Principles of PIXE and PIGE
advanced techniques and applications

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ASBeST

A 7-Beryllium electron capture STudy for nuclear and solid state physics

Nuclear Physics meets Electronic Technology - Summer School
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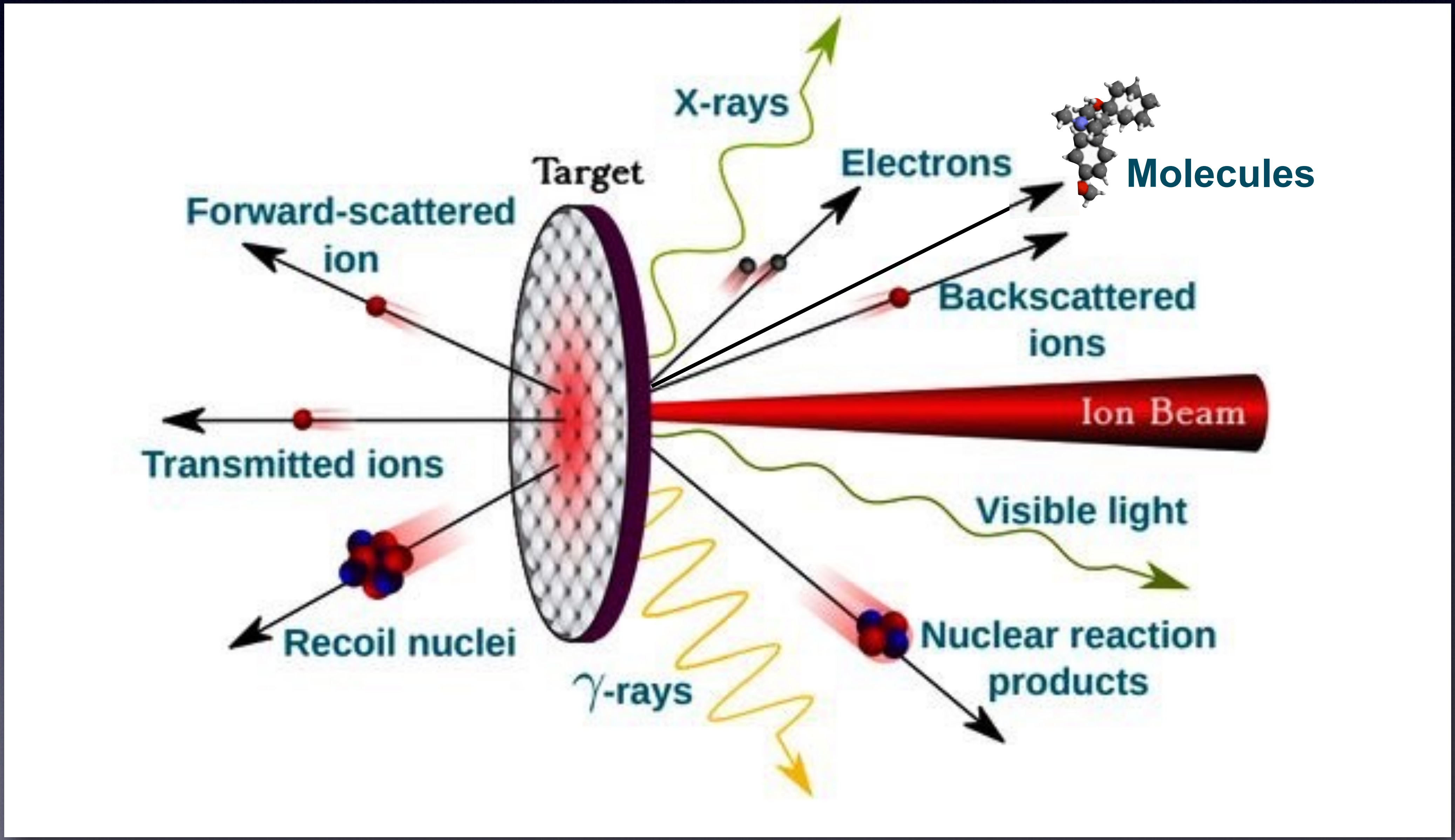
Outline

- Introduction to Particle Induced X-ray Emission and Particle Induced Gamma-ray Emission techniques
- External beams
- Examples of applications (environment, cultural heritage, forensics, geology, material science)
- Future technological advances

IBA

Ion Beam Analysis



IBA are like a superhero team…

PIXE

Particle Induced X-ray Emission

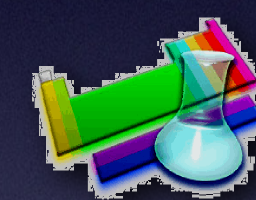
Emission of characterisic X-rays following ioniziation from incident ions

Z>10

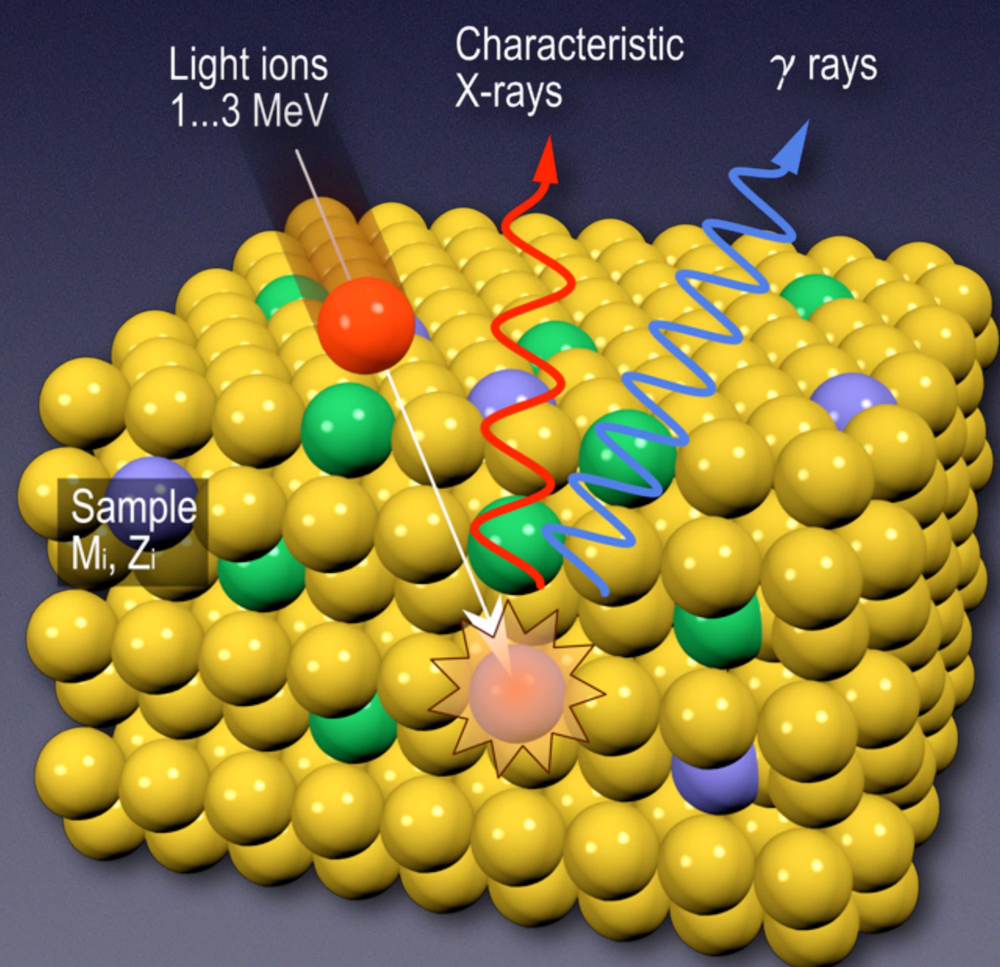
PIGE

Particle Induced Gamma-ray Emission

Prompt emission of gamma-rays during the ion beam irradiation



Li, Be, B, F, Na, Al...

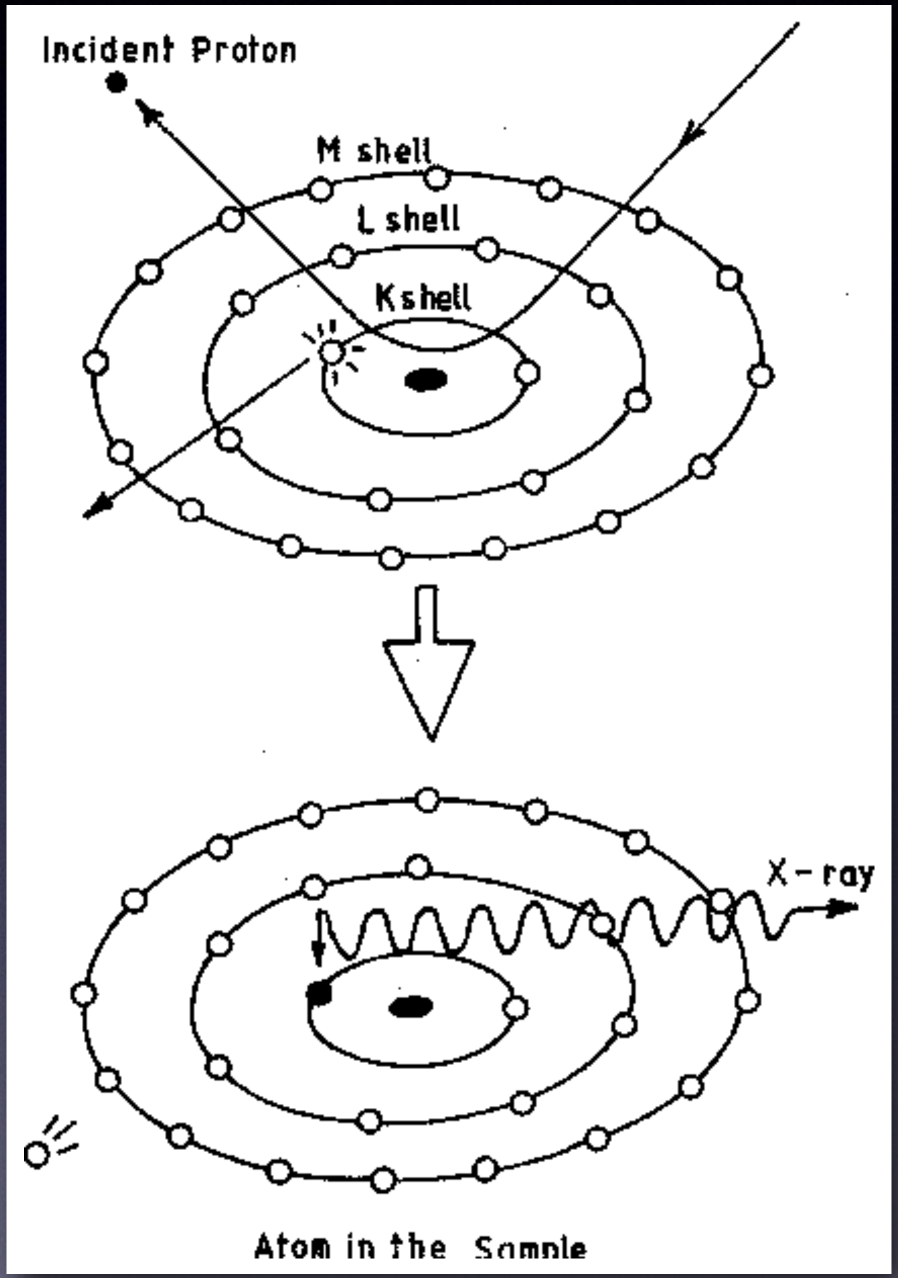


General features of PIXE/PIGE

- Multielemental
- Quantitative analysis
- High sensitivity (1-100 ppm in at/cm^3; 10^{11}-10^{12} in at/cm^2)
- Surface analysis (up to tens of µm)
- "No" depth profiling
- Ambient pressure/external beam
- Non-destructive
- No sample pre-treatment
- Microanalysis (lateral resolution <1 µm)
- Imaging capability (2D mapping)

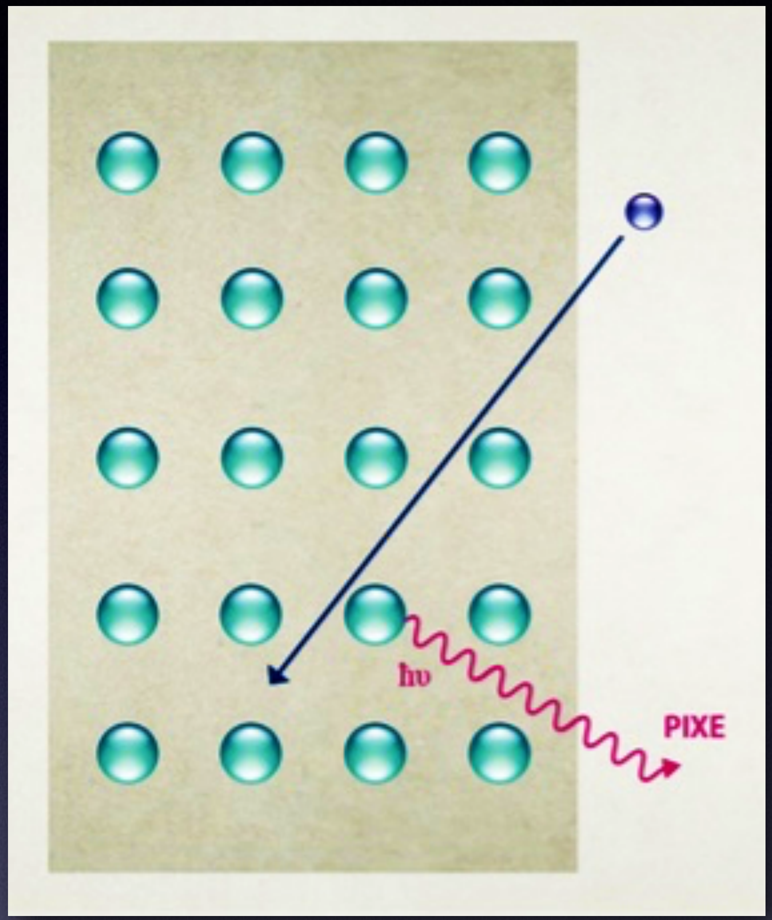
Basics of PIXE technique

- Inner-shell electrons from target atoms are ejected after the impact with the energetic incident ion
- The electron binding energies in the different atomic shells are characteristic of a given atomic species
- The difference between the electron binding energies, i.e. the X-ray energies, are thus a characteristic "fingerprint" of the emitting atoms



