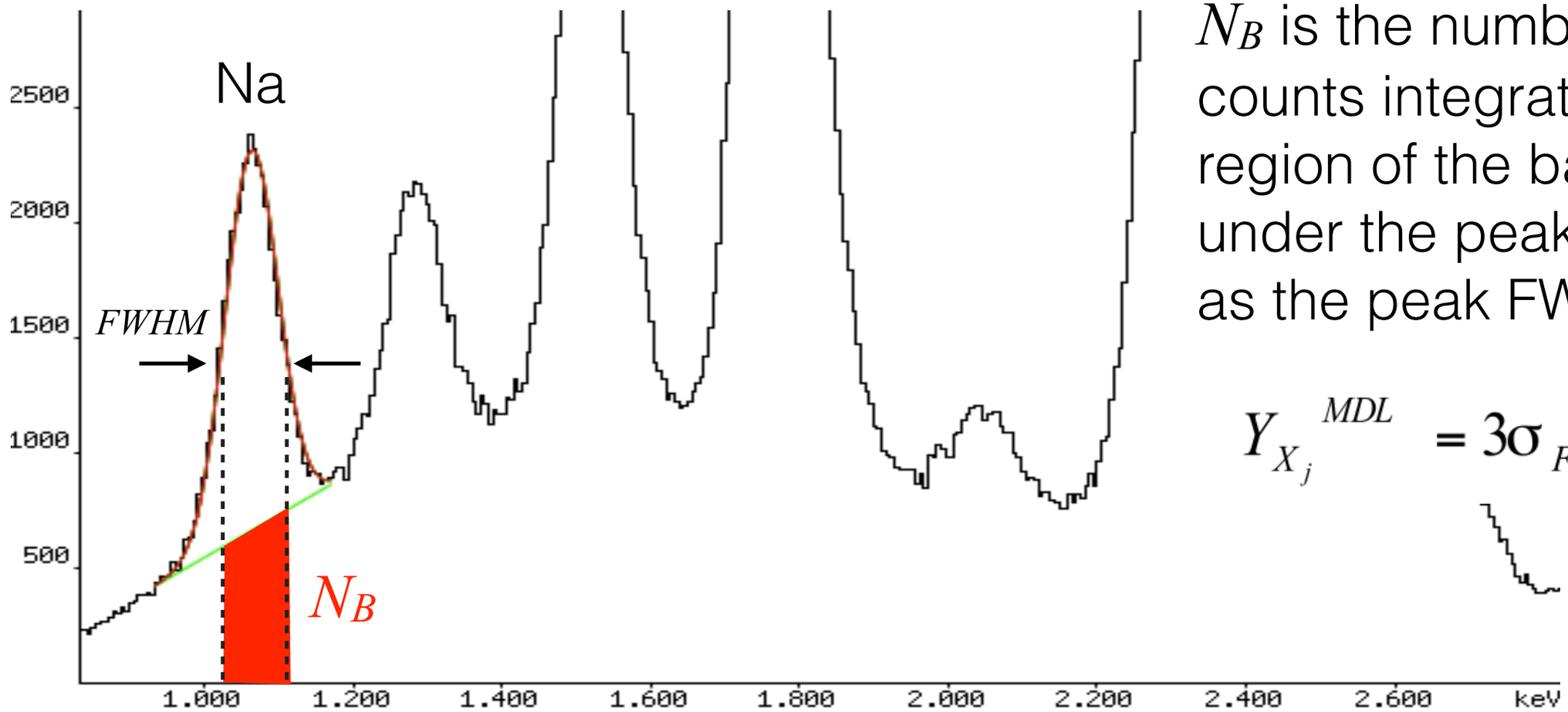
Mainly due to *Secondary Electron Bremsstrahlung* radiation (for E < 10 keV)

PIXE spectrum background



Possible contribution from Compton interaction of gamma-rays in the detector active volume (for E > 10 keV)

Minimum Detection Limit (MDL)



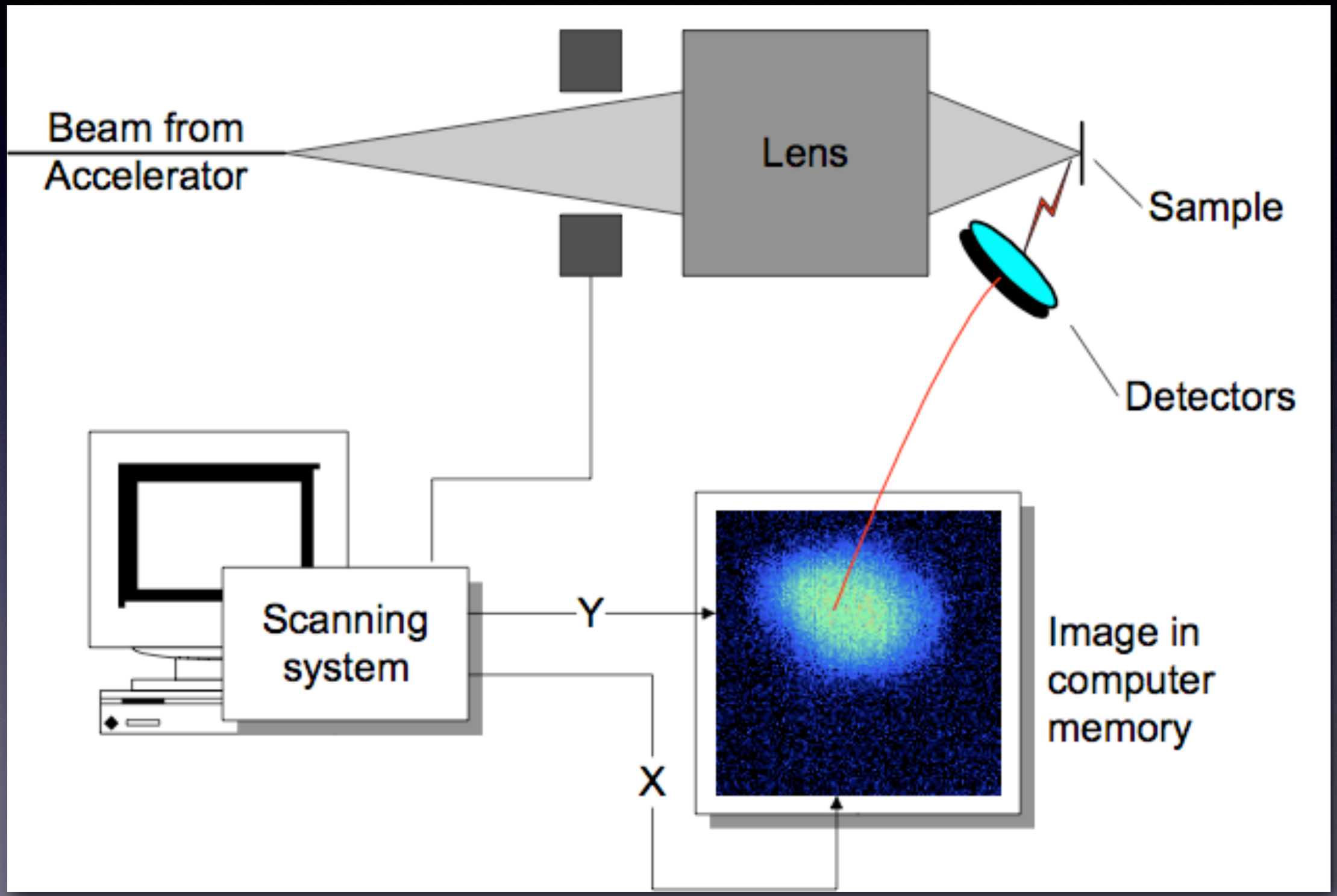
N_B is the number of counts integrated in a region of the background under the peak as wide as the peak FWHM

$$Y_{X_j}^{MDL} = 3\sigma_F = 3\sqrt{N_B}$$

In terms of areal density (i.e. μg/cm²) the PIXE MDL can be calculated as:

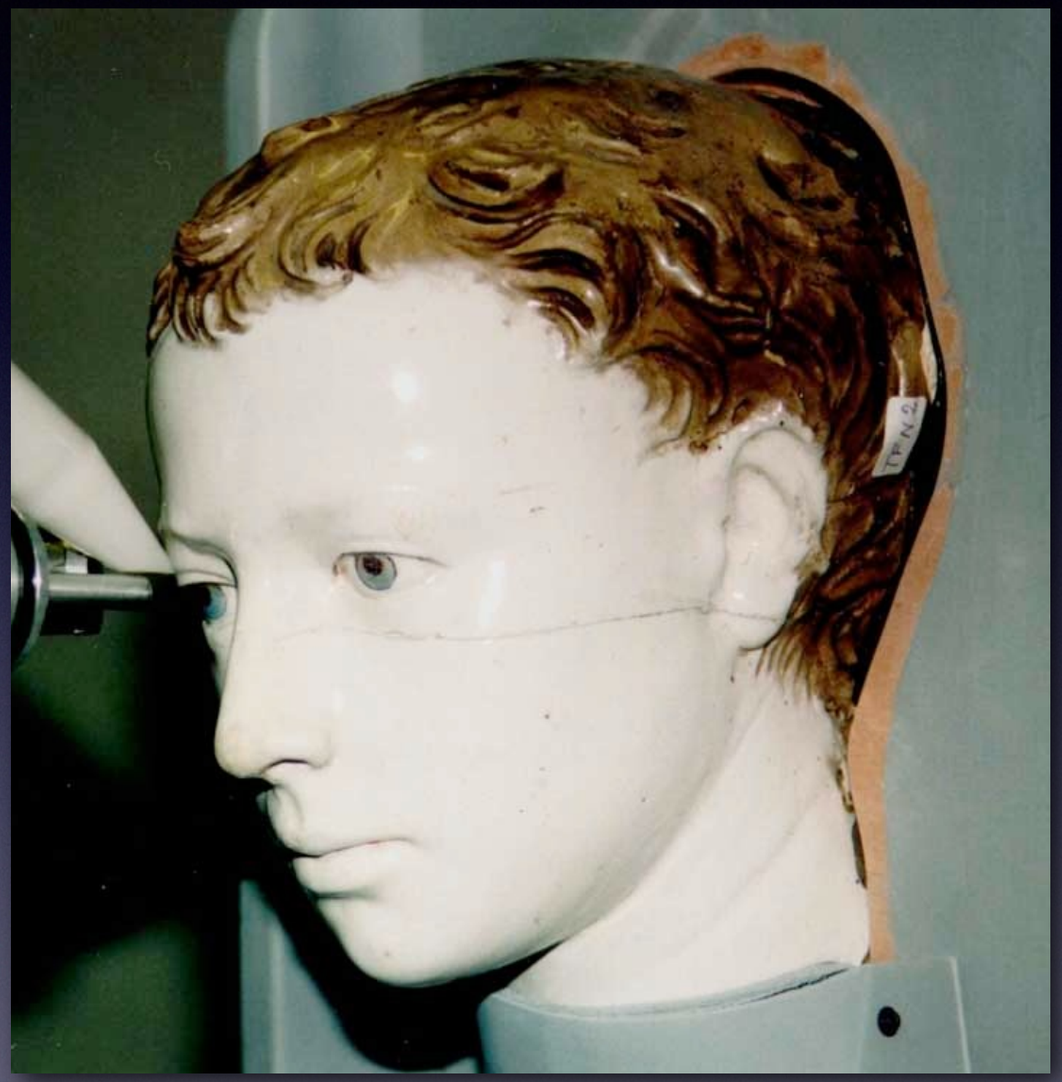
$$MDL_Z = \frac{3 \cdot \sqrt{N_B}}{\eta_Z \cdot Q}$$

Nuclear microscopy



External beam PIXE of ancient manuscripts, ...ceramics,

PIXE analysis of the frontispiece of Pl.16,22, from Biblioteca Laurenziana in Florence