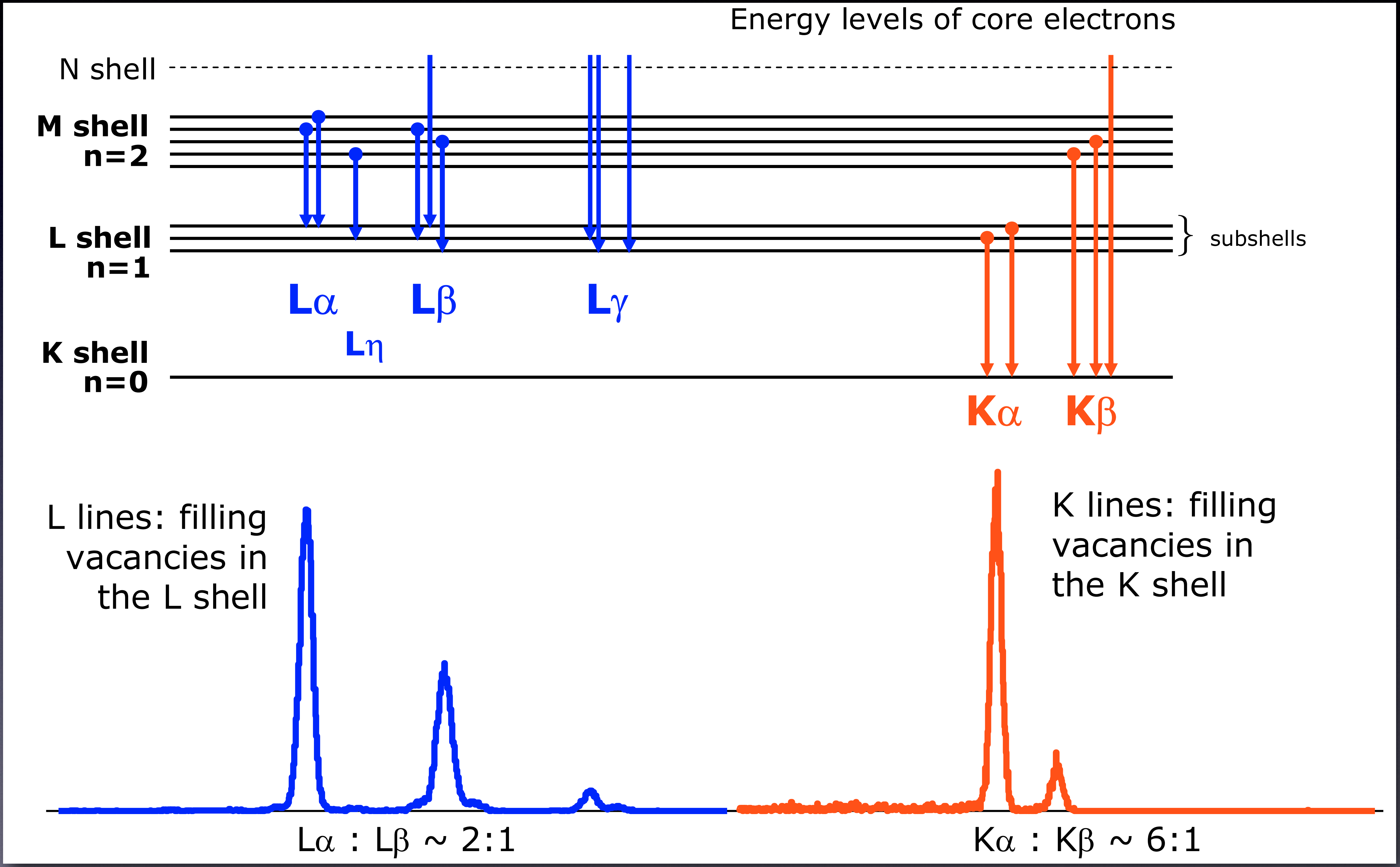
Basics of PIXE technique

- Detecting the emitted X-ray it is possibile to identify and to quantify the different atomic elements in the sample
- Because X-rays do not lose energy as they cross the sample, so they come from the near probed depth; PIXE determines total amounts, not depth profiles