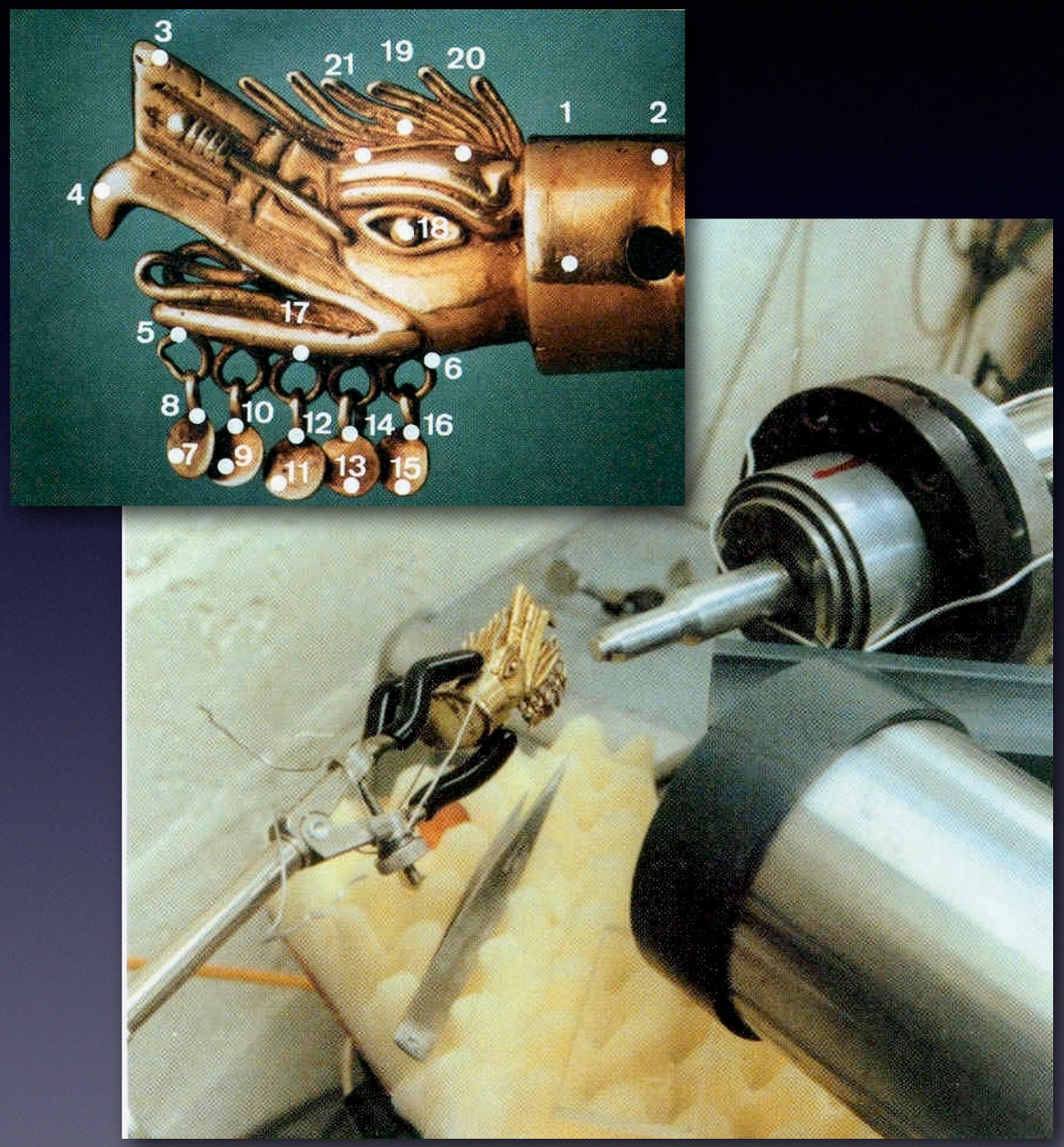


Analysis of the Ritratto di fanciullo by Luca Della Robbia – before restoration at the Opificio delle Pietre Dure in Florence

… drawings,

Micro-PIXE measurements of Portrait of Lucas de Leyde by Alfred Dürer
A.Duval et al., (Louvre laboratory)

... jewels,

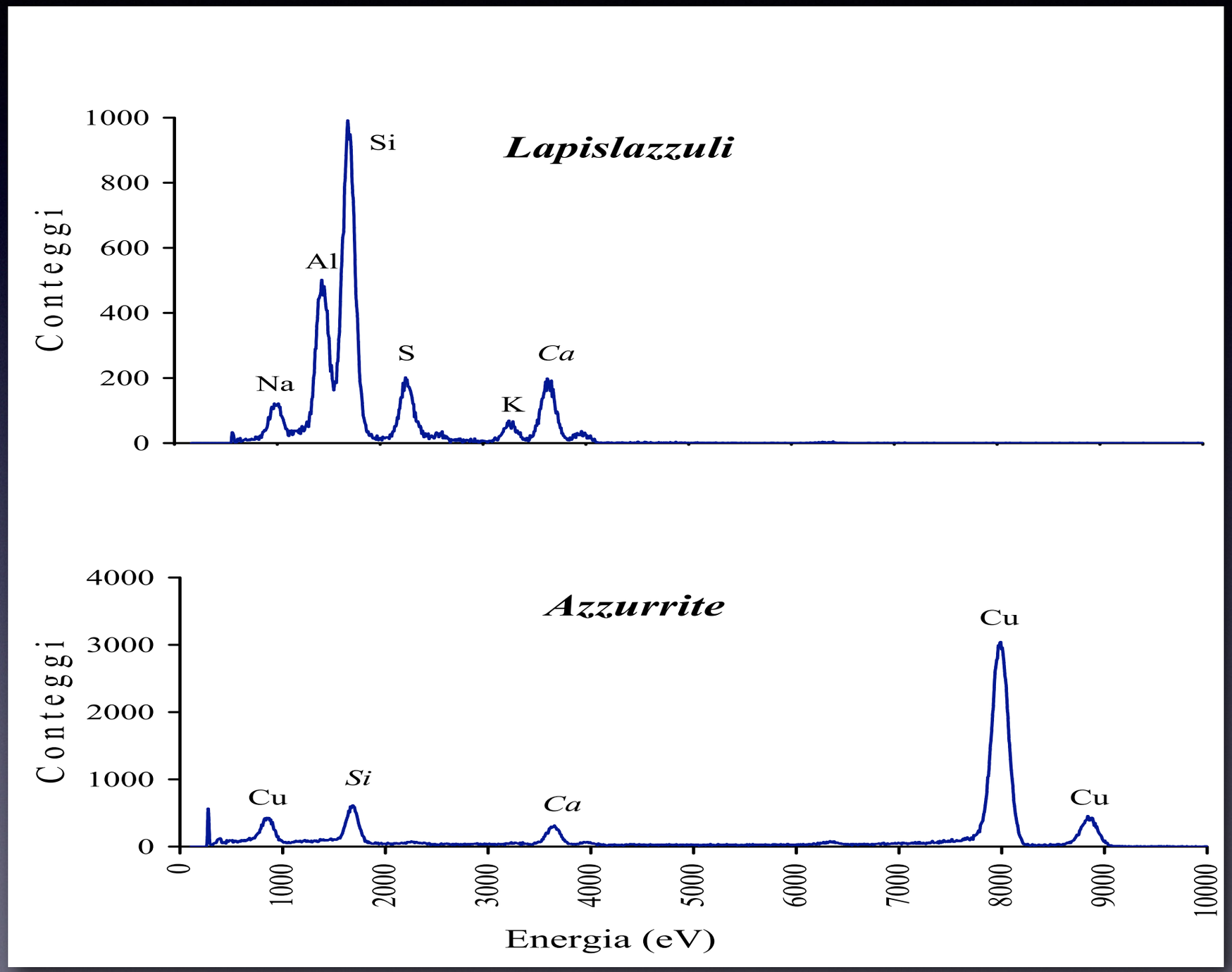


Micro-PIXE measurements of a Mexican gold alloy ornament
G.Demortier and J.L.Ruvalcaba Sil (Namur)

...paintings

PIXE analysis of a painting by
Lucas Cranach the Elder
C. Neelmeijer et al.
(Rossendorf Forschungszentrum, Dresda)

Blue Temperas



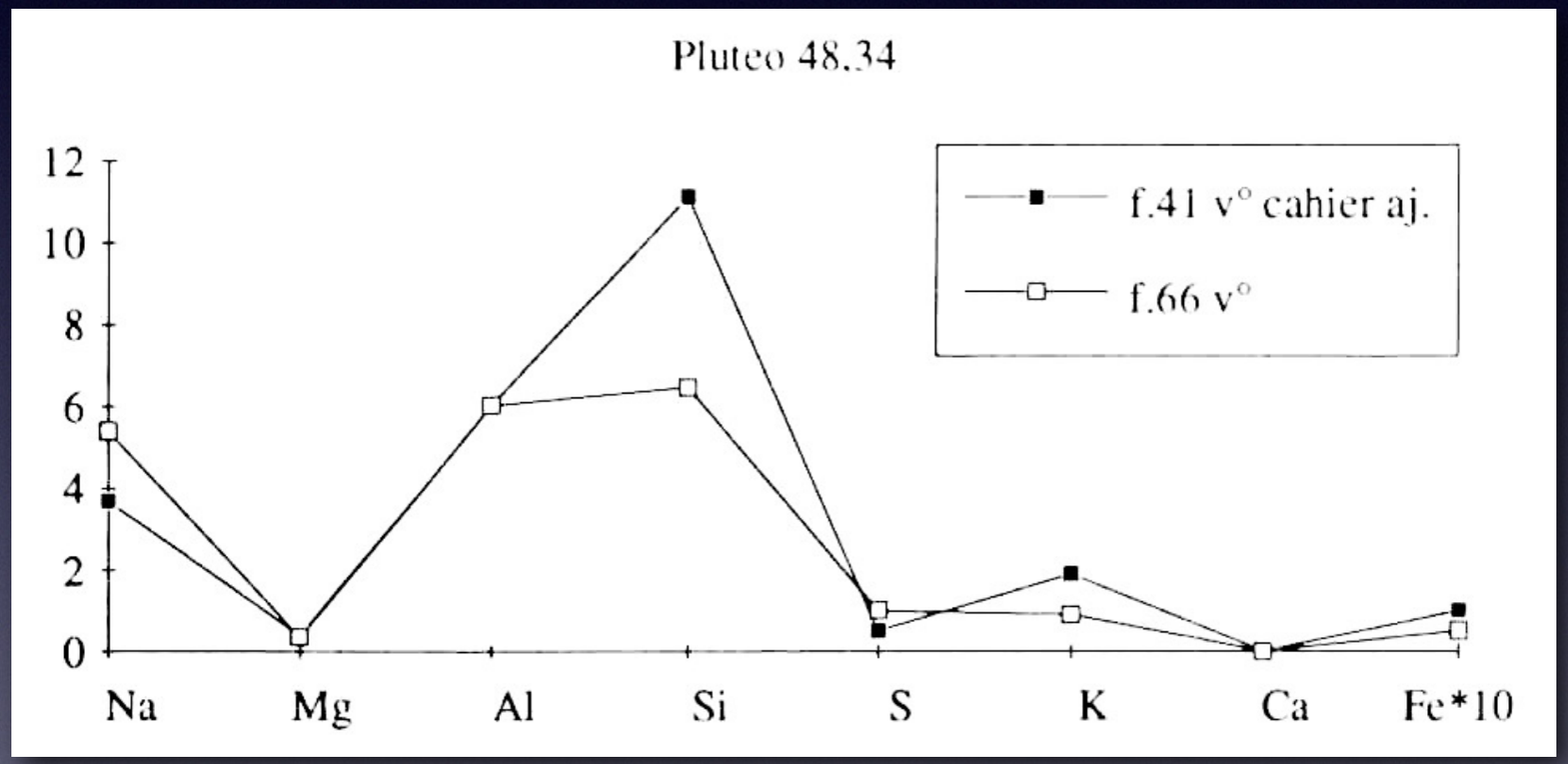
Example of PIXE spectra of two blue pigments

Blue Temperas

Extensive use of lapislazuli starting from XI century

Pluteo 48, 34, f. 66 v°

Pluteo 48, 34, f. 41 v°

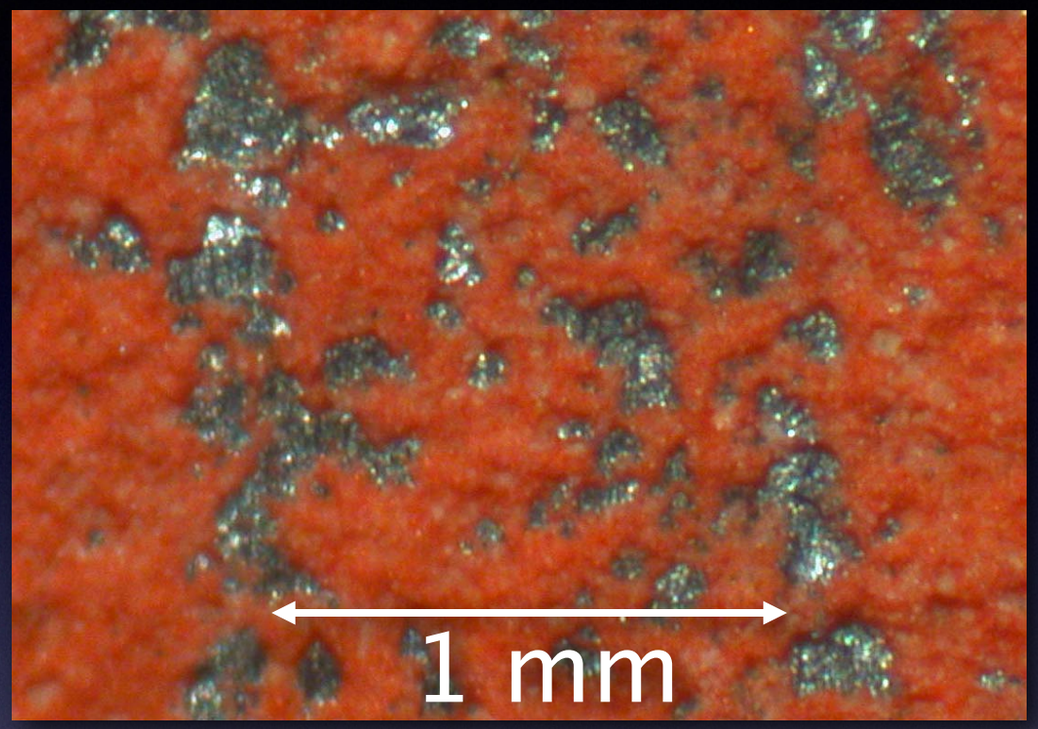


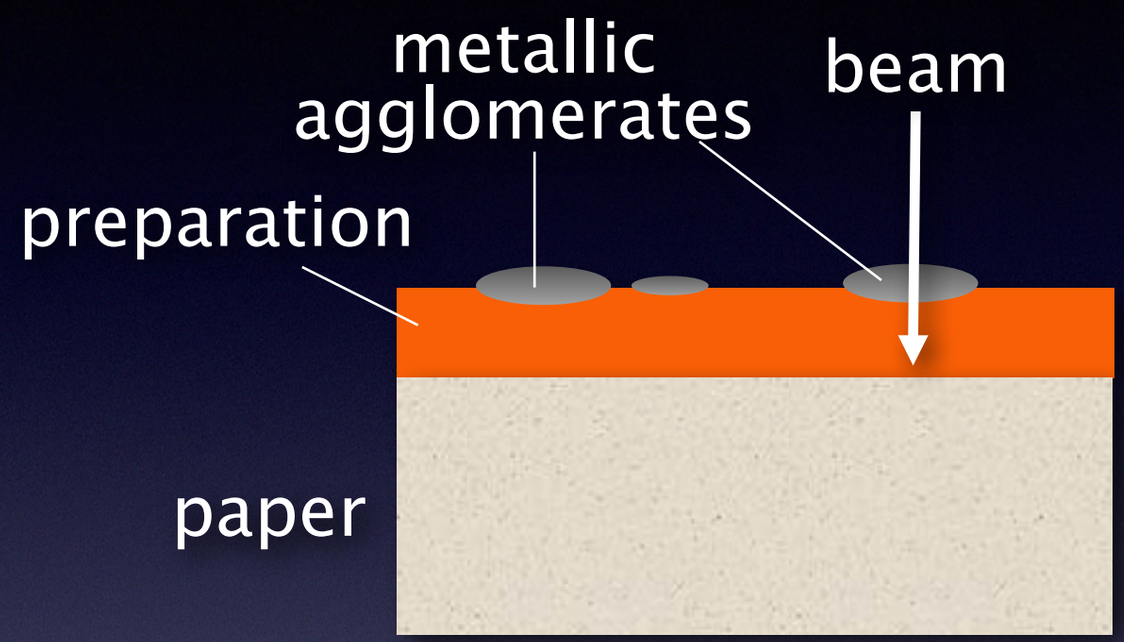
Metal point drawings

LEONARDO DA VINCI
STUDY OF A DRAPERY
Roma, Istituto Nazionale per la Grafica

metal point, lead white
red prepared paper

Characteristics of metal point drawings





The extension of the metallic agglomerates on the surface is some tens of μm

The beam can pass through the trace and hit the preaparation

The beam size does not allow a detailed analysis

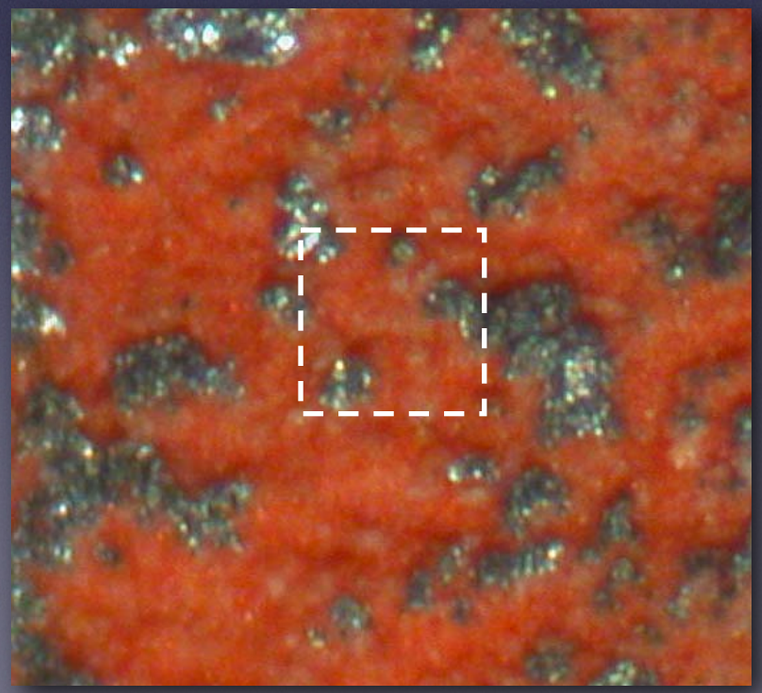
The contribution of the preparation must be taken into account

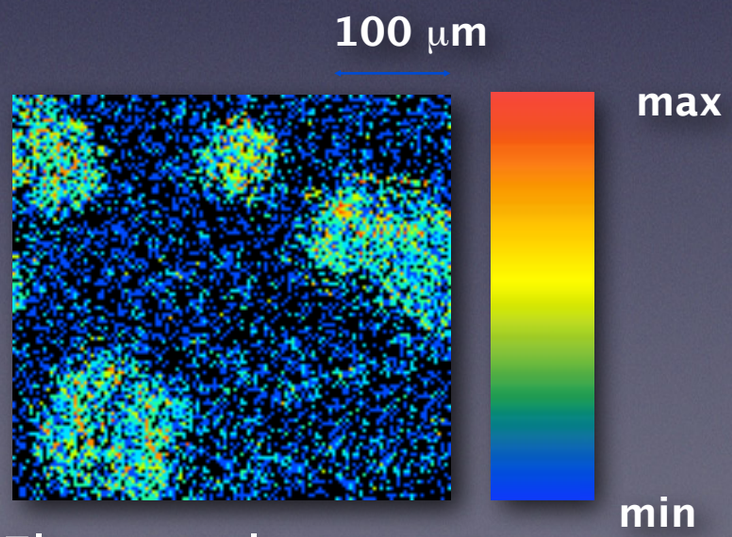
MicroPIXE analysis of metal point drawings

Four metallic points:
silver, lead, gold, copper

Red preparation:
cinnaber, yellow ochre, lead white, bone white

Au Cu Pb



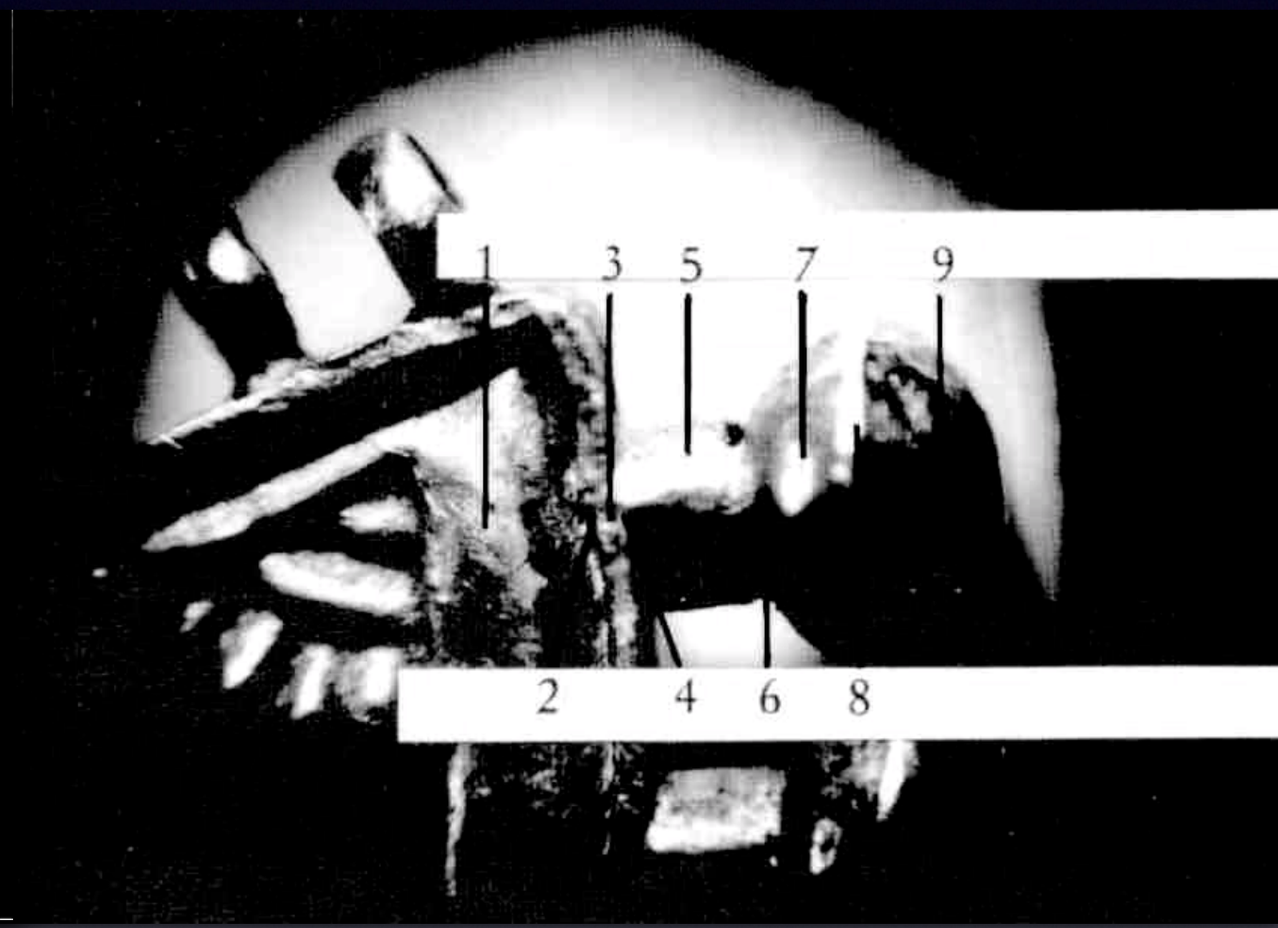


Elemental map on 0.4×0.4 mm^2

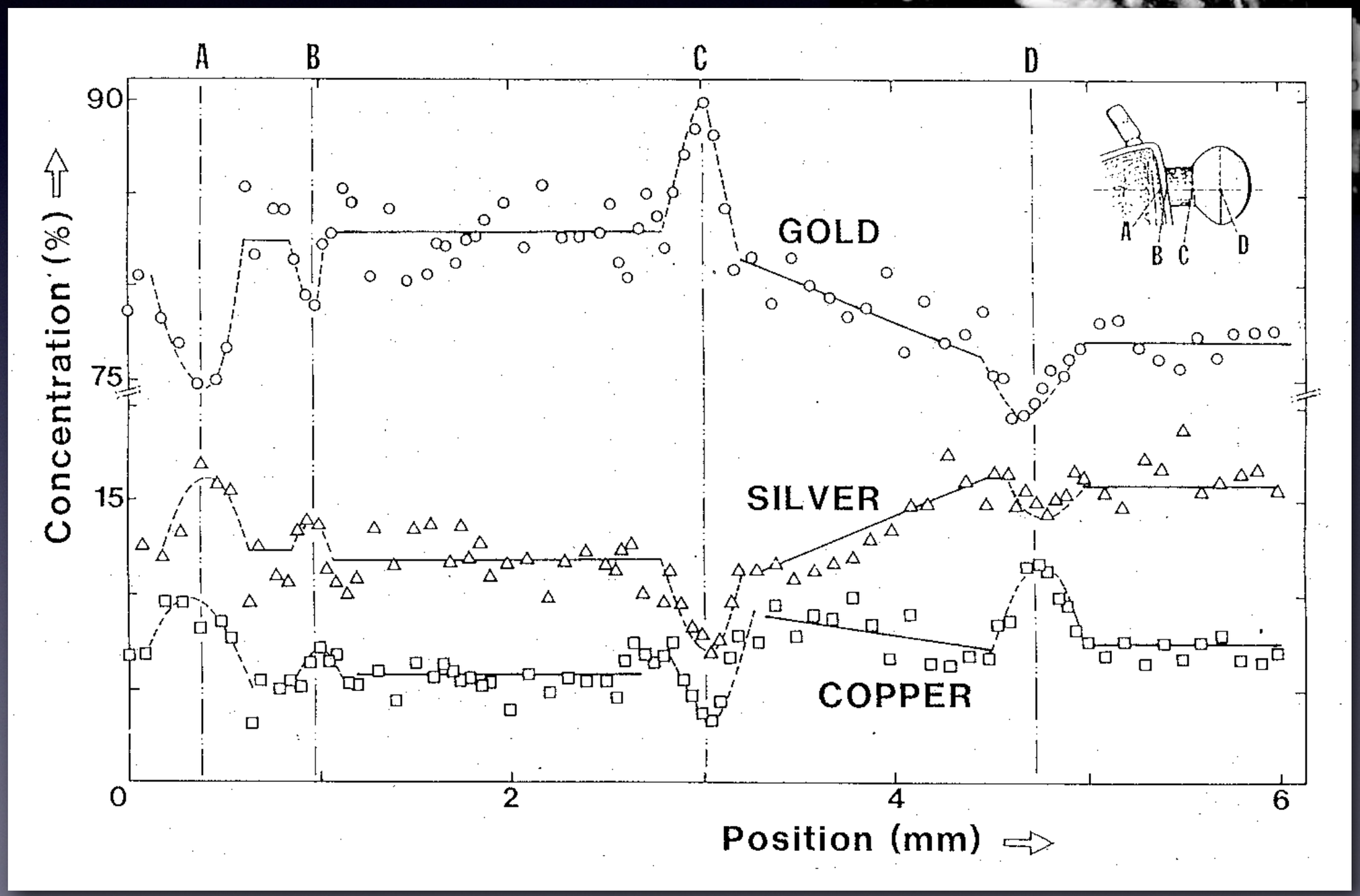
Lead stylus
(**Pb**, trace of Sn)

Red preparation
(S, Hg, Pb, Fe, P, Ca)

Micro-PIXE measurements of an Achemenide pendant (IV century BC)



Micro-PIXE measurements of an Achemenide pendant (IV century BC)

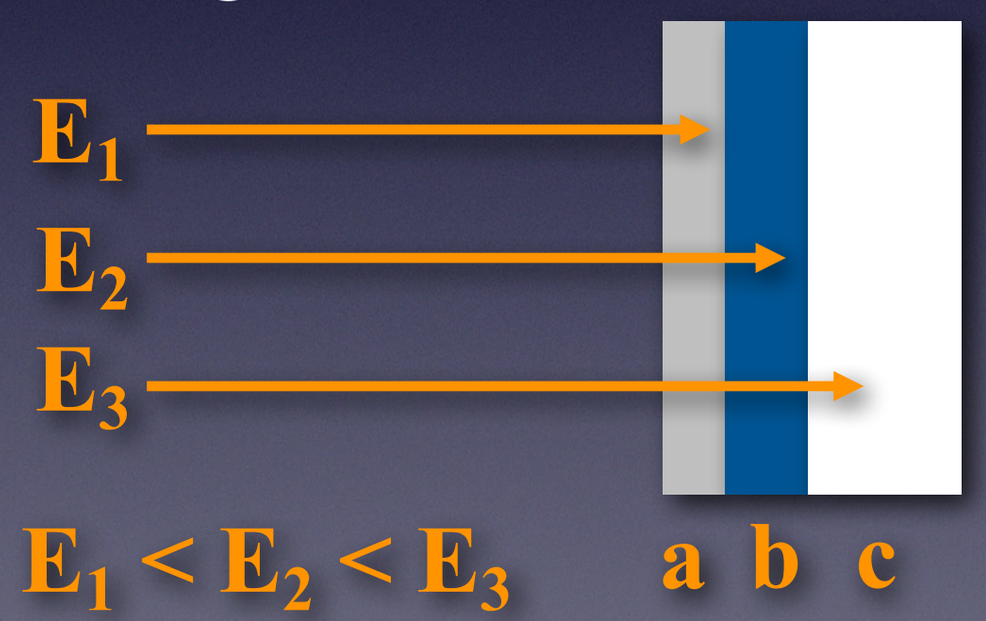


Differential PIXE

Whereas PIXE does not provide elemental depth profiles, "Differential PIXE" measurements can provide semi-quantitative stratigraphical information on cultural heritage objects (works mainly by the groups in Florence, Ljubljana and Namur).