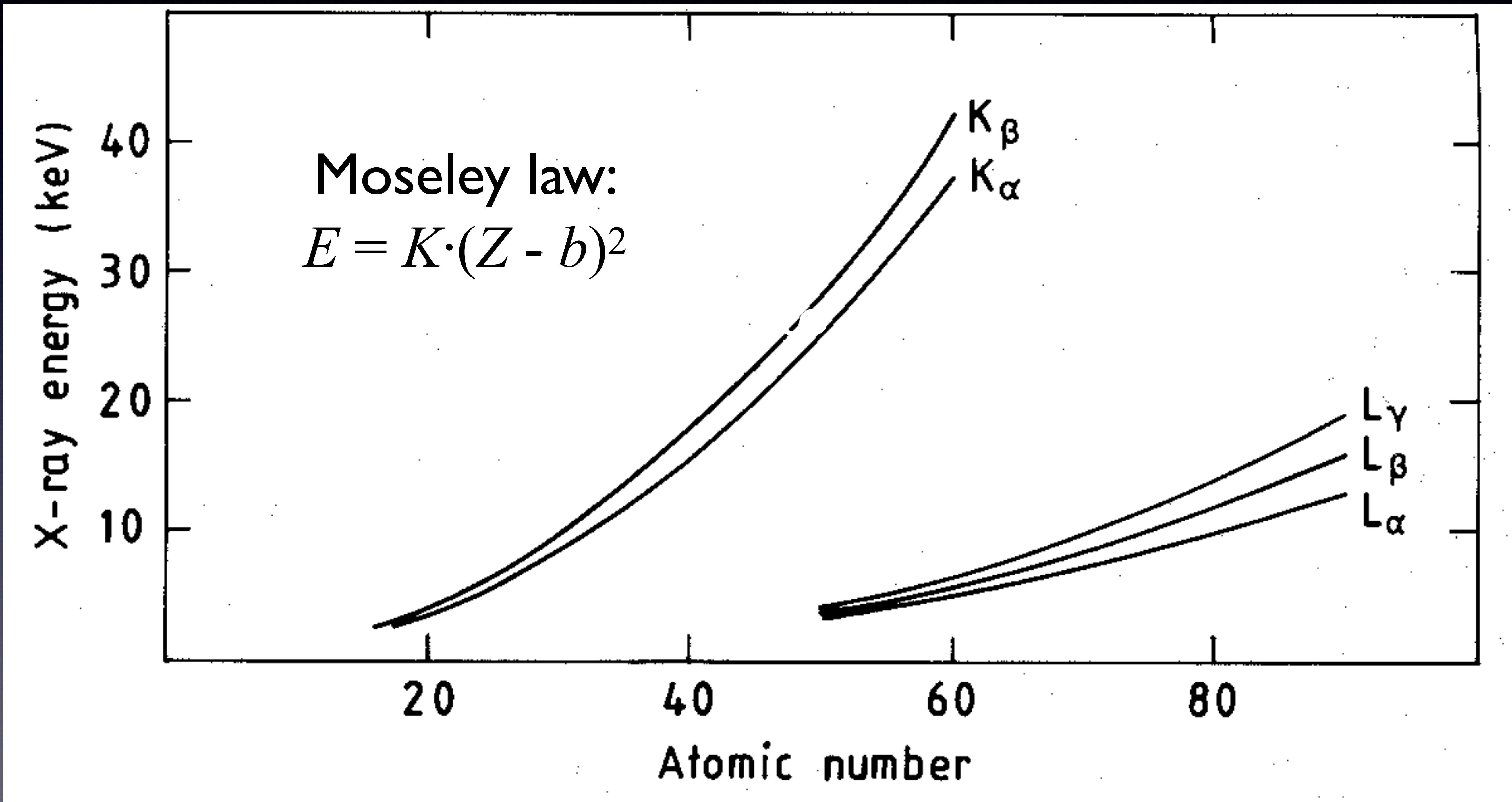


what?
how much?
~~where?~~

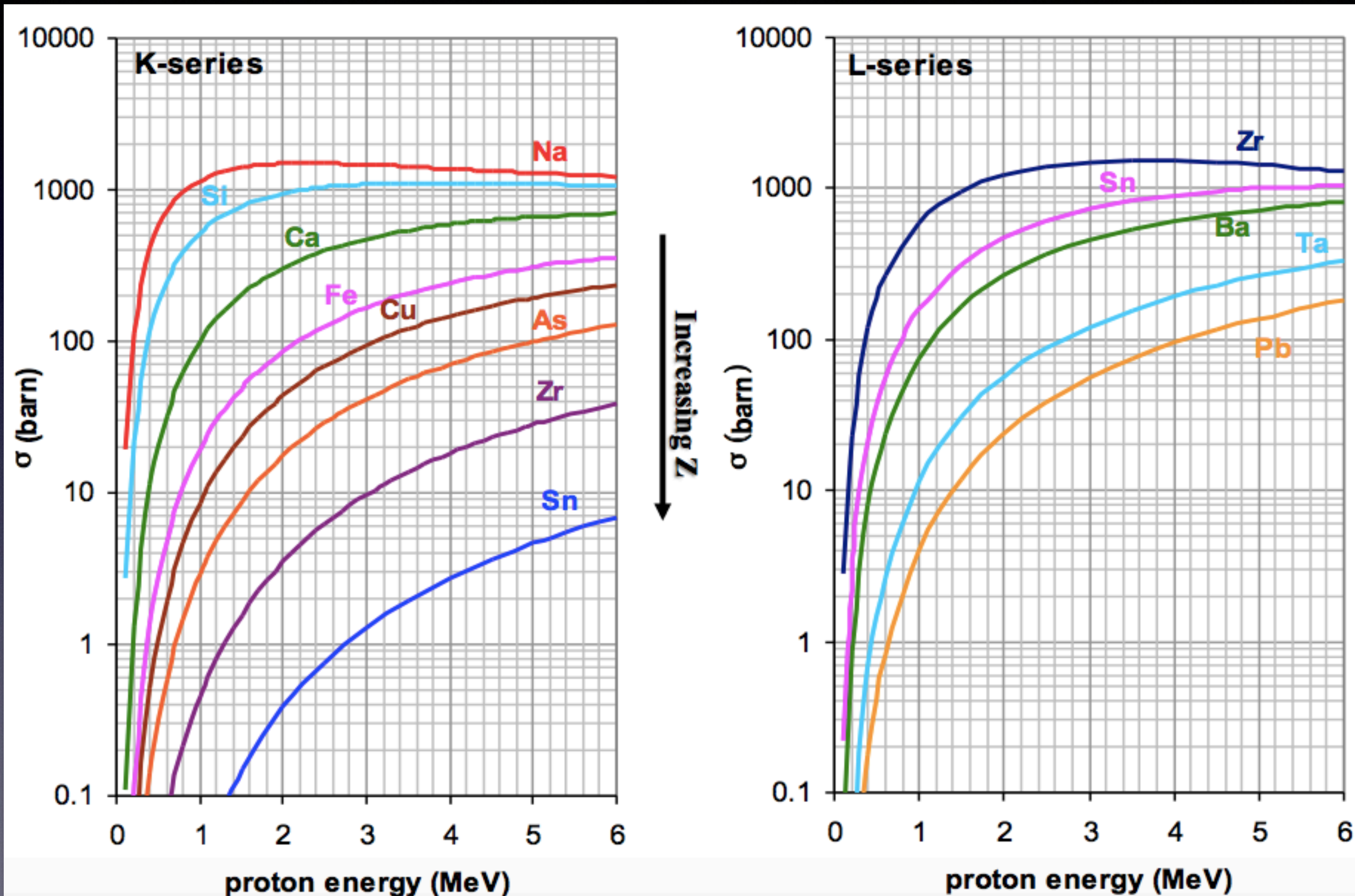
Energy of characteristic X-rays



Energy of characteristic X-rays



X-ray production cross sections



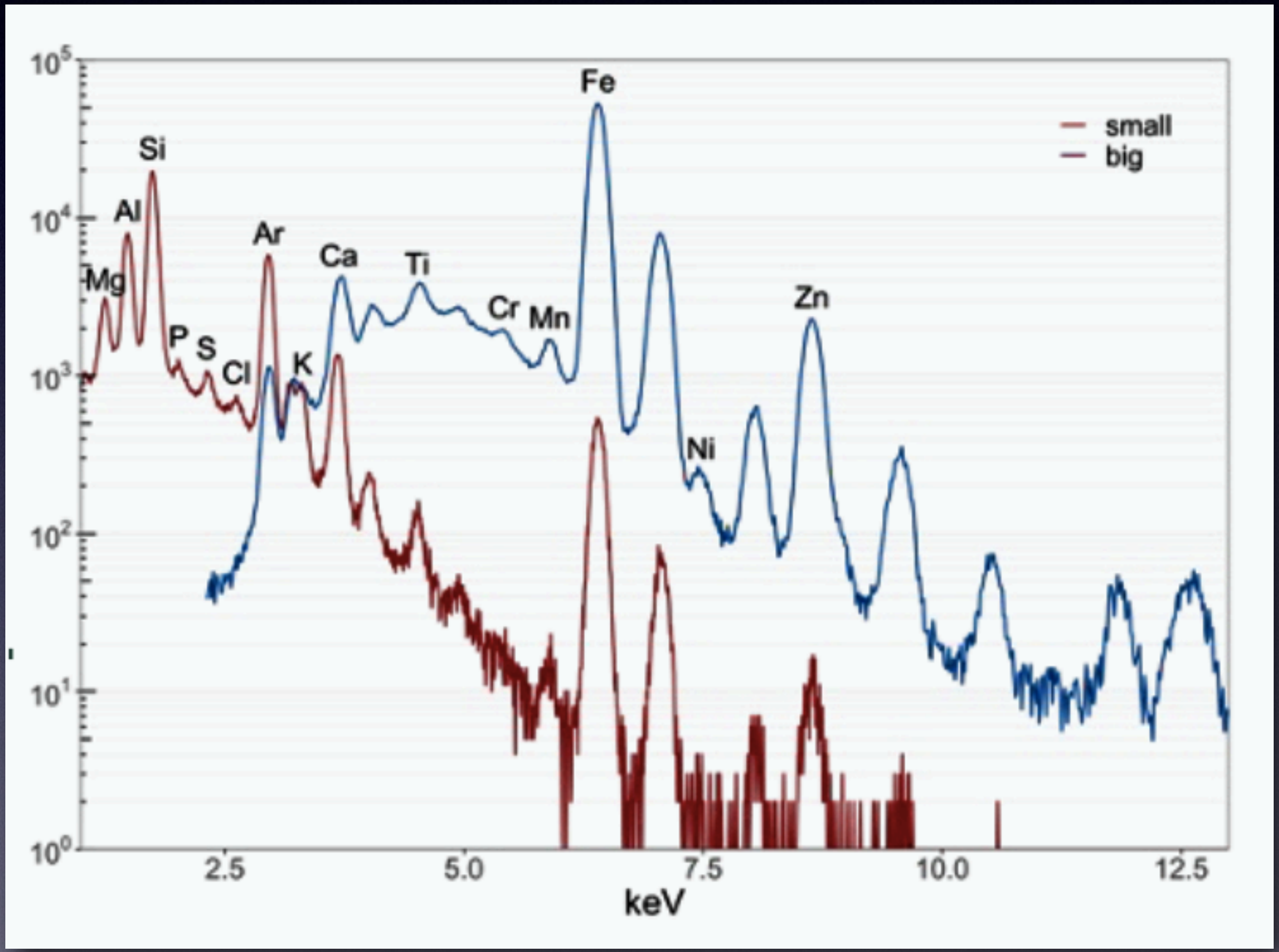
Advantages of PIXE

- Very fast, high sensitivity, non destructive analysis
- Quantitative analysis
- All the elements starting from Na are quantifiable simultaneously (minimum energy of detected X-rays typically ~1 keV)
- Can be performed at ambient pressure (external beam set-up)

Limitations of PIXE

- No information on the organic components
- No information on chemical states
- No direct information on the stratigraphy and the depth distribution of the elements

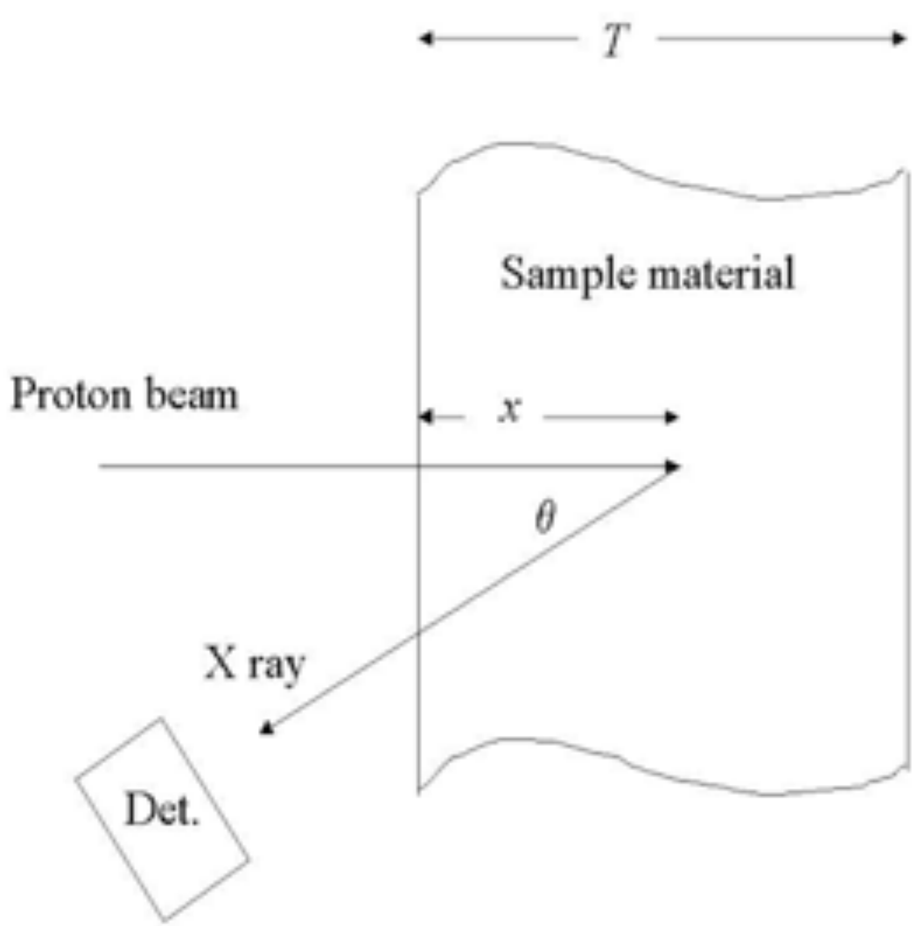
Example of PIXE spectra



PIXE spectra of a PM_{10} aerosol sample, using Silicon Drift Detectors (SDDs)

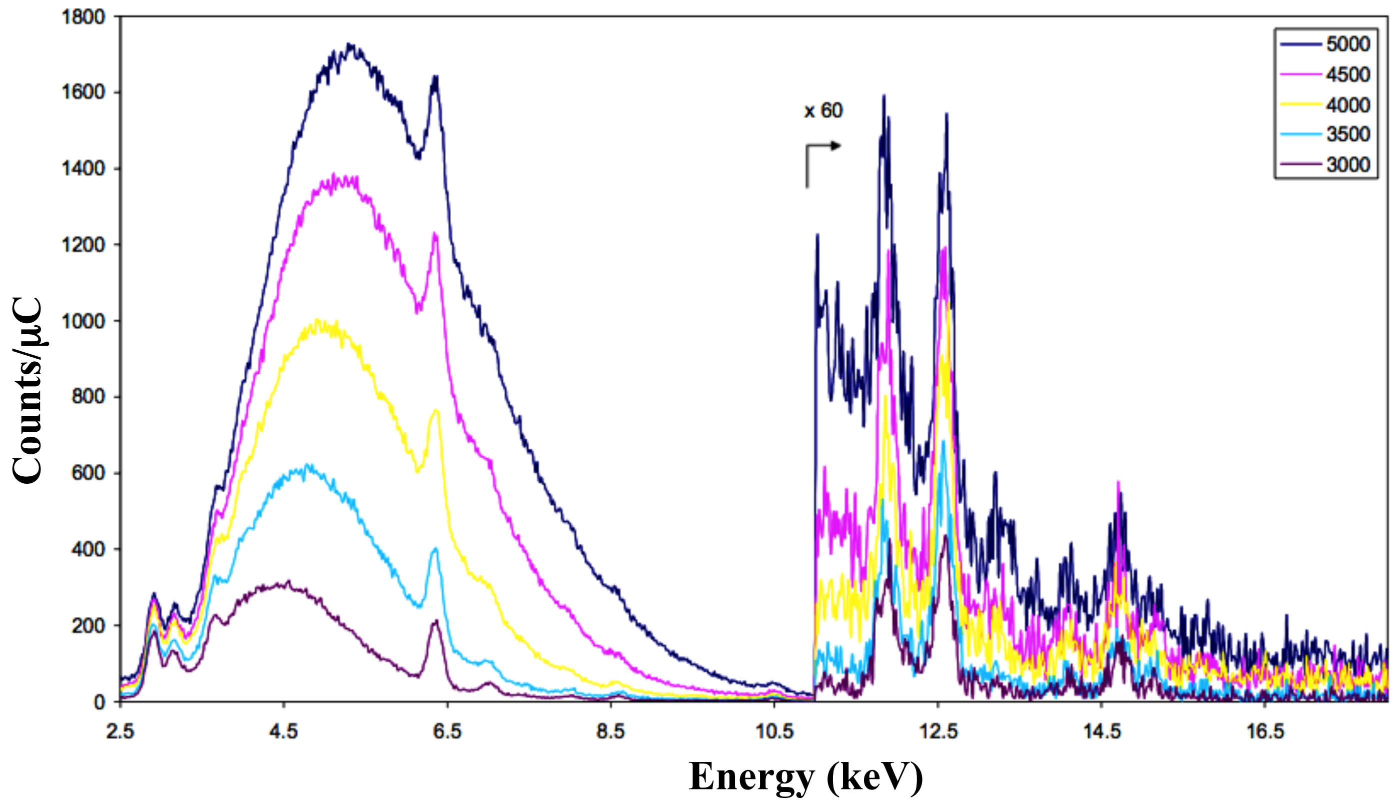
PIXE quantitative analysis of thick targets

$$A_X(Z) = \frac{\Omega}{4\pi}\varepsilon_{det} \cdot \frac{N_{Av}}{A} \cdot N_p \cdot c_Z \cdot \alpha_Z \cdot \int_0^{E_0} \sigma_X(E,Z) \cdot e^{-\frac{\mu \int_E^{E_0} \frac{d\xi}{\rho \cdot S(\xi)}}{\cos\theta}} \cdot \frac{dE}{S(E)}$$

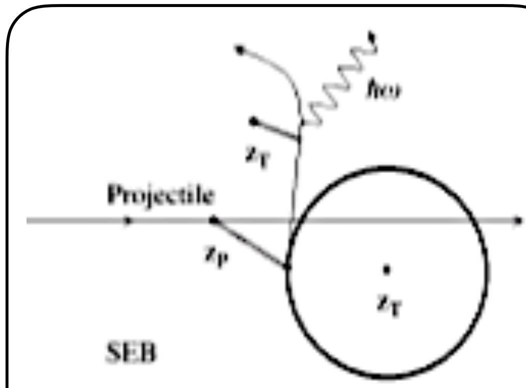


- *A*, area of the X-ray peak
- *Ω*, detector solid angle
- *ε*, detector efficiency
- N_{Av}, Avogadro number
- *A*, element mass
- N_p, number of impinging particles
- c_Z, elemental concentration
- α_Z, attenuation term due to absorbers (if any)
- E_0, energy of the incident ion
- σ_X, X-ray production cross-section
- *μ*, X-ray attenuation factor
- *ρ*, sample density
- *S*, stopping power