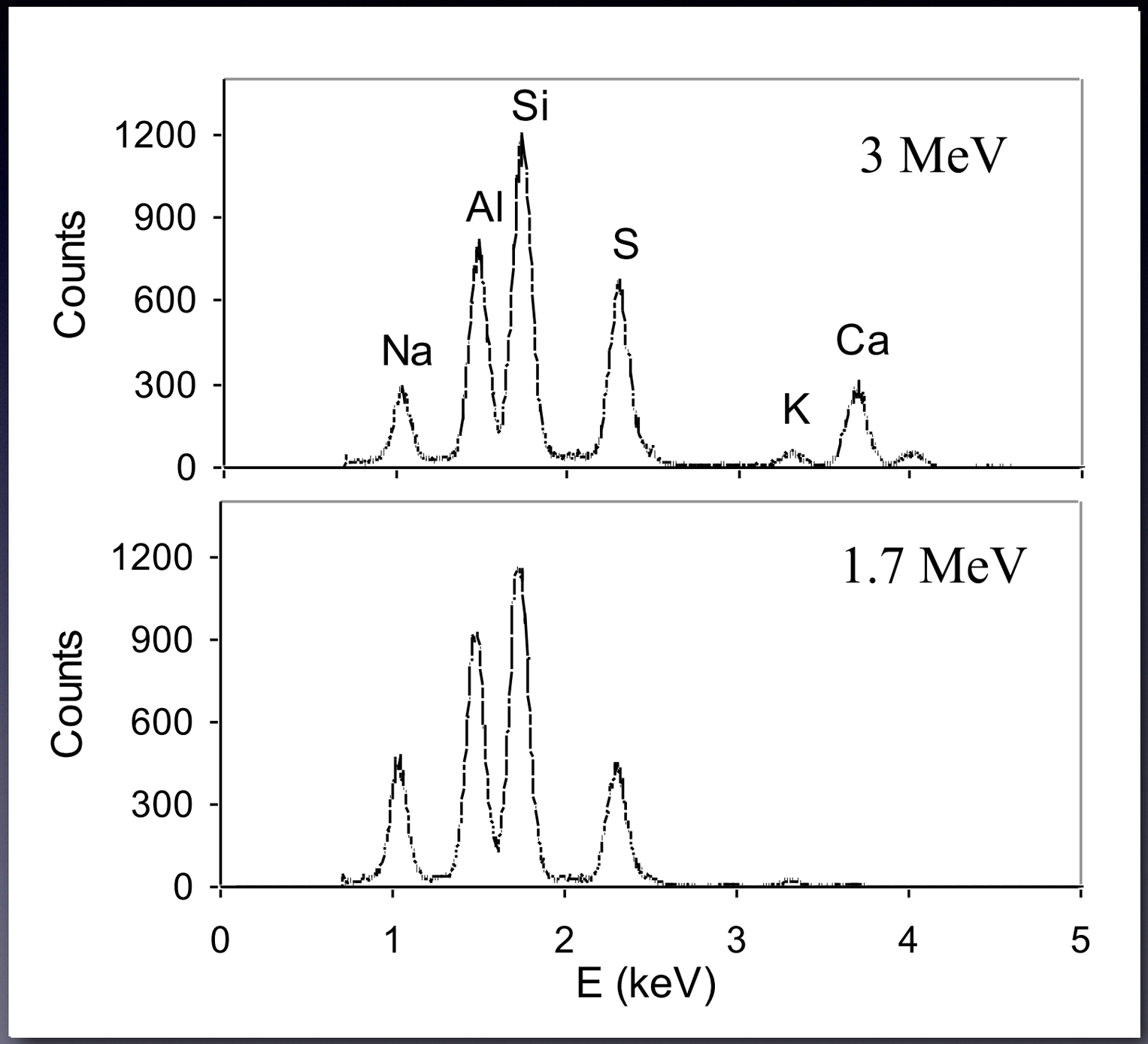
"Differential PIXE" consists in performing measurements on the same area with beams of different energies

At different energies proton beam ranges are different



By comparing X-ray spectra taken at different energies, stratigraphic information can be obtained

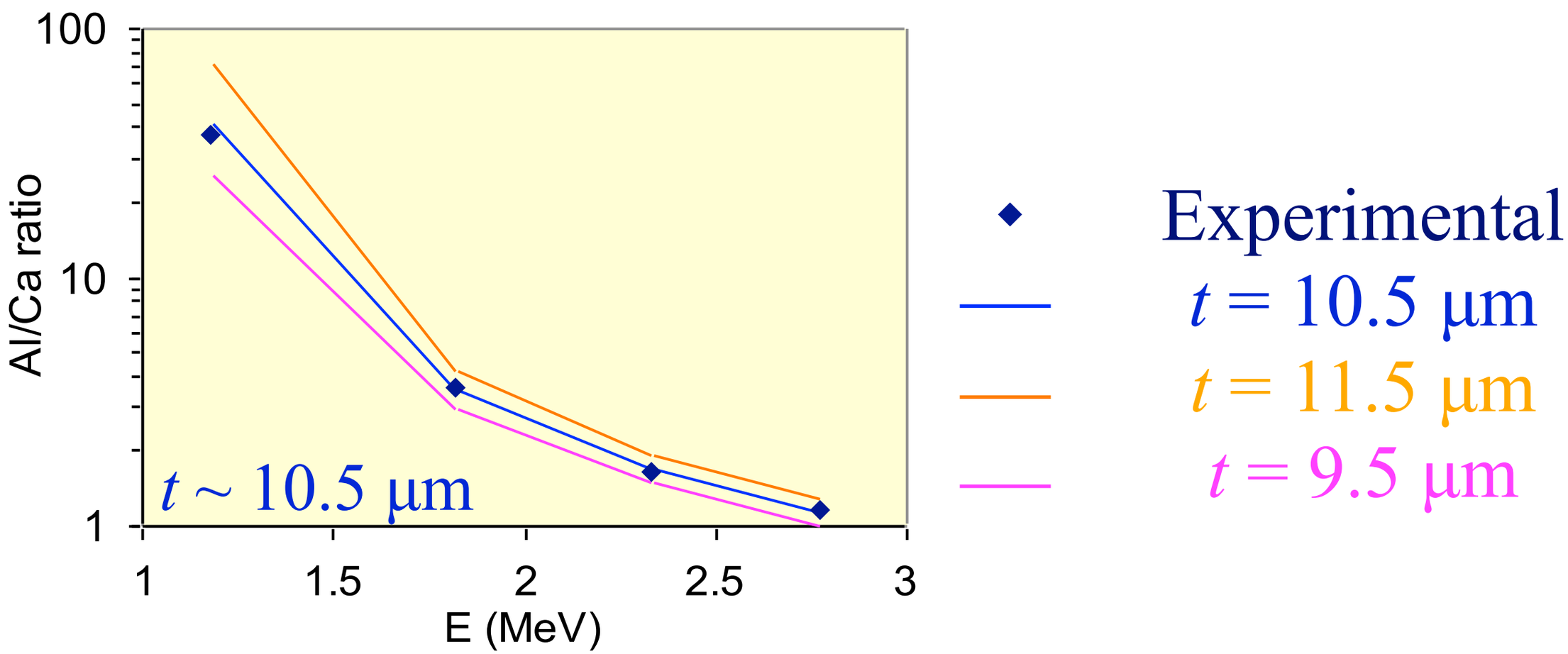
PIXE spectra at different energies



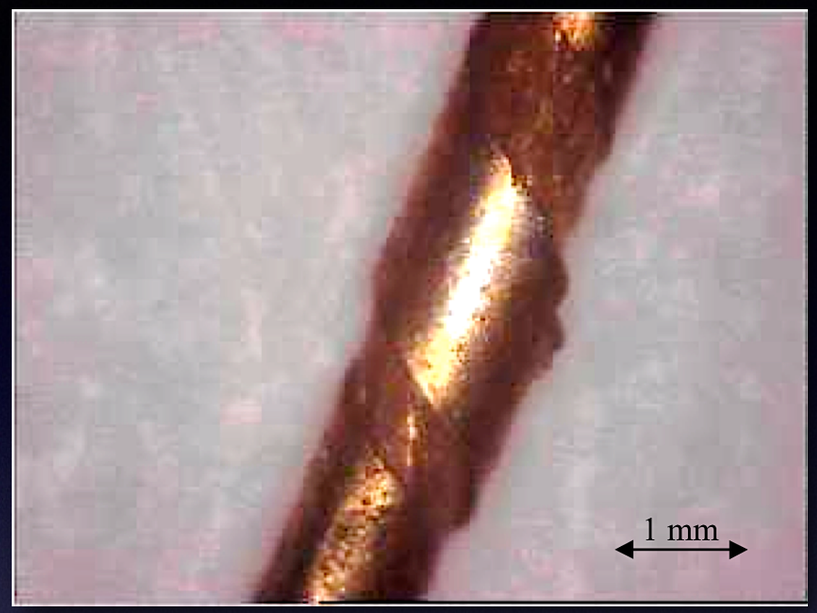
Blue paint layer (lapislazuli) on a substrate of calcium sulphate