The continuous background in PIXE spectra

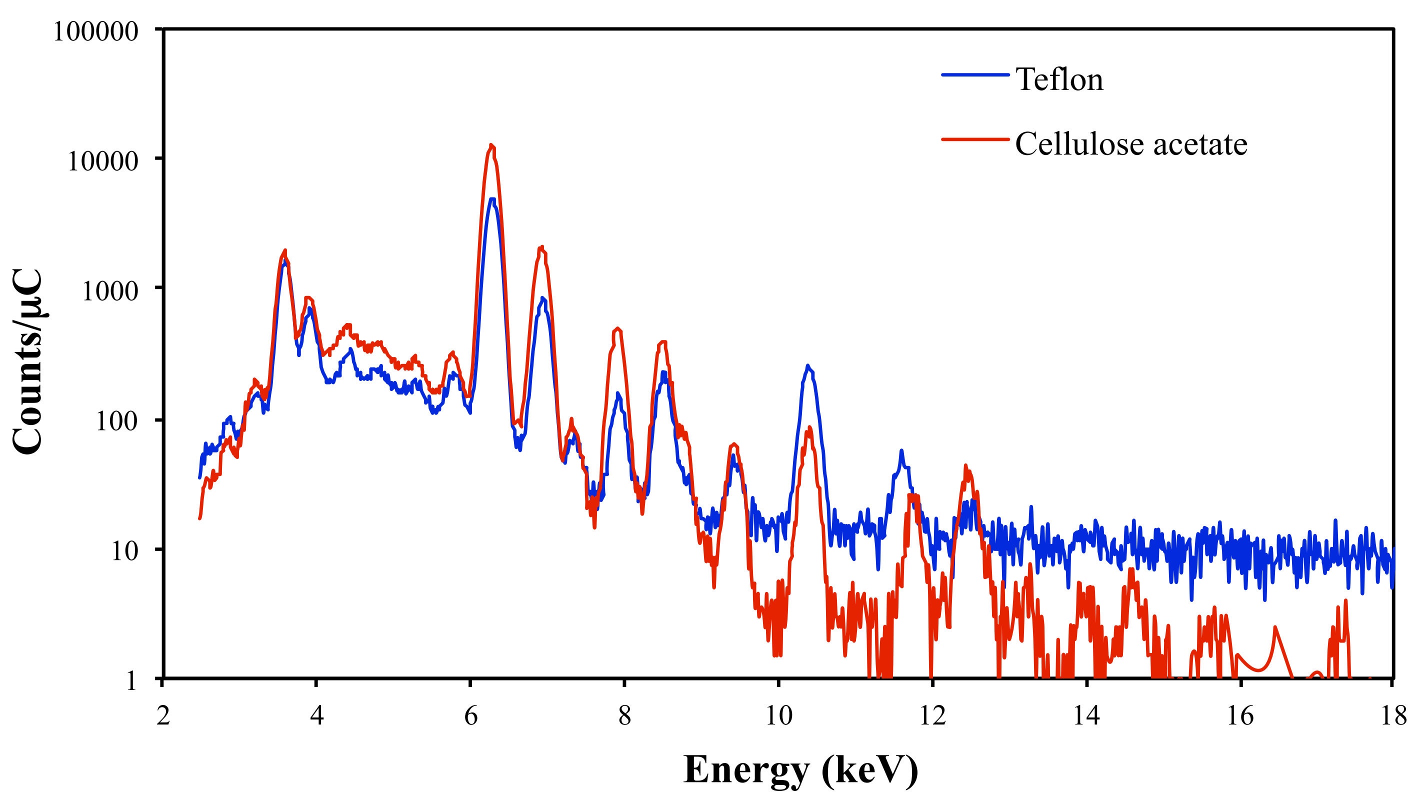


- Mainly due to *Secondary Electron Bremsstrahlung* radiation for energies typically below 10 keV



$$T_m = 4 m_e E_0 / m_p$$

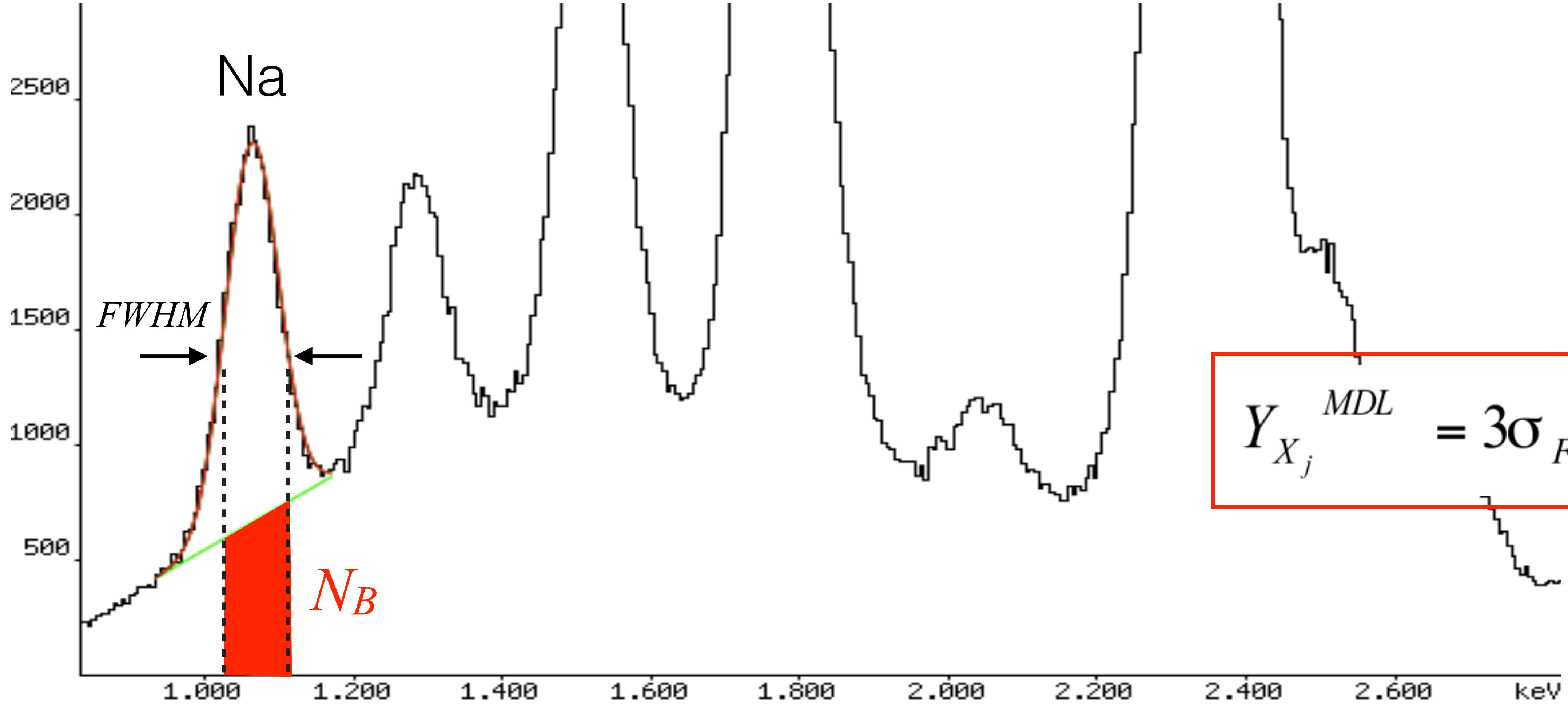
Endpoint energy of the SEB radiation spectrum



- Possible contribution from Compton interaction in the X-ray detector active volume from gamma-rays - promptly emitted by the target - for energies above 10 keV

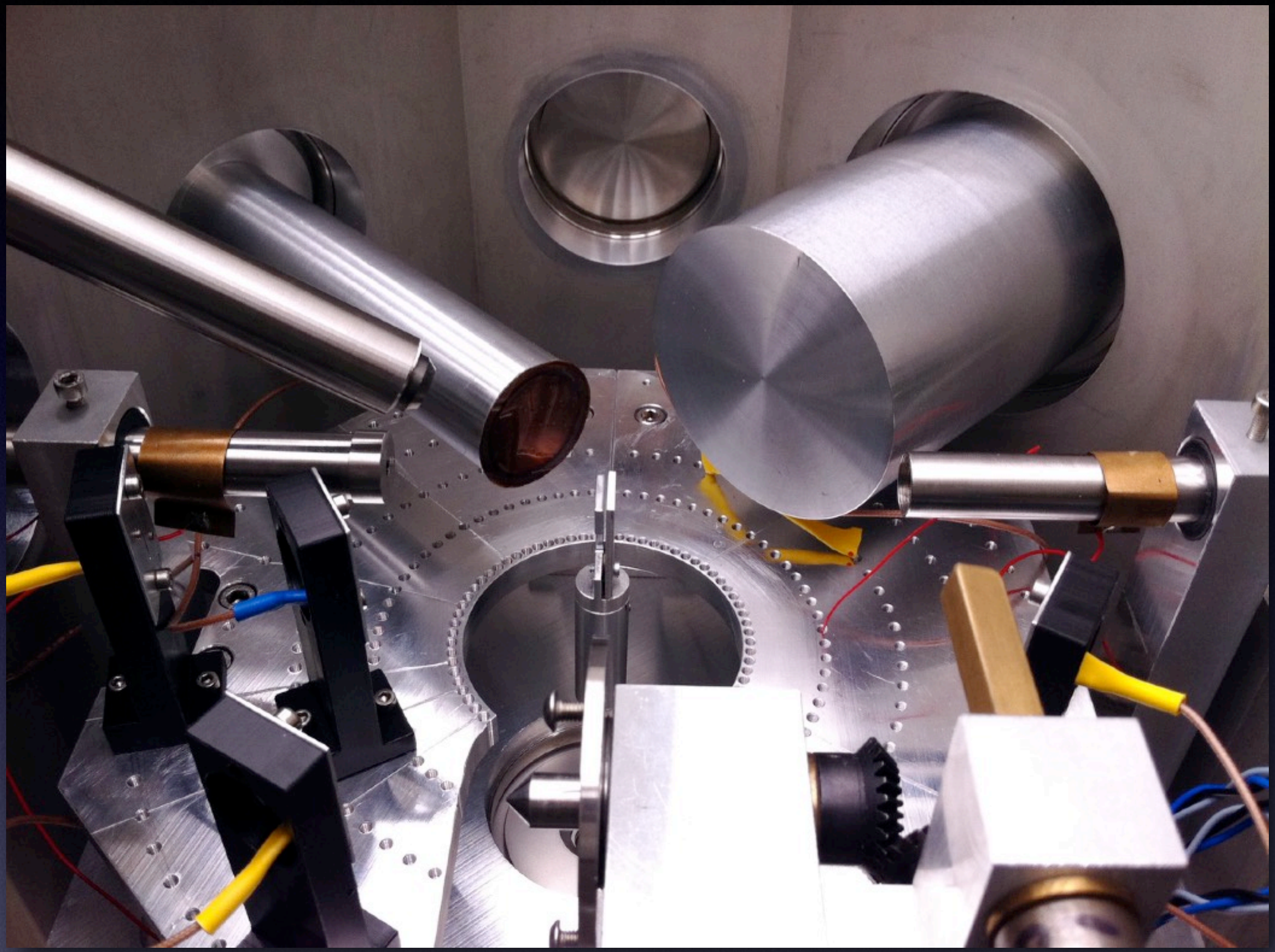
PIXE Minimum Detection Limit (MDL)

The PIXE MDL can be calculated assuming an equivalent area (Y_X^{MDL}) equal to three times the square root of the number of counts (N_B) integrated in a region of the background under the X-ray peak as wide as the peak FWHM



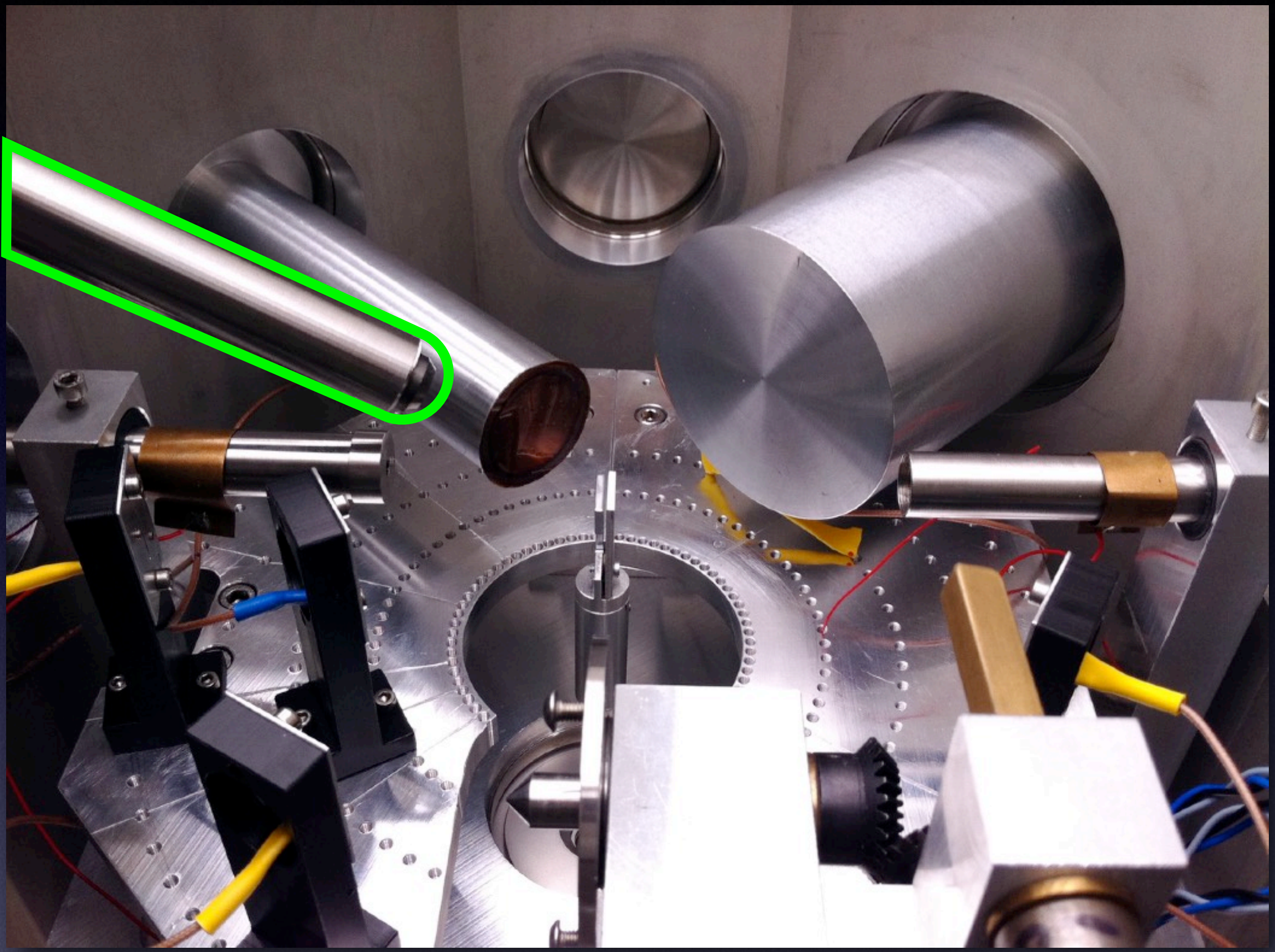
$$Y_{X_j}^{MDL} = 3\sigma_F = 3\sqrt{N_B}$$

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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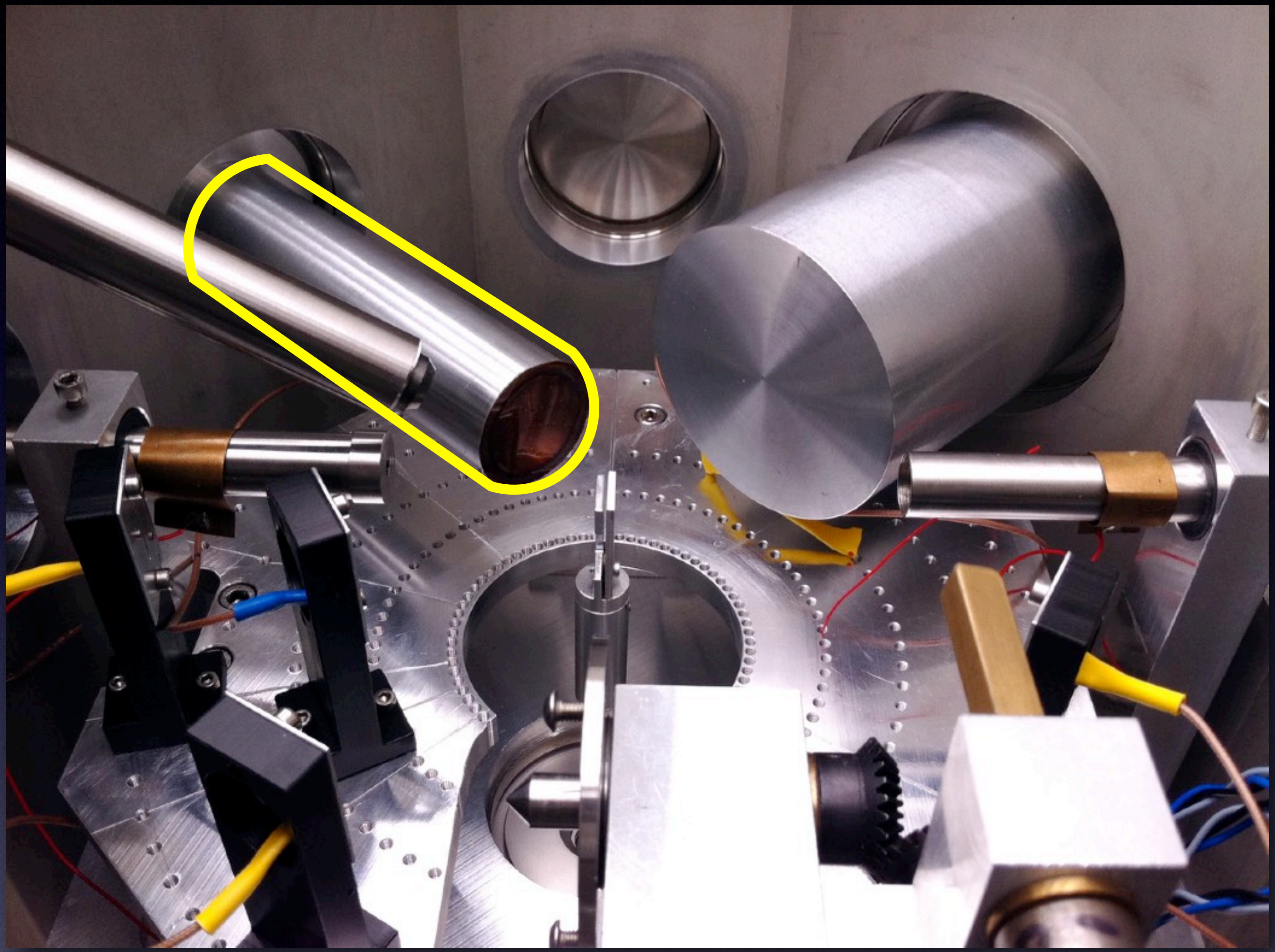

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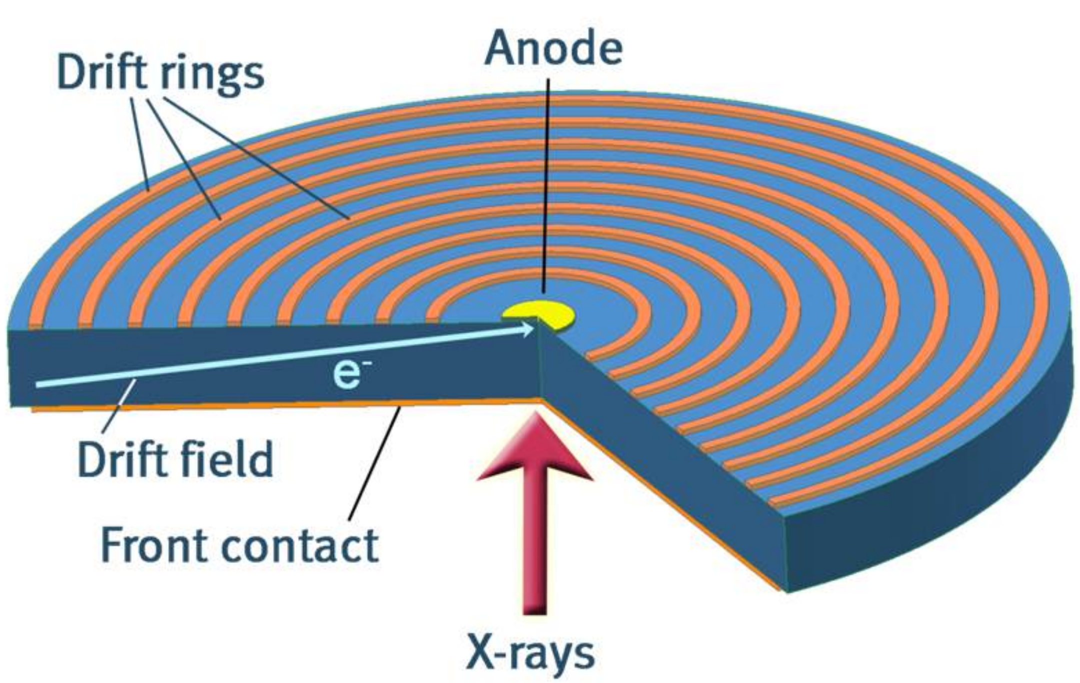
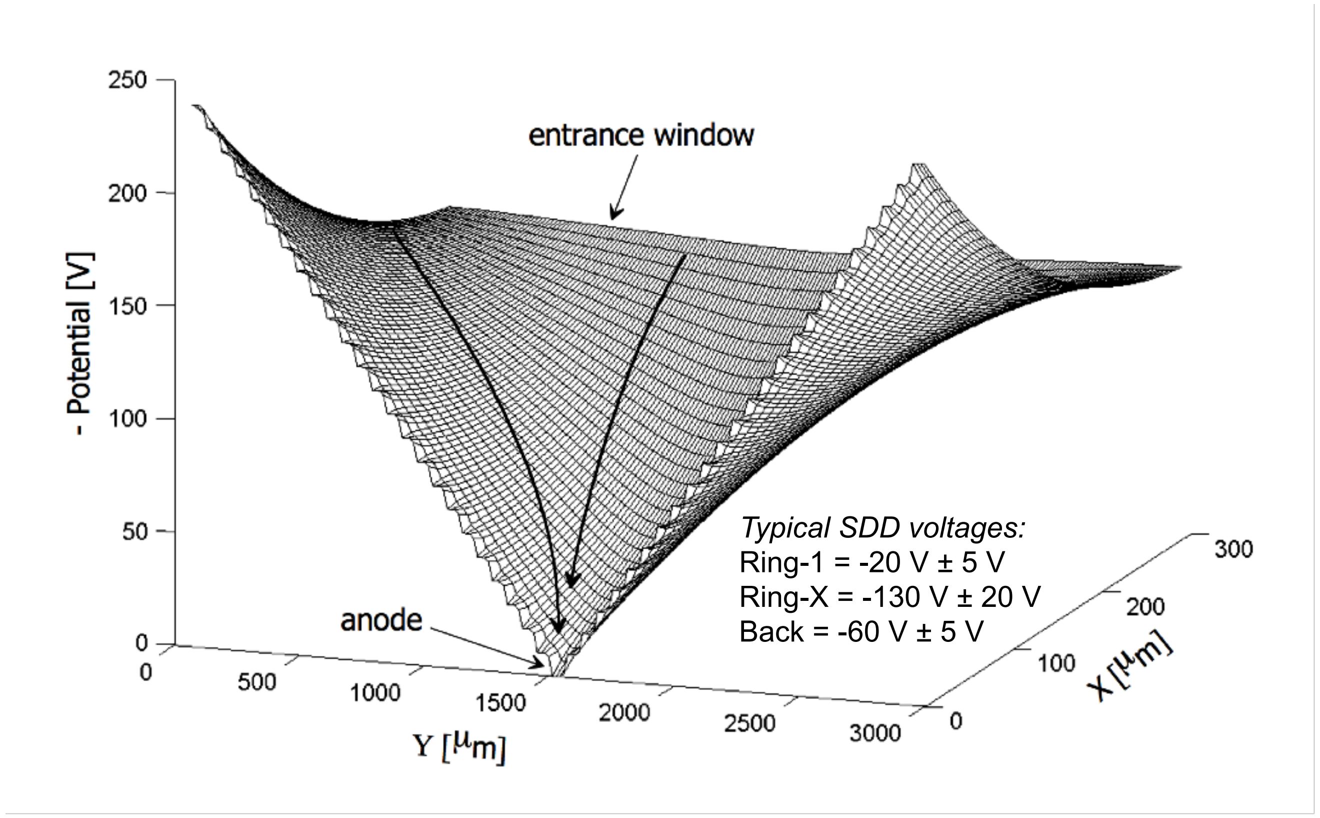
The working principle of Silicon Drift Detectors

- 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

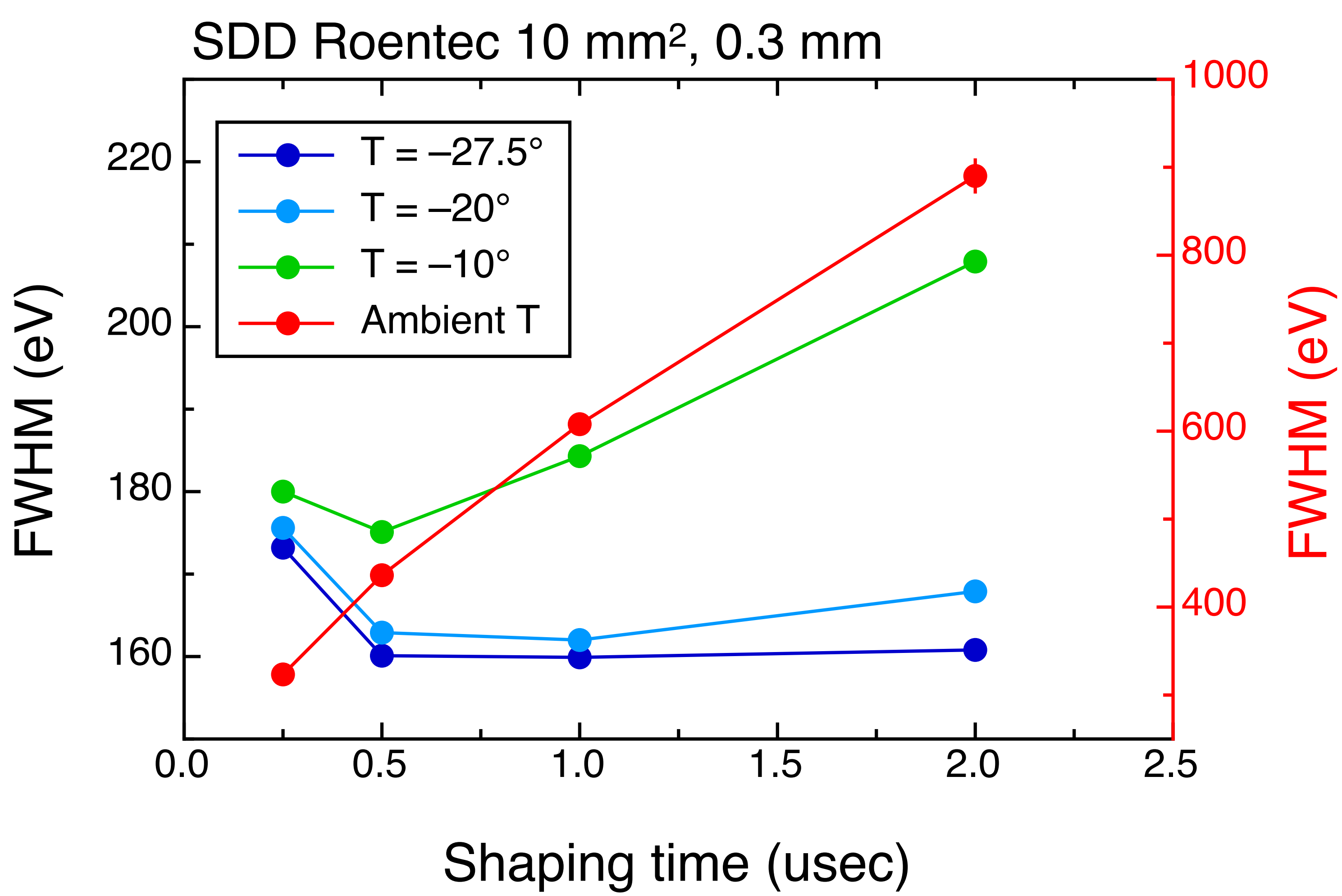


Energy potential for electrons inside a SDD with homogeneous entrance window.