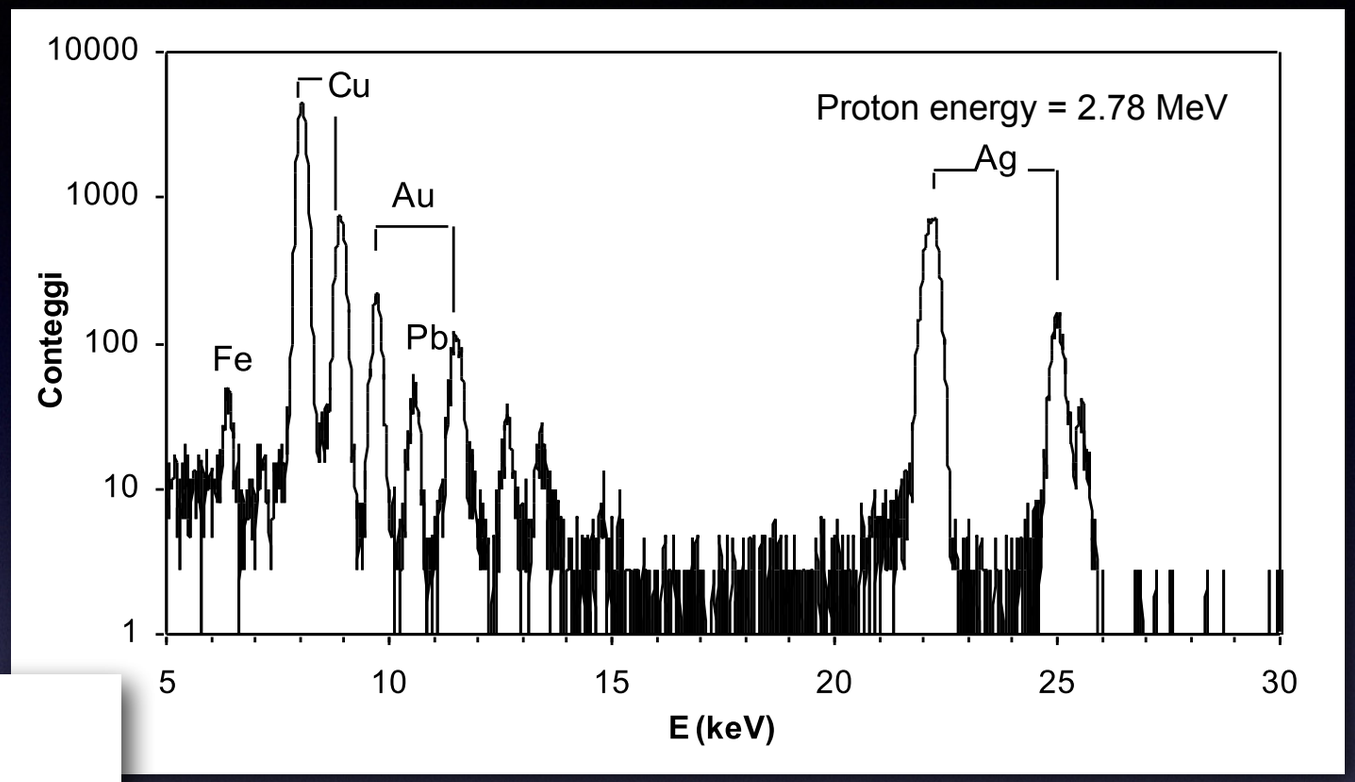
Estimate of the paint layer thickness

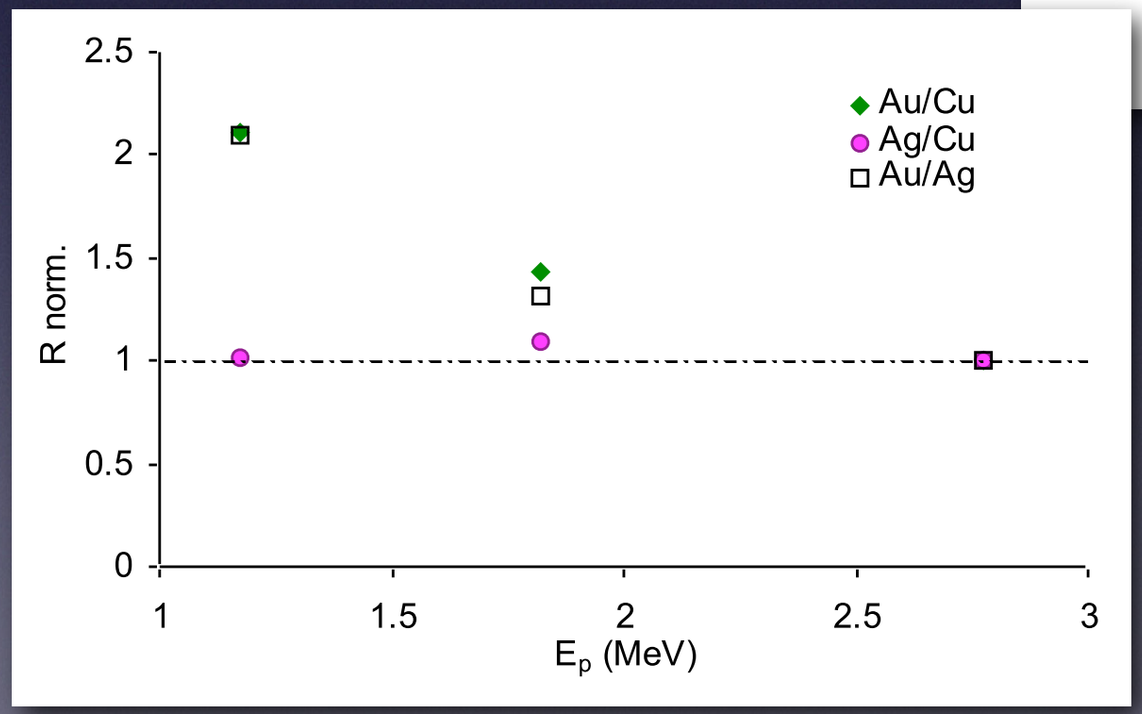
$$\frac{Y_{\mathrm{Al}}}{Y_{\mathrm{Ca}}} = \frac{C_{\mathrm{Al}}}{C_{\mathrm{Ca}}} \frac{\int_{E_{\mathrm{p}}}^{E_{\mathrm{p}}-\Delta E_{\mathrm{lap}}(t)} \sigma_{\mathrm{X}}^{(\mathrm{Al})}(E) \mathrm{e}^{-\mu_{\mathrm{lap}}^{(\mathrm{Al})} \frac{x(E)}{\cos\theta}} \frac{\mathrm{d}E}{S_{\mathrm{lap}}(E)}}{\mathrm{e}^{-\mu_{\mathrm{lap}}^{(\mathrm{Ca})} \frac{t}{\cos\theta}} \int_{E_{\mathrm{p}}-\Delta E_{\mathrm{lap}}(t)}^{0} \sigma_{\mathrm{X}}^{(\mathrm{Ca})}(E) \mathrm{e}^{-\mu_{\mathrm{white}}^{(\mathrm{Ca})} \frac{x'(E)}{\cos\theta}} \frac{\mathrm{d}E}{S_{\mathrm{white}}(E)}}$$

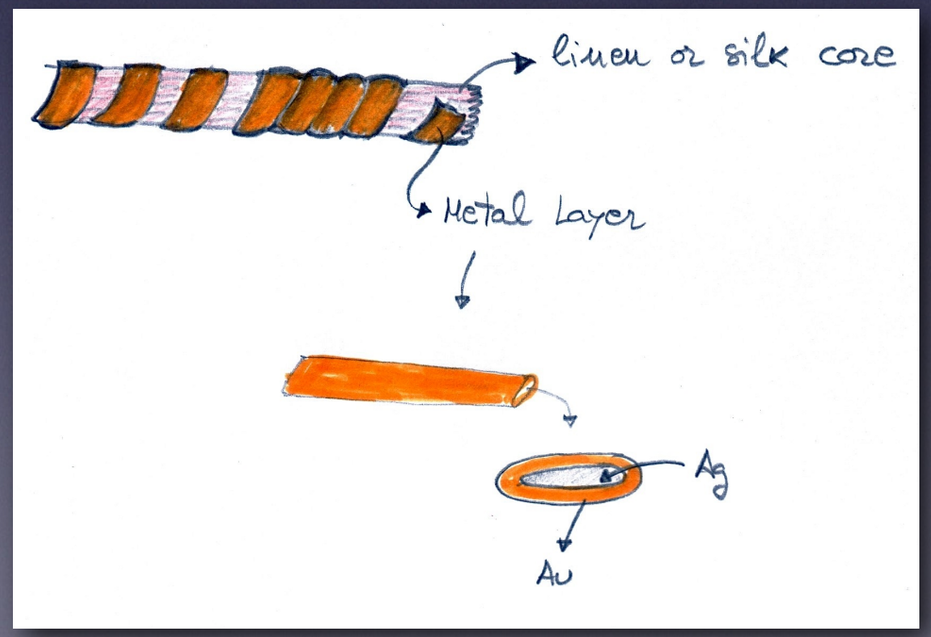


Metal threads (Alhambra, Granada)



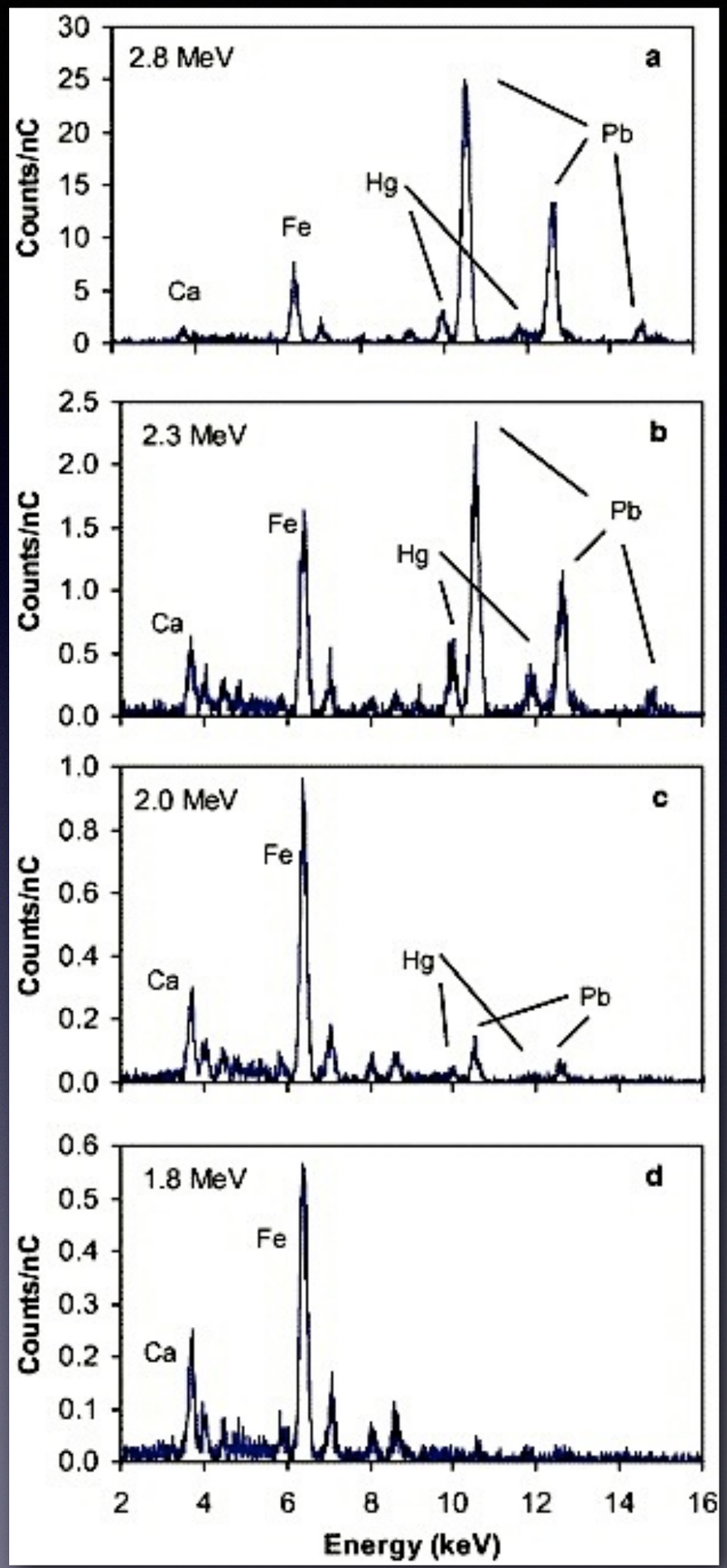


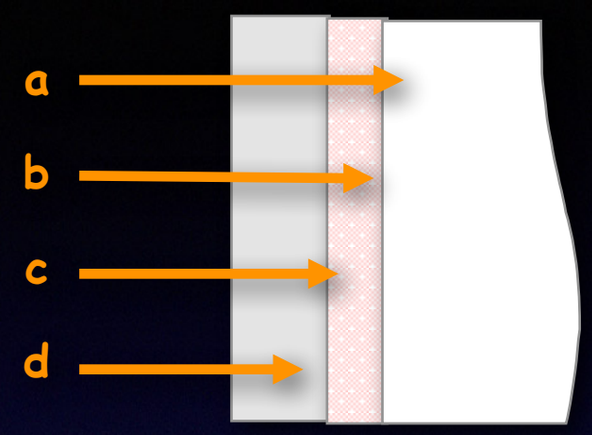


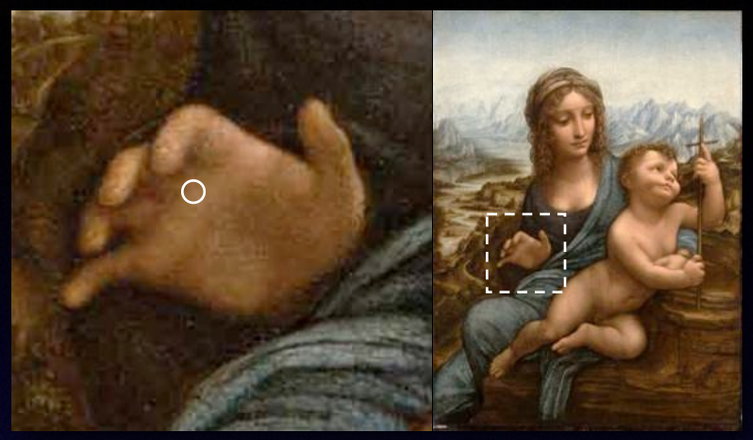


Enrichment of gold on the surface

“Incarnato”







paint layer:

cinnabar (HgS, red pigment)+lead white

preparation:

lead white

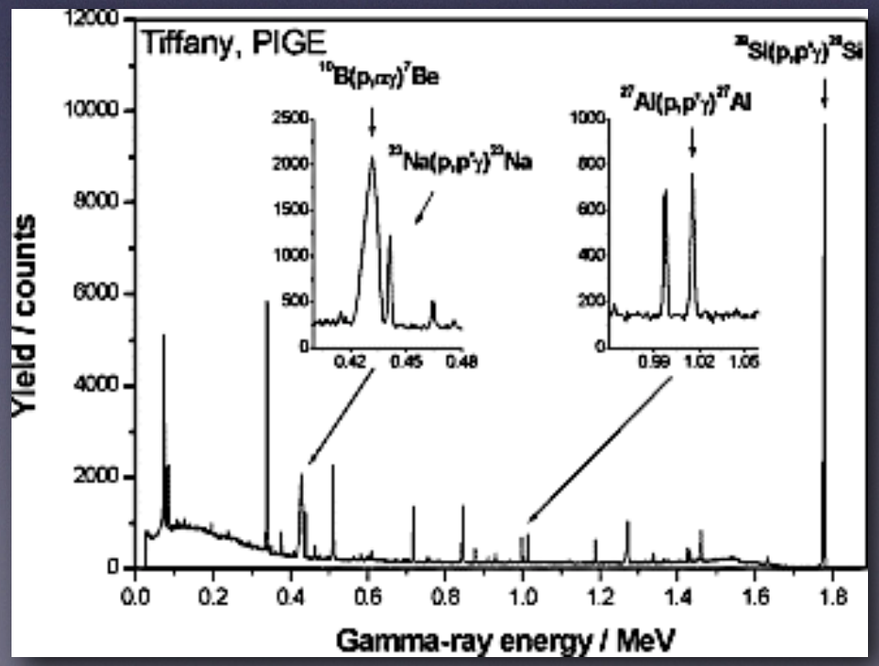
Ca and Fe are in the varnish

Complementary PIXE/PIGE

Particle Induced Gamma-ray Emission (PIGE) technique is an invaluable tool, complementary to PIXE, to quantify low-Z elements (Li, B, F, Na, Mg, Al, Si, ...) in cultural heritage objects.

In this respect PIGE can be considered a "sidekick" of PIXE

Sherlock Holmes and ***Doctor Watson***



Batman and ***Robin***

Frodo and ***Sam***

Lapis-lazuli pigment in paint layers

"Maddonna dei fusi", Leonardo da Vinci (1501)

Lapis-lazuli is a blue pigment, mainly composed of lazurite ($3Na_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2Na_2S$)

Limited possibility of identifying lapis-lazuli by PIXE in canvas and wood paintings:

- *low-energy X-rays absorption in the varnish and in the paint layer itself*
- *signal interference from other pigments*

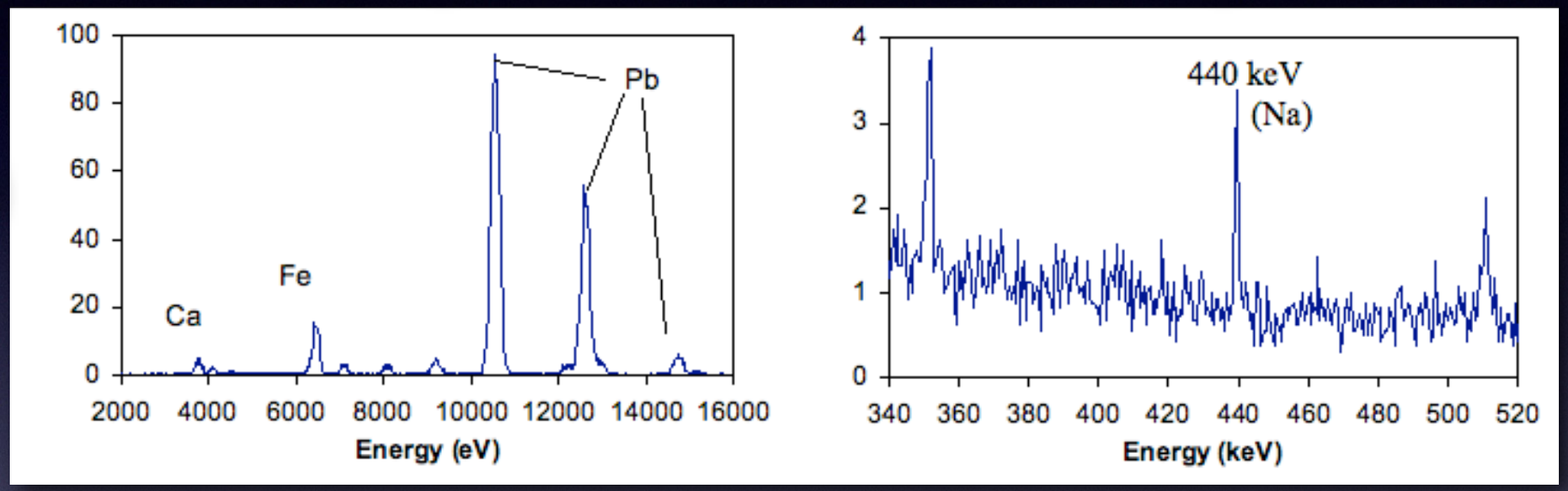
Lapis-lazuli pigment in paint layers

PIXE spectra

PIGE spectra

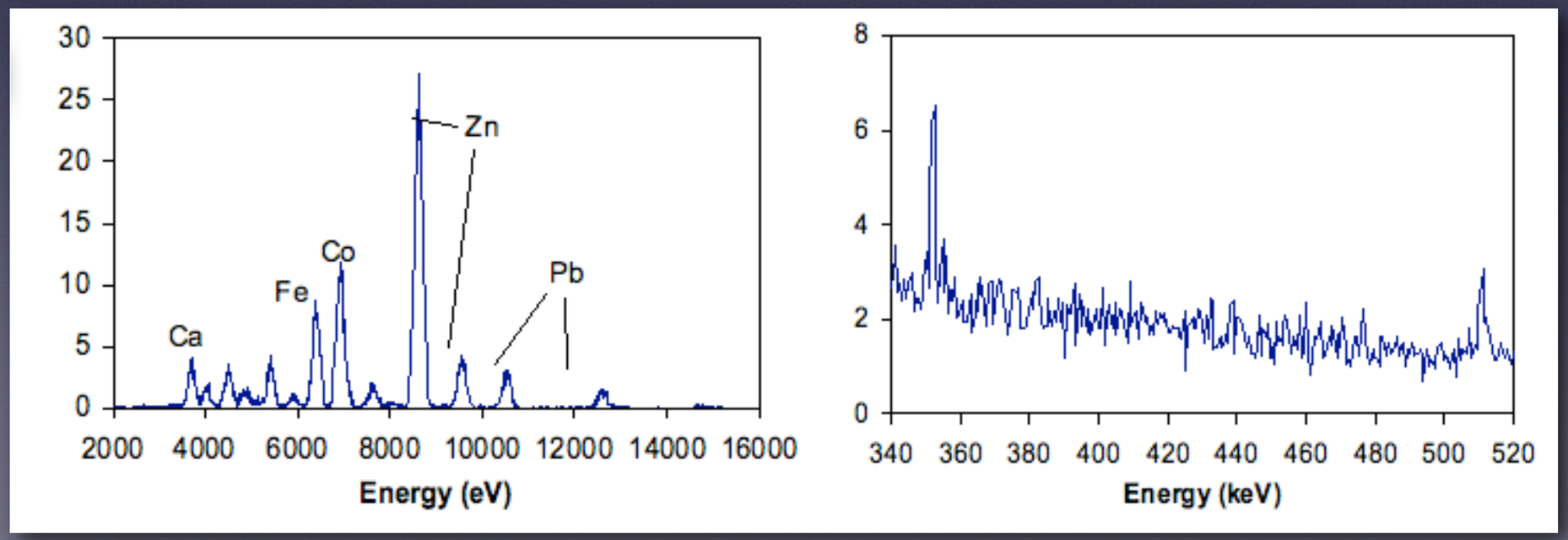
Original

Blue pigment mixed with Lead white (Ca and Fe from the varnish)



Restored

Cobalt blue and Zinc white (used only from XIX century!)



Analysis of ancient Roman glasses

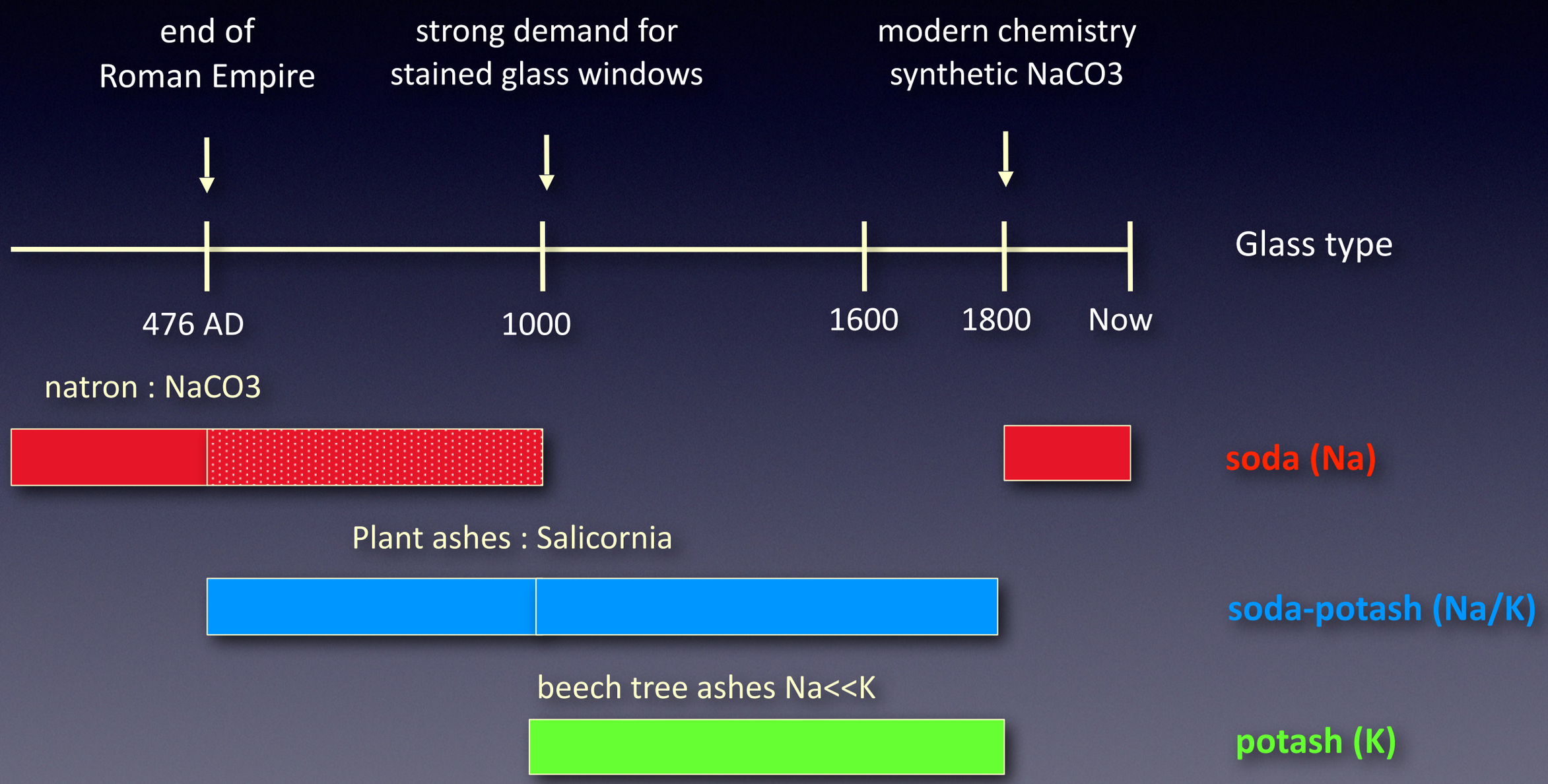
Quantification of sodium is of great importance for the characterisation of ancient glasses

Roman glass mosaic *tesserae* from Villa Adriana, Tivoli (Italy)

There are two basic typologies of Western glasses:

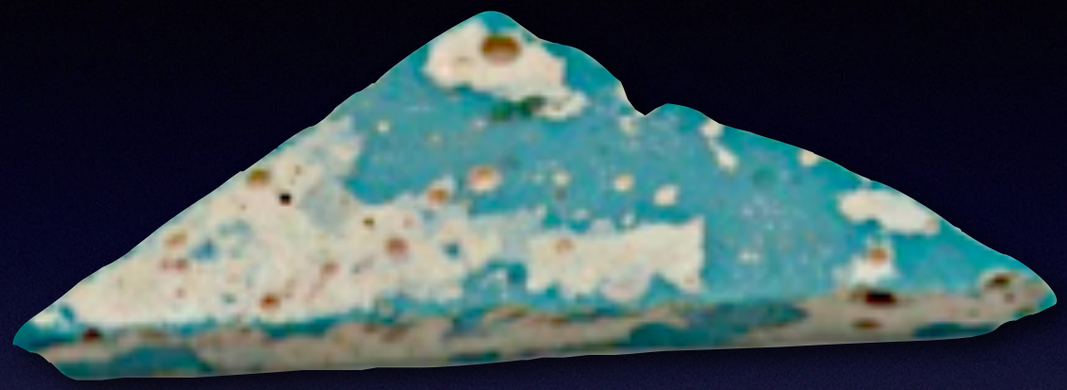
- **natron**
  (high Na_2O, low K_2O and MgO content)
  Roman and High Middle Ages
- **plant ash**
  (low Na_2O, high K_2O content)
  since Middle Ages

Evolution of glass manufacture technology



Sodium in Roman glasses

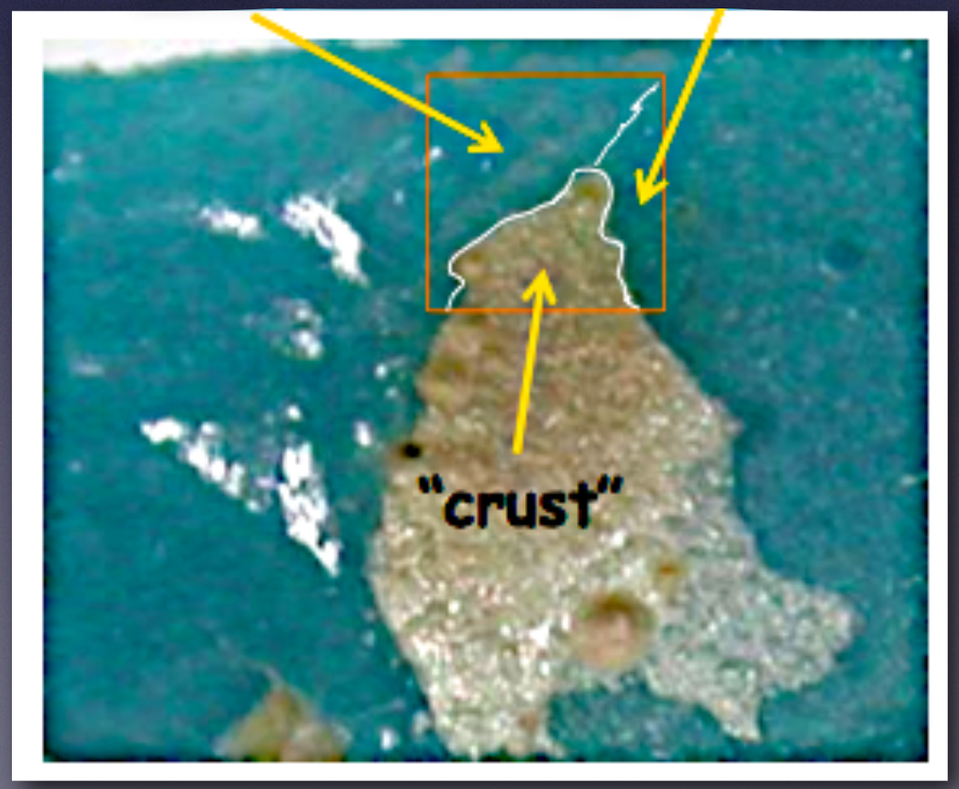
X-rays fom the lightest elements strongly absorbed by crusts and *patinae*