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/cm²) and the low leakage current (1-2 nA/cm² at room temperature) resulting in improved energy resolution

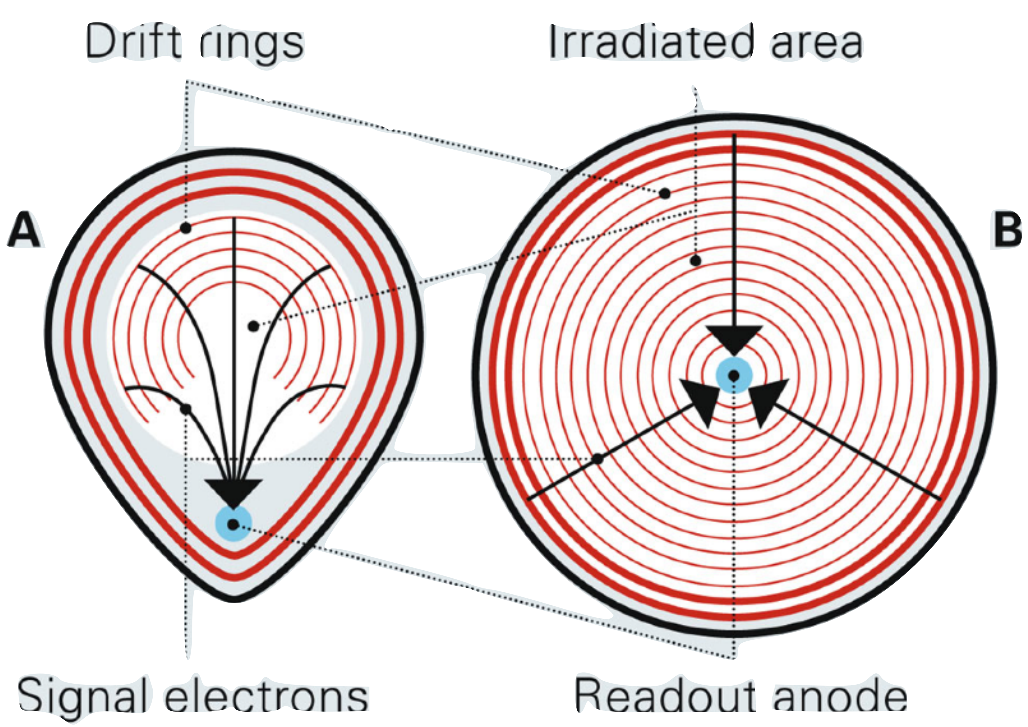
$$\mathrm{ENC} = \left[\frac{k_1 \cdot \langle e_w^2 \rangle \cdot (C_d + C_i + C_p)^2}{\tau} + k_3 A_{1/f} (C_d + C_i + C_p)^2 + 2k_2 q I_l \tau \right]^{1/2}$$



	SDD	Si(Li)
Energy resolution	125-150 eV	180-200 eV
Shaping time	1 μs	6 μs
Sustainable count-rate	50 kHz	5 kHz
Cooling	-40/-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

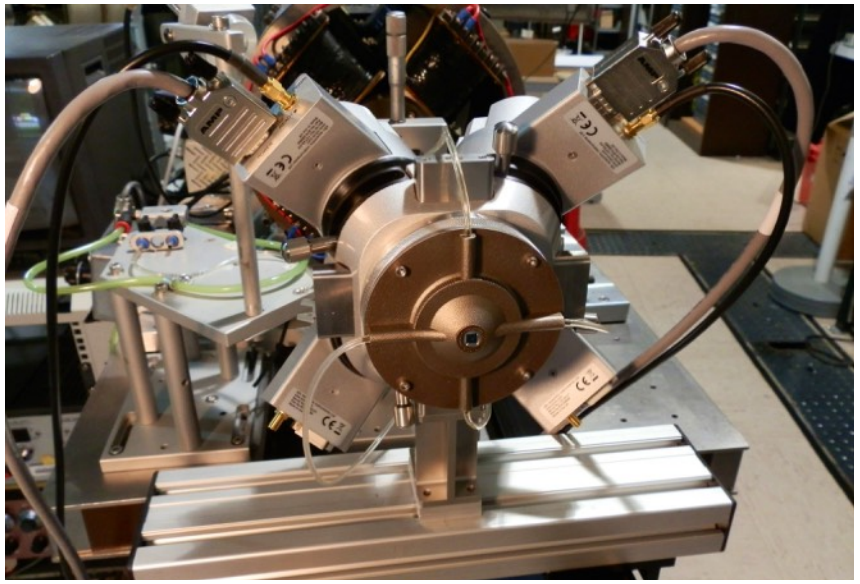
XGLAB
X and Gamma Ray Electronics

BRUKER

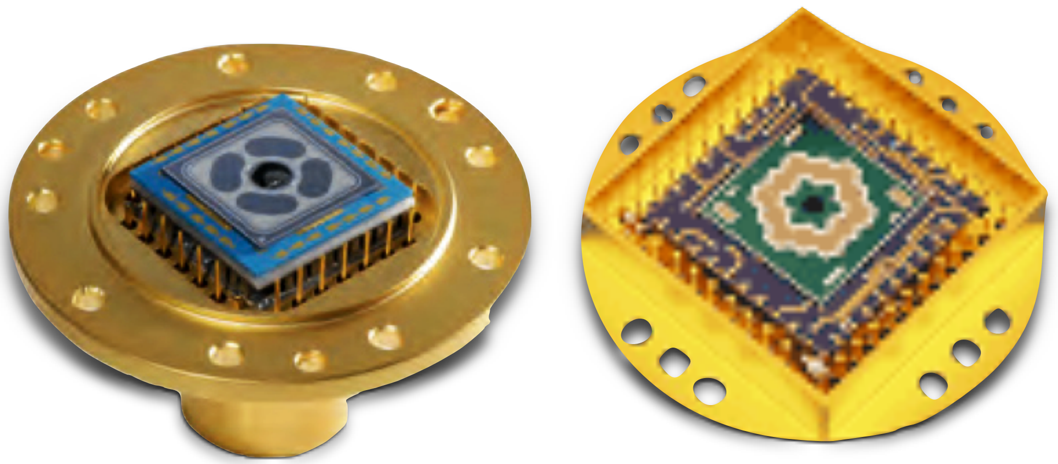
Hitachi High-Technologies Science America, Inc.

Large area SDD

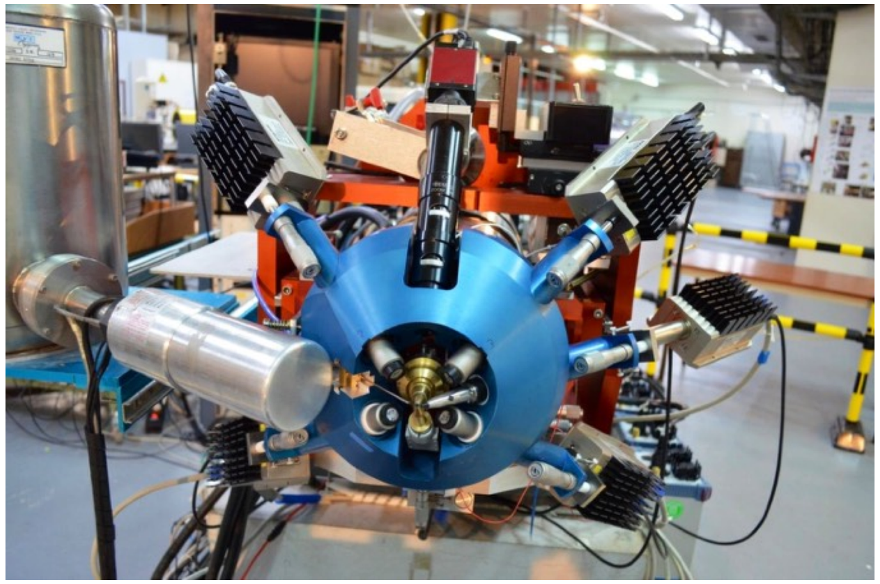
- A single SDD with active area up to 150 mm^2 is now commercially available (Ketek Gmbh)
- Larger areas can be obtained using arrays of individual systems or integrated multi-channel SDDs



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



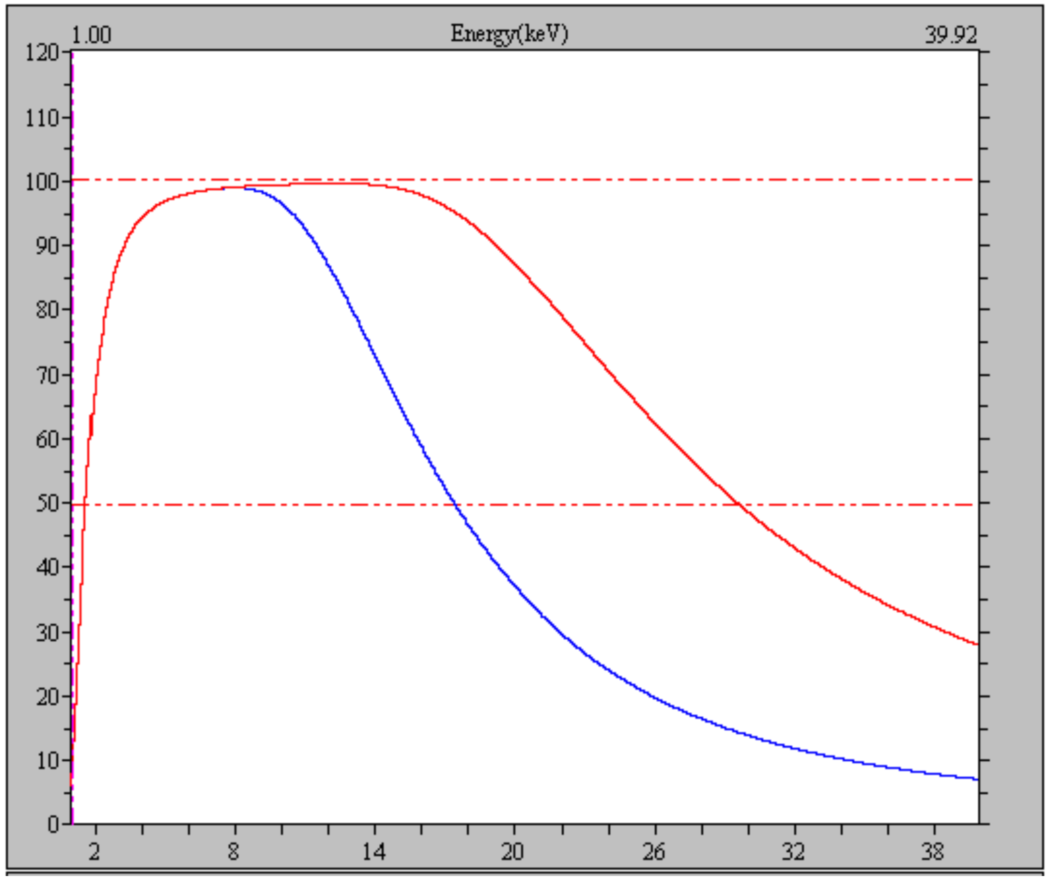
Ring-shaped multi cell SDD with 12 x 5 mm^2 hexagonal cells (PN Detectors, Germany)



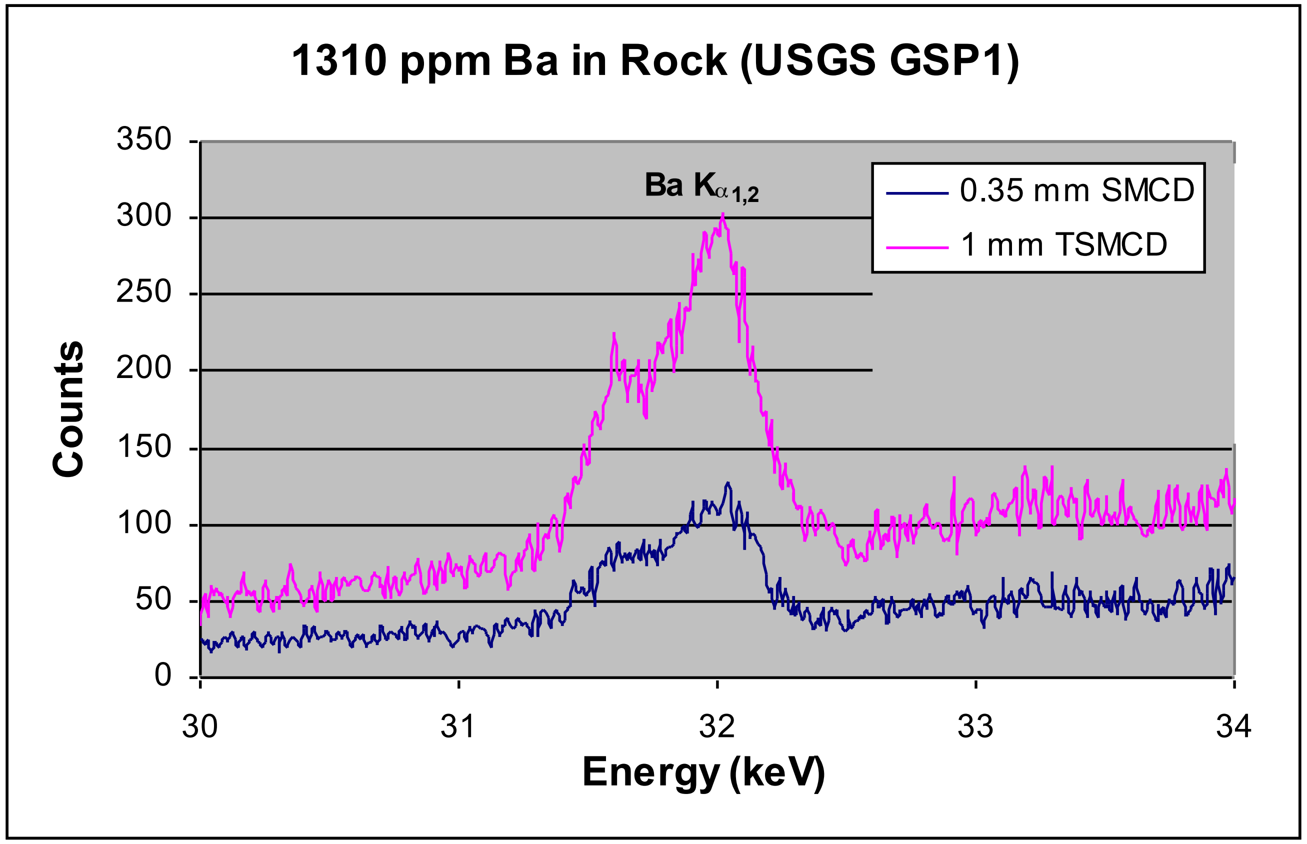
Multi SDD PIXE system (1 low and 4 high energy), total solid angle 500 msr, at AGLAE, Paris (Ketek Gmbh, Germany)

Increased thickness SDD

- Single SDD with active thickness of 1 mm (Amptek, Inc) and 1 or 2 mm (Hitachi High-Technologies Science America, Inc) are now commercially available



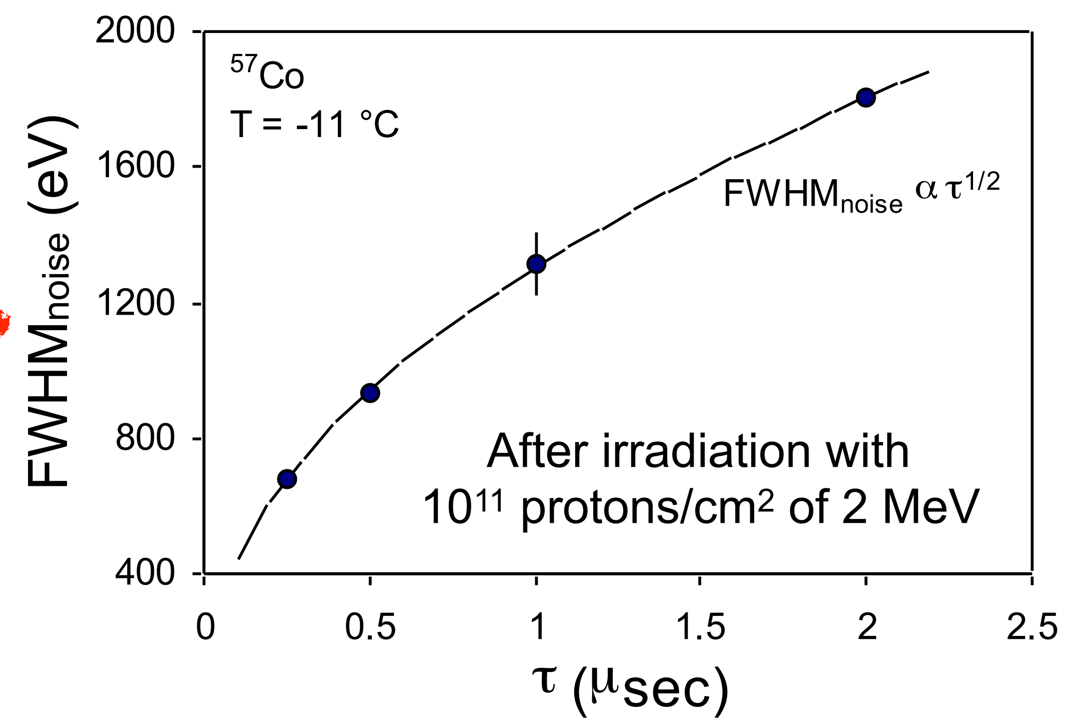
Eff. (0.45 mm) = 50% @17 keV; 10% @34 keV
Eff. (2.0 mm) = 95% @17 keV; 40% @34 keV

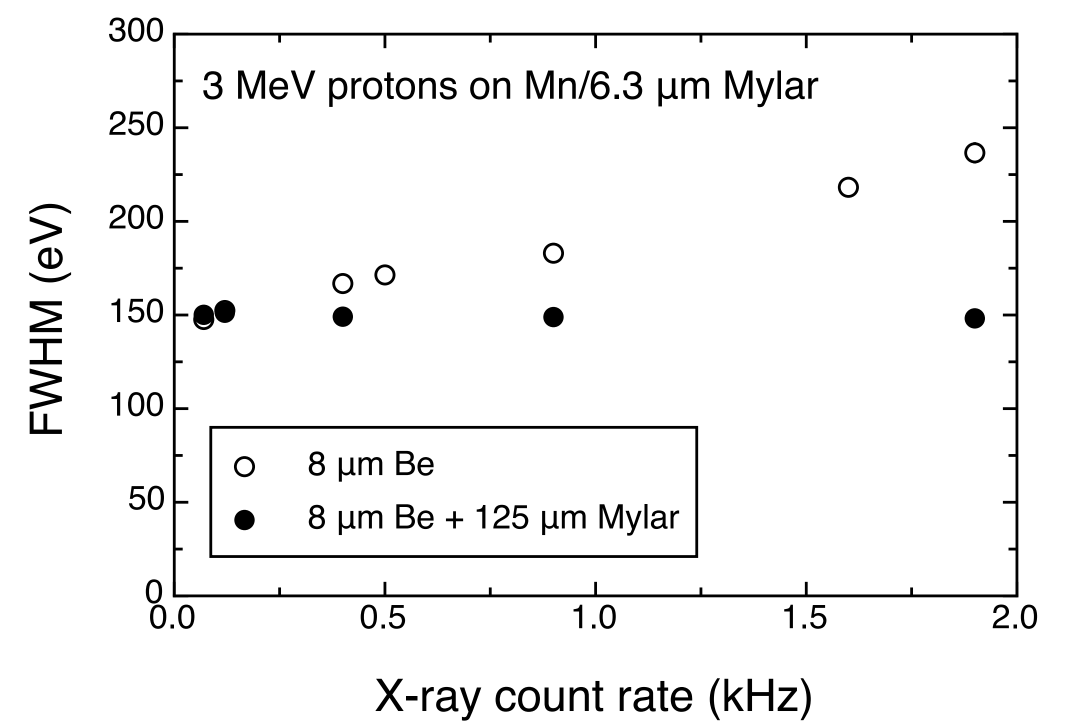


32 keV Ba spectra from USGS GSP1 – Rh tube, 50 kV, 1 mA, 0.5 mm Cu + 6 mm Al Filter, 0.5 μs peaking time, 300 sec. livetime. (Gordon Myers, Hitachi High-Technologies Science America, Inc.)

Backscattered protons effects on SDD

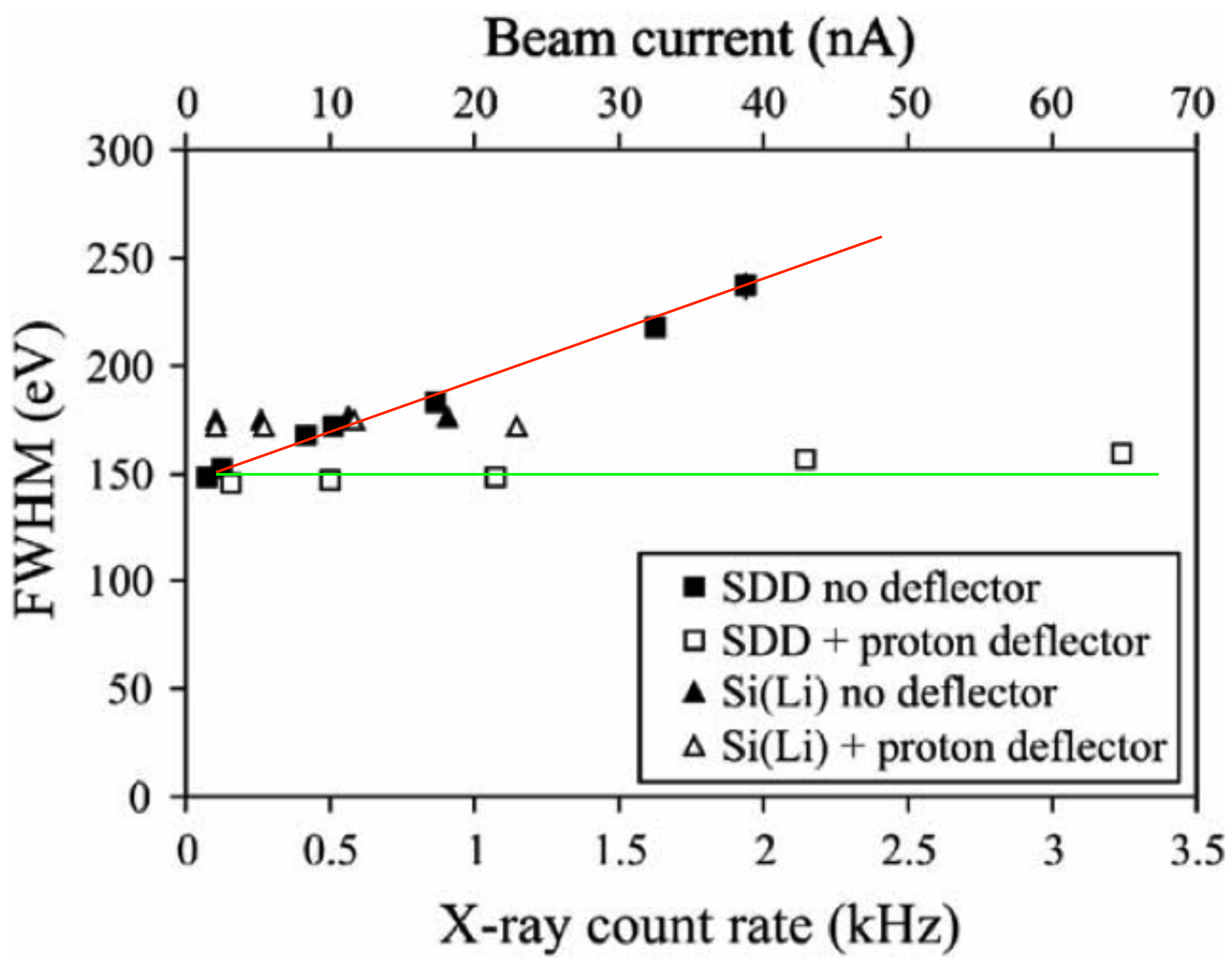
- PIXE detectors with thin entrance window used in presence of a large backscattered protons flux from the sample can suffer unrecoverable damages (long-term effects) and worsening of the energy resolution under beam irradiation (short-term effects)