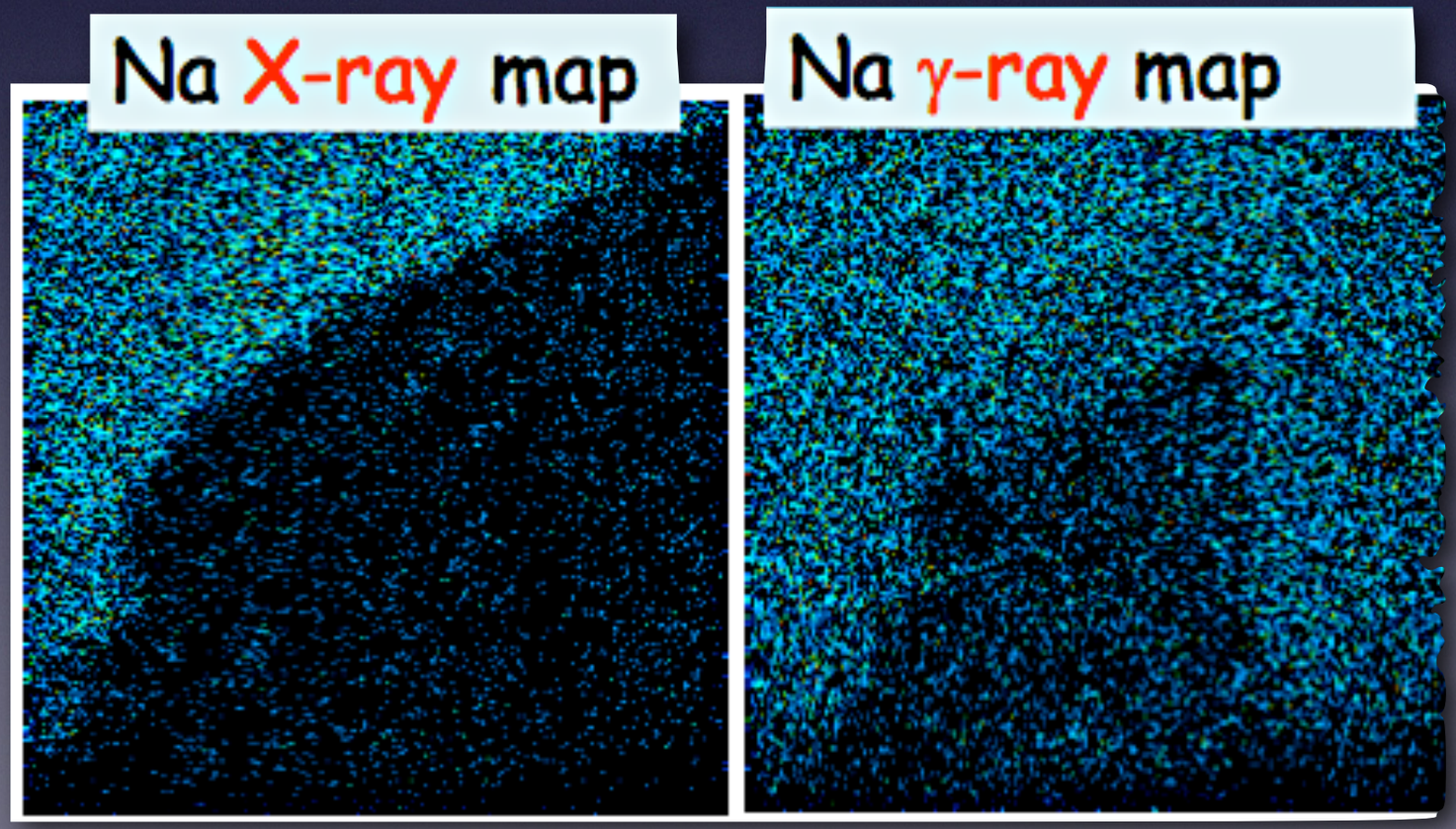


Roman glass mosaic *tesserae*

"freshly cut" zone

coloured but more opaque zone

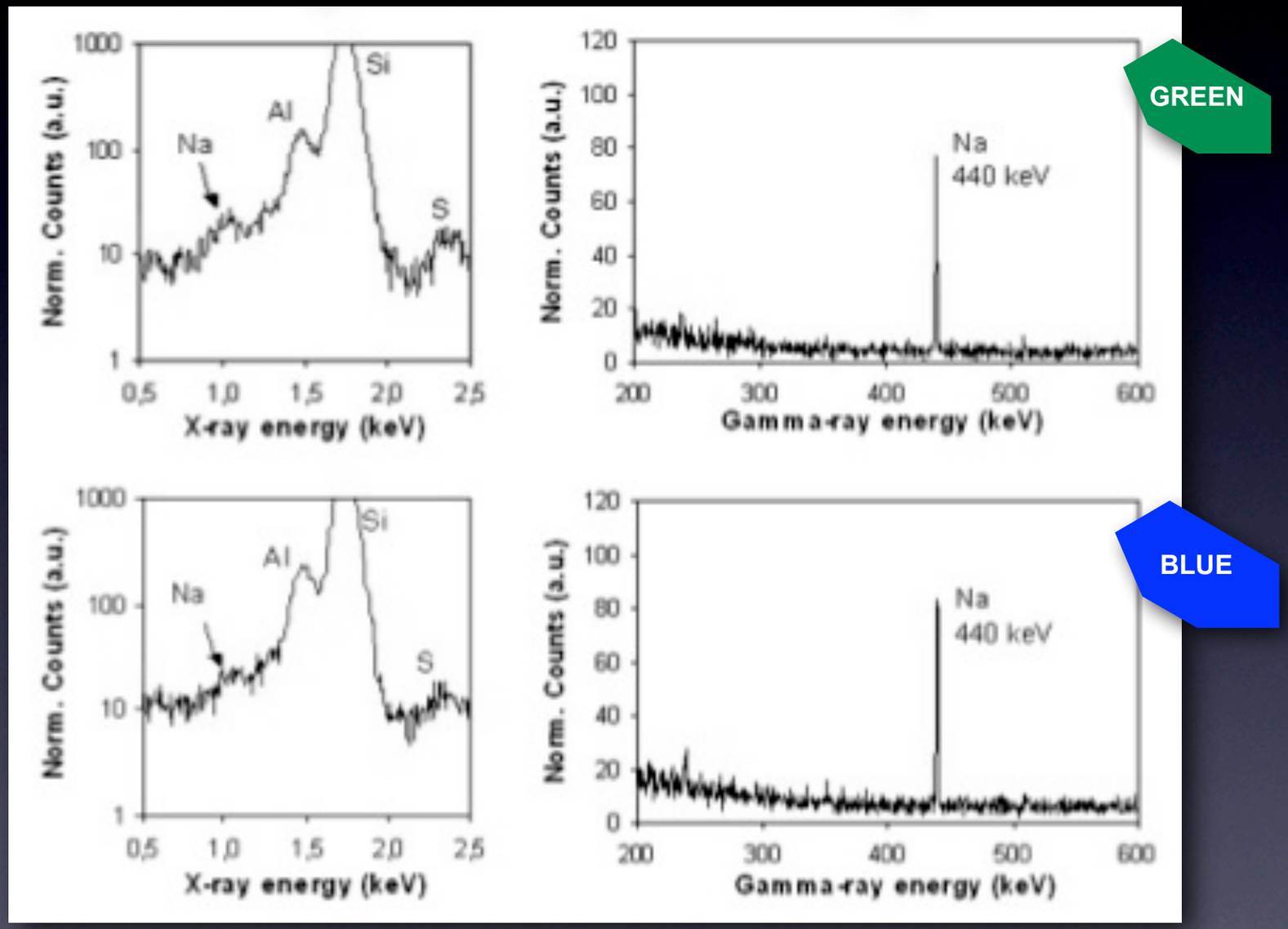




2 mm

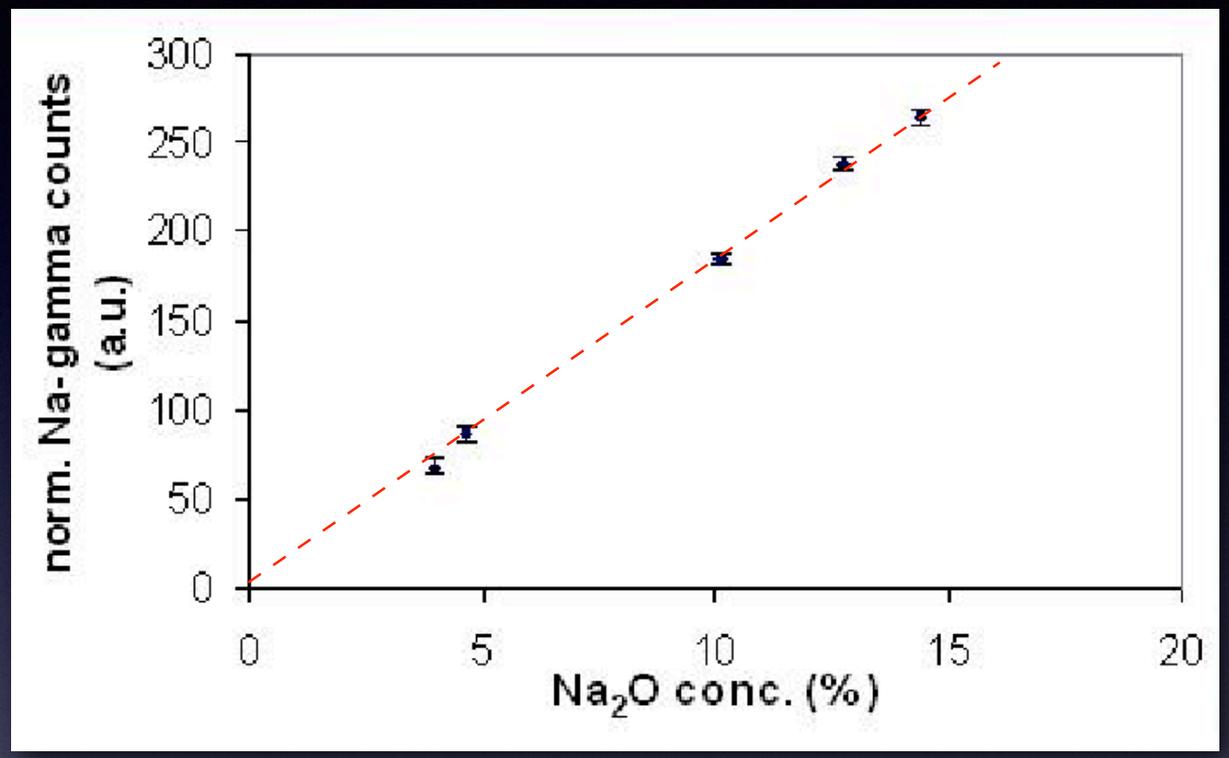
Sodium in Roman glasses

PIXE spectra PIGE spectra



X-rays from the lightest elements strongly absorbed by crusts and *patinae*

Sodium in Roman glasses



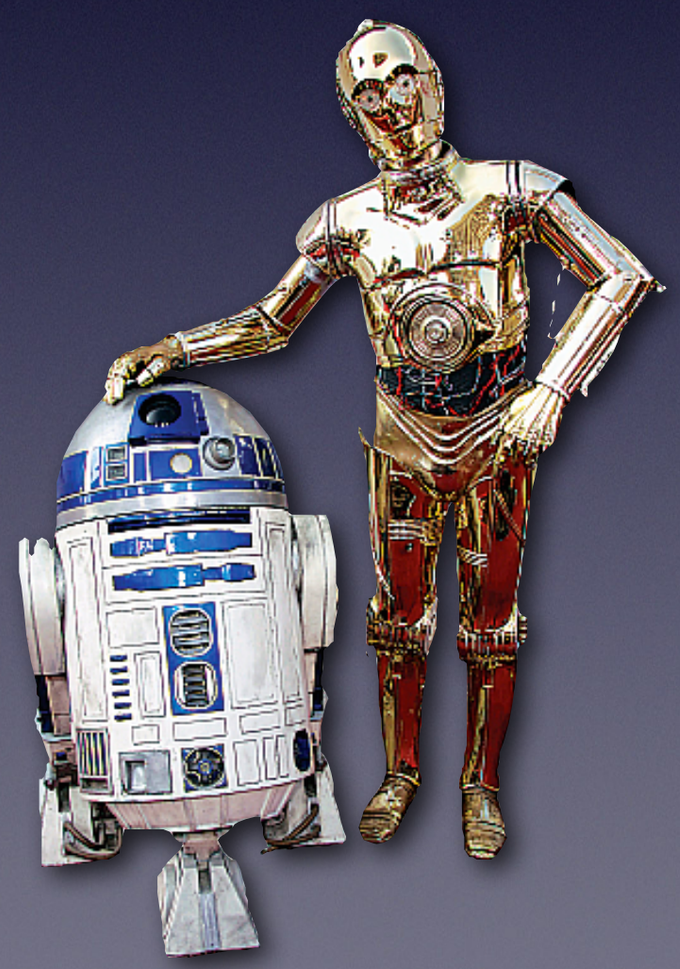
Estimate of Na content by comparing gamma-ray yields to those of thick glass standards (NIST SRM) with certified Na_2O concentration

Concentration ranges perfectly compatible with the typical Roman soda-lime-silica glass

glass colour	main oxides (%)			
	Na_2O	SiO_2	CaO	PbO
green	~20	55-60	5-9	1-3
blue	~20	60-65	5-9	<0.1
turquoise	~20	55-60	5-9	<0.3
yellow	~15	55-60	5-9	5-8
red	~10	35-40	5-9	30-35

Complementary PIXE/RBS

Whereas PIXE and Rutherford Backscattering Spectroscopy (RBS) separately give only partial information, in samples with a layered structure these analyses can be performed simultaneously and their synergic use permits to derive detailed data about composition and elemental depth distribution of the analysed material (aka "Total IBA")



PIXE strenghts

- High sensitivity
- Excellent specificity

RBS weaknesses

- Low sensitivity
- Poor mass resolution

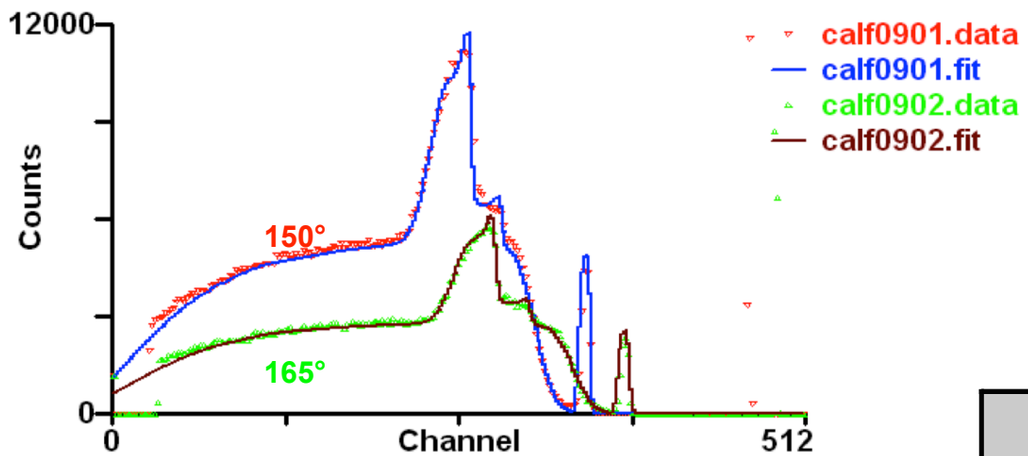
RBS strenghts

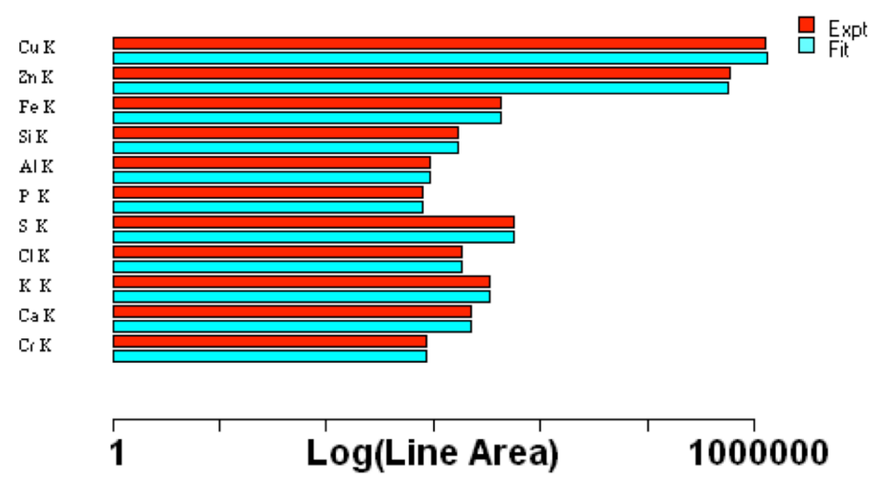
- Traceable accuracy
- Excellent depth resolution

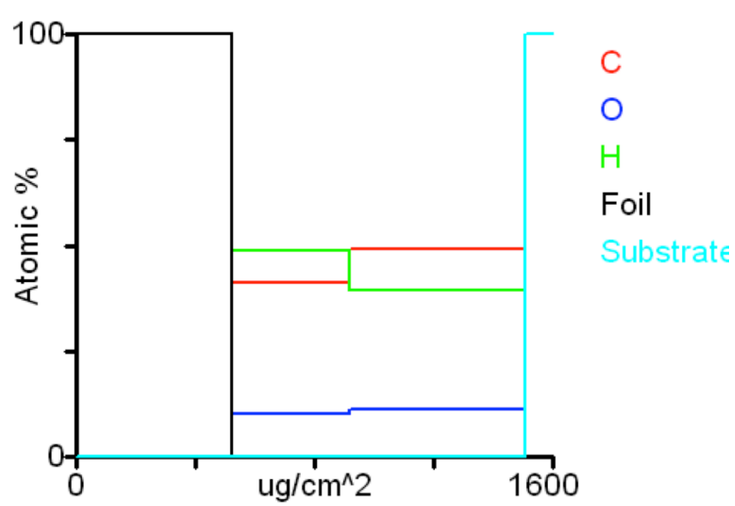
PIXE weaknesses

- Poor traceability
- Poor depth resolution

“Total IBA” of 1-layered brass test sample



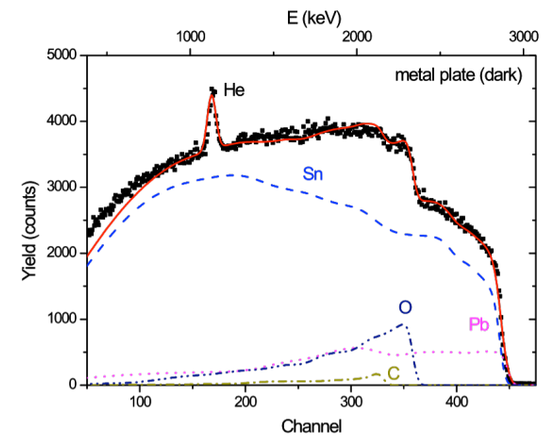




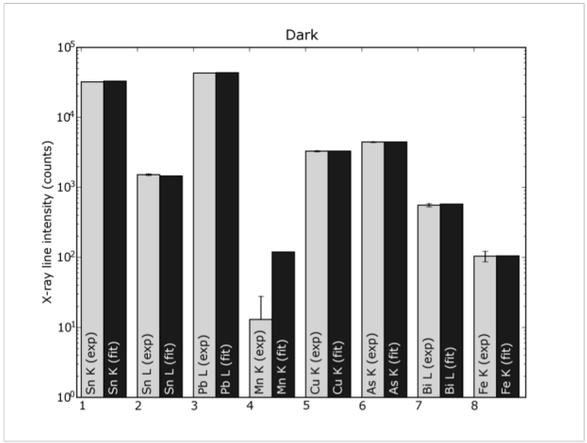
	DataFurnace	SIMNRA	GUPIX
Gilding	Cu 94% Zn 2% Fe 1%, 510 µg/cm	Cu 89% Zn 11%, 390 µg/cm	
Mordant	H 40-49% C 41-49% O 10-11%, 1.0 mg/cm	H 51% C 41% O 8%, 1.0 mg/cm	
Bulk	Cu 65% Zn 35%	Cu 65% Zn 35%	Cu 66%, Zn 34% H&Q 0.946

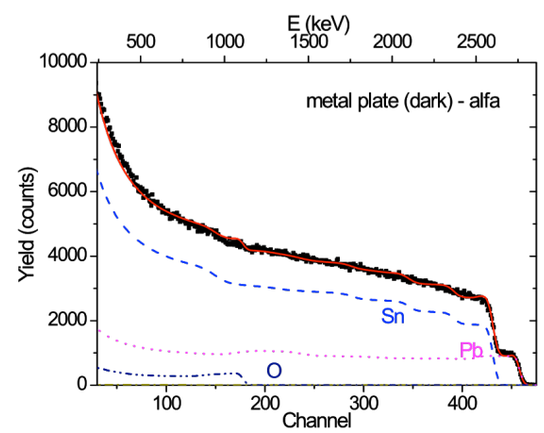
Analysis of stratigraphies in cultural heritage by PIXE/RBS analysis

"View from the Window at Le Gras", the oldest surviving camera photograp ("heliography") created by Nicéphore Niépce (in 1826 or 1827) at Saint-Loup-de-Varennes

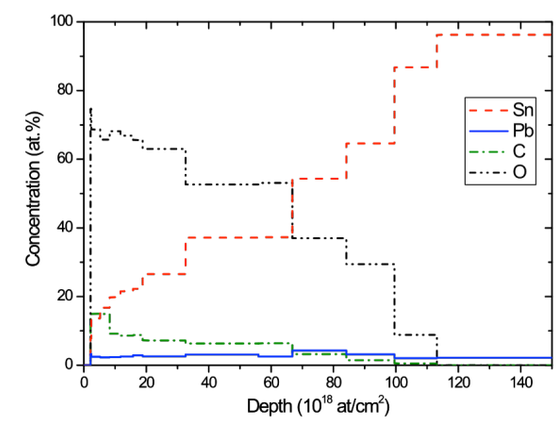


Fitted RBS spectrum for 3 MeV H^+ beam on the dark spot (corroded area). Calculated partial spectra for each element are also shown





Fitted RBS spectrum for 3 MeV $^4He^+$ beam on the dark spot (corroded area). Calculated partial spectra for each element are also shown

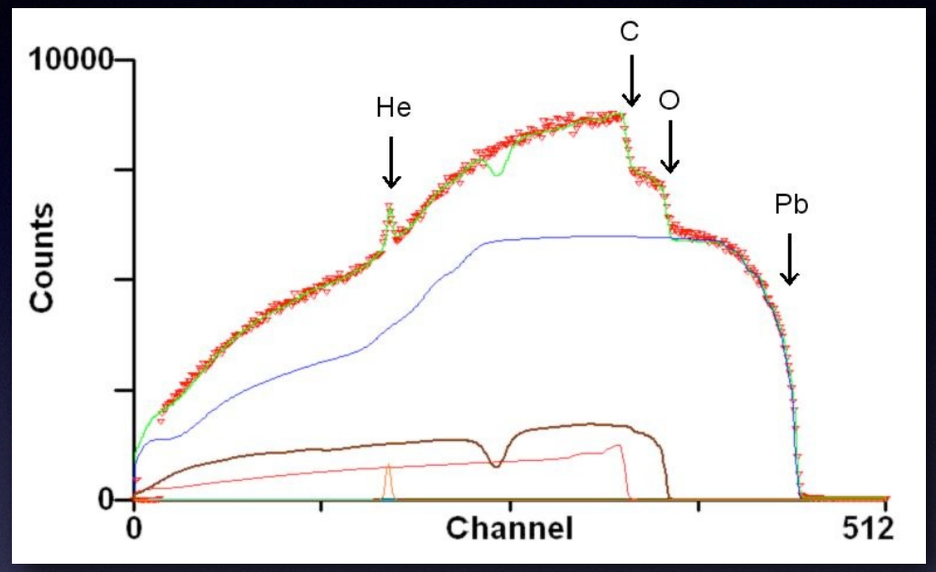


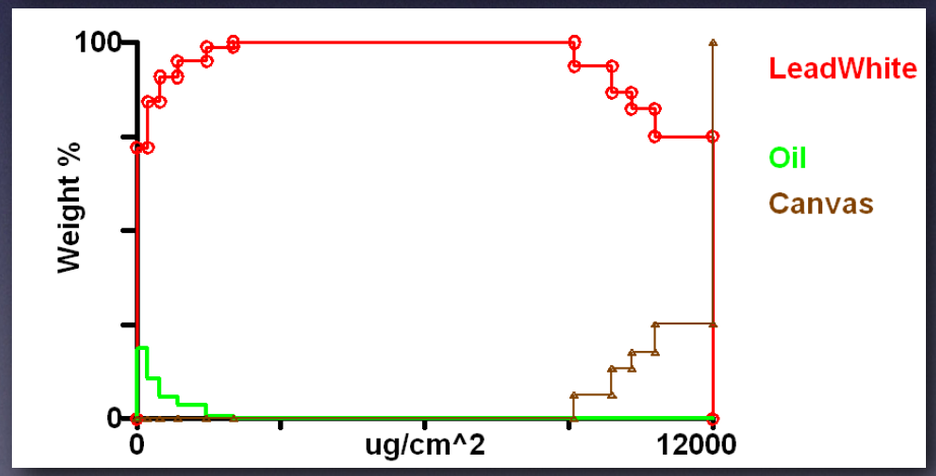
Concentration profiles for the dark spot (corroded area), as obtained from a simultaneous fit to 3 MeV proton PIXE and RBS, and 3 MeV alpha RBS.

PIXE/RBS analyses reveal that the corrosion proiducts are lead oxides in a Sn/Pb matrix

Characterization of paint layers by simultaneous PIXE/RBS analysis

"La Bohémienne", Frans Hals (1630)





The canvas is schematized as carbon plus chalk ($CaCO_3$)

Ochre pigment (ematite) detected and quantified thanks to simultaneous PIXE/RBS measurements: $440 \cdot 10^{15}$ atoms/cm^2 Fe_2O_3 in $7000 \cdot 10^{15}$ atoms/cm^2 of oil ($C_{13}O_5$)

Thanks for your attention!