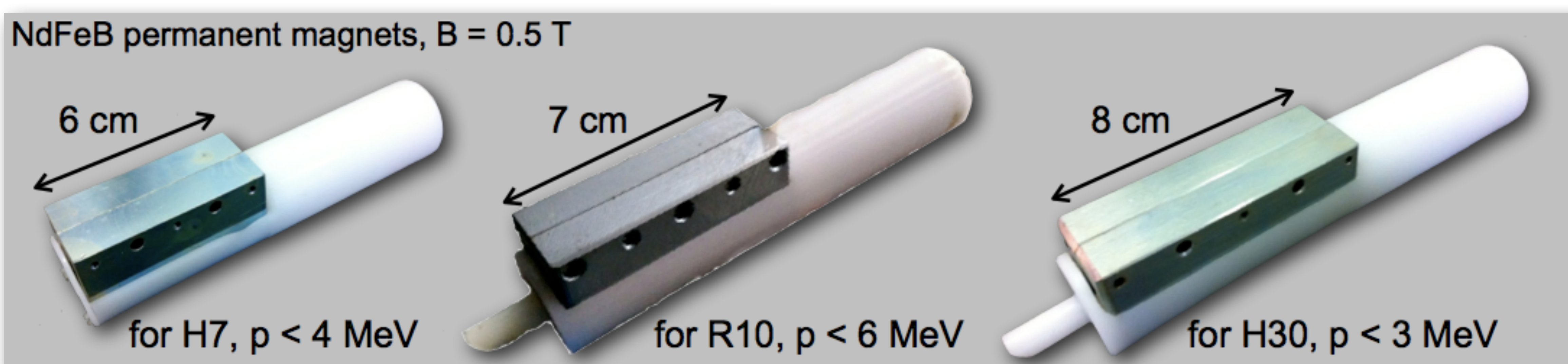




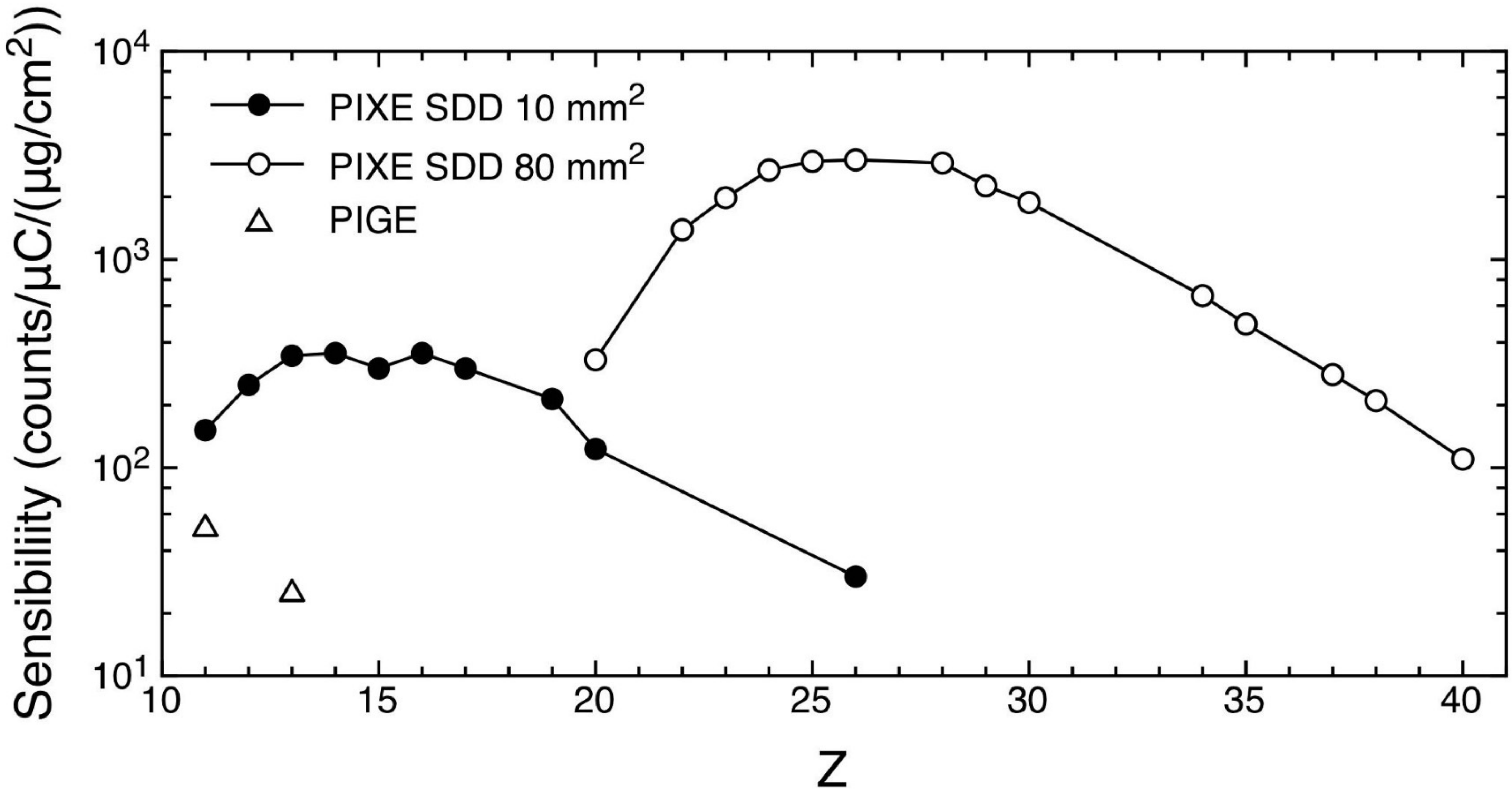
Magnetic proton deflector

- 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





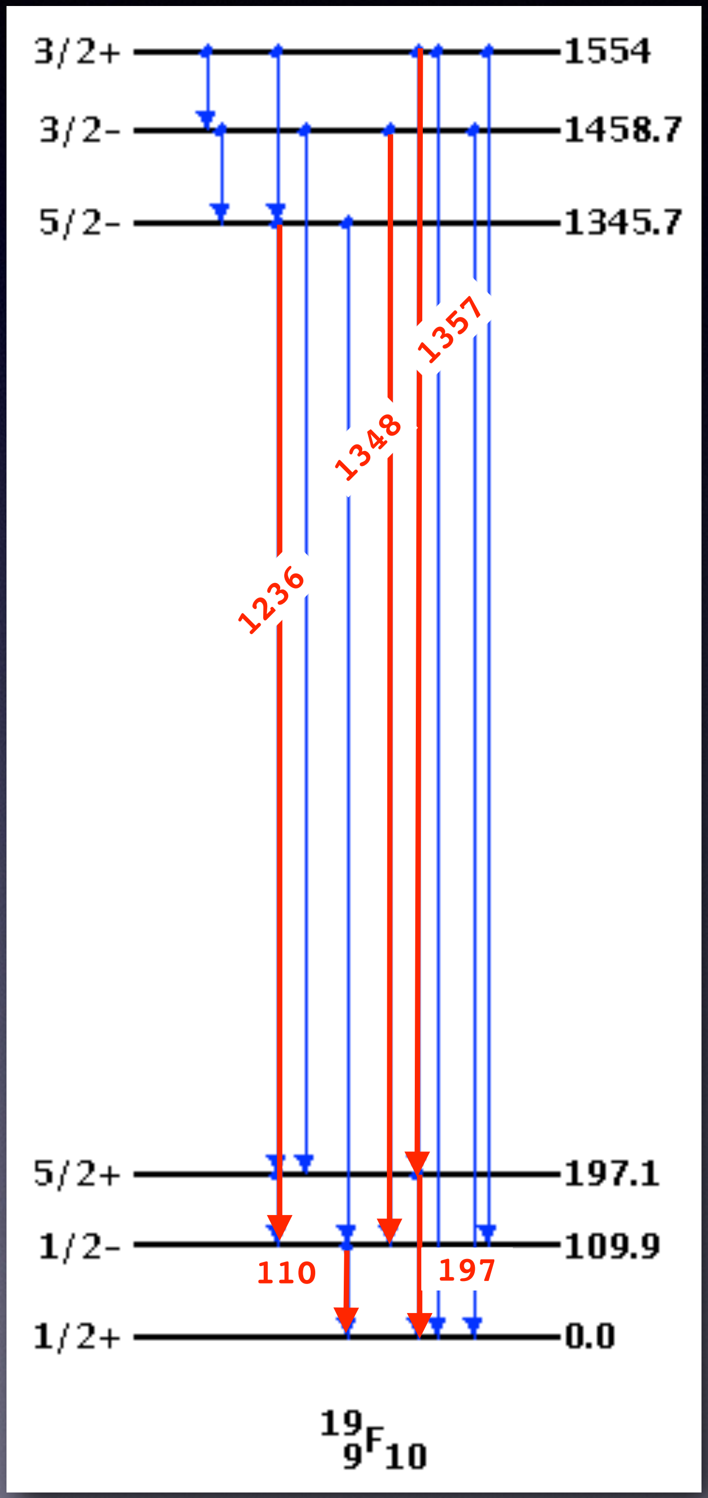
Sensibility curve for a 2-SDD set-up obtained from a set of thin elemental standards



- Use a set of thin mono- or bi-elemental standards (NaCl, MgF_2, Al, SiO, CuSx, KCl, CaF_2, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ge, Se, CsBr, SrF_2, MoO_3, Pb) from MicroMatter deposited on Mylar or Nuclepore with concentrations in the 40-50 µg/cm^2 range

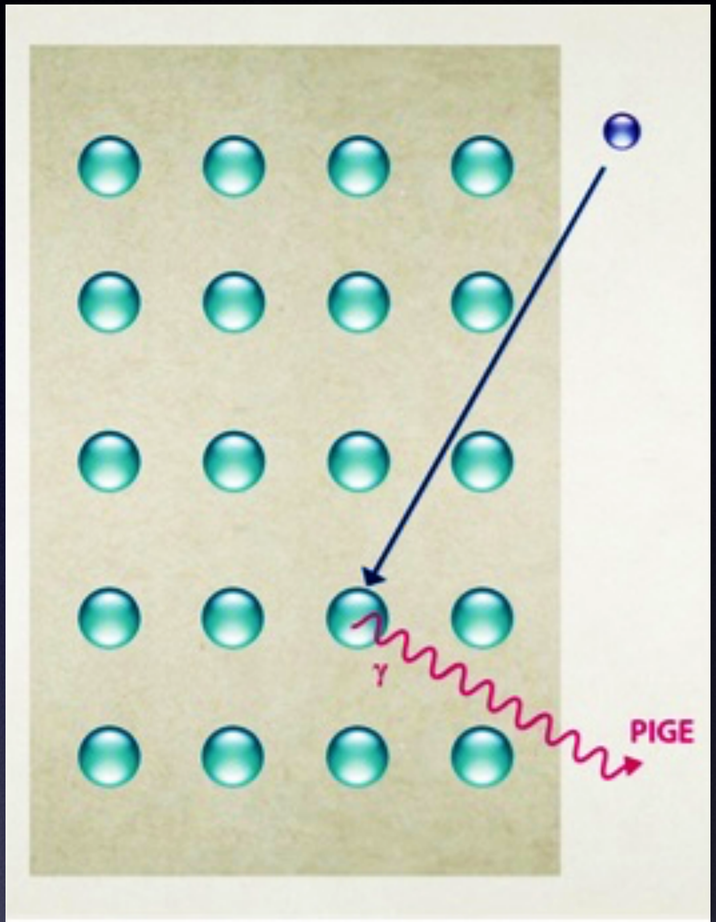
Basics of PIGE technique

- For low-Z target elements, the incident beam particles can reach closer to the target nuclei (weaker Coulomb repulsion) and the short range nuclear interaction comes into play
- The target nucleus can be excited and the de-excitation of the nucleus occurs through the “prompt” emission of a gamma-ray
- The gamma-ray energies are a characteristic “fingerprint” of the emitting isotopes



Basics of PIGE technique

- Detecting these gamma-rays it is possible to identify and to quantify the low-Z (typically) isotopes in the sample
- Because gamma-rays do not lose energy as they cross the sample, so they come from the near probed depth; PIGE determines total amounts, not depth profiles



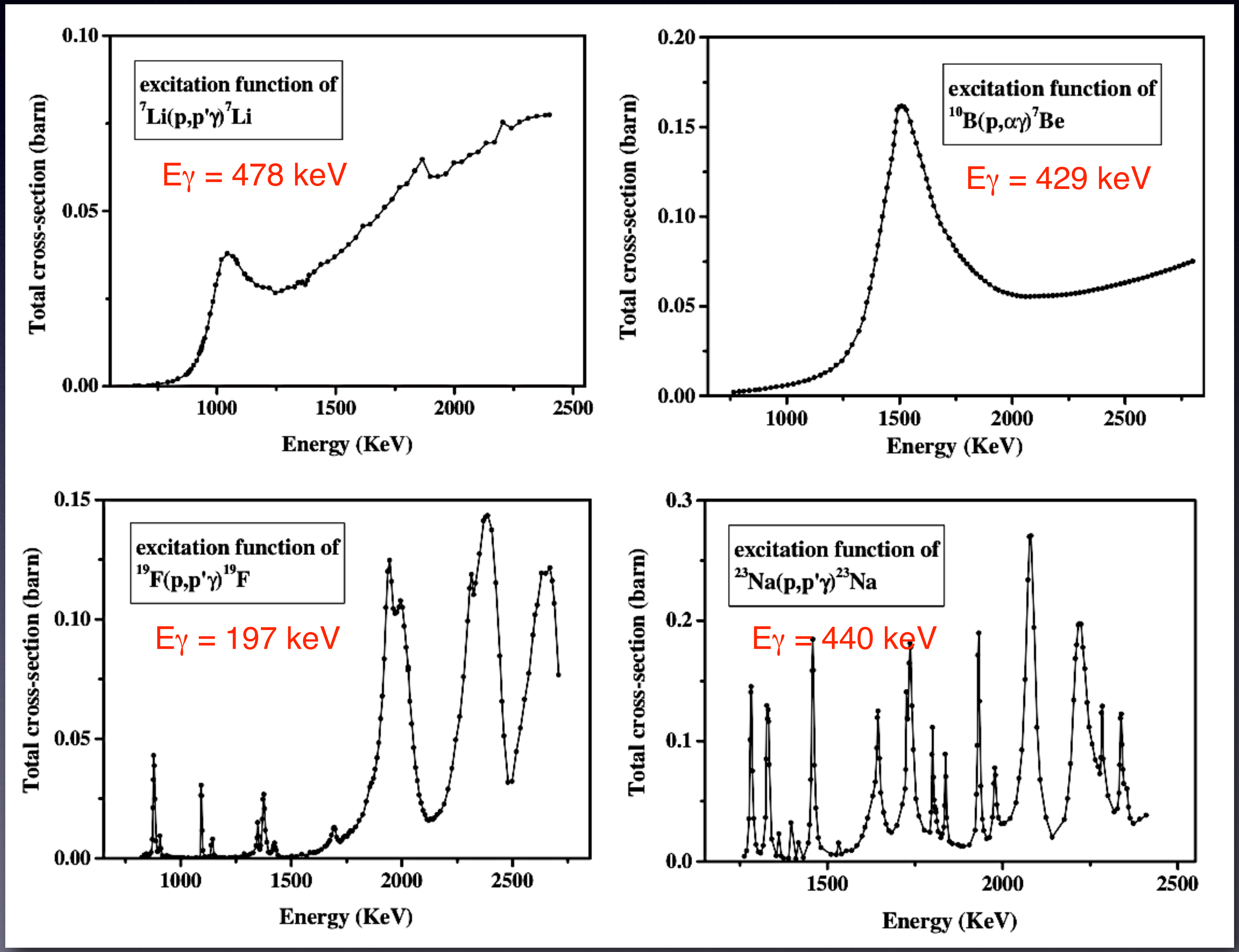
what?
how much?
~~where?~~

List of proton-induced reactions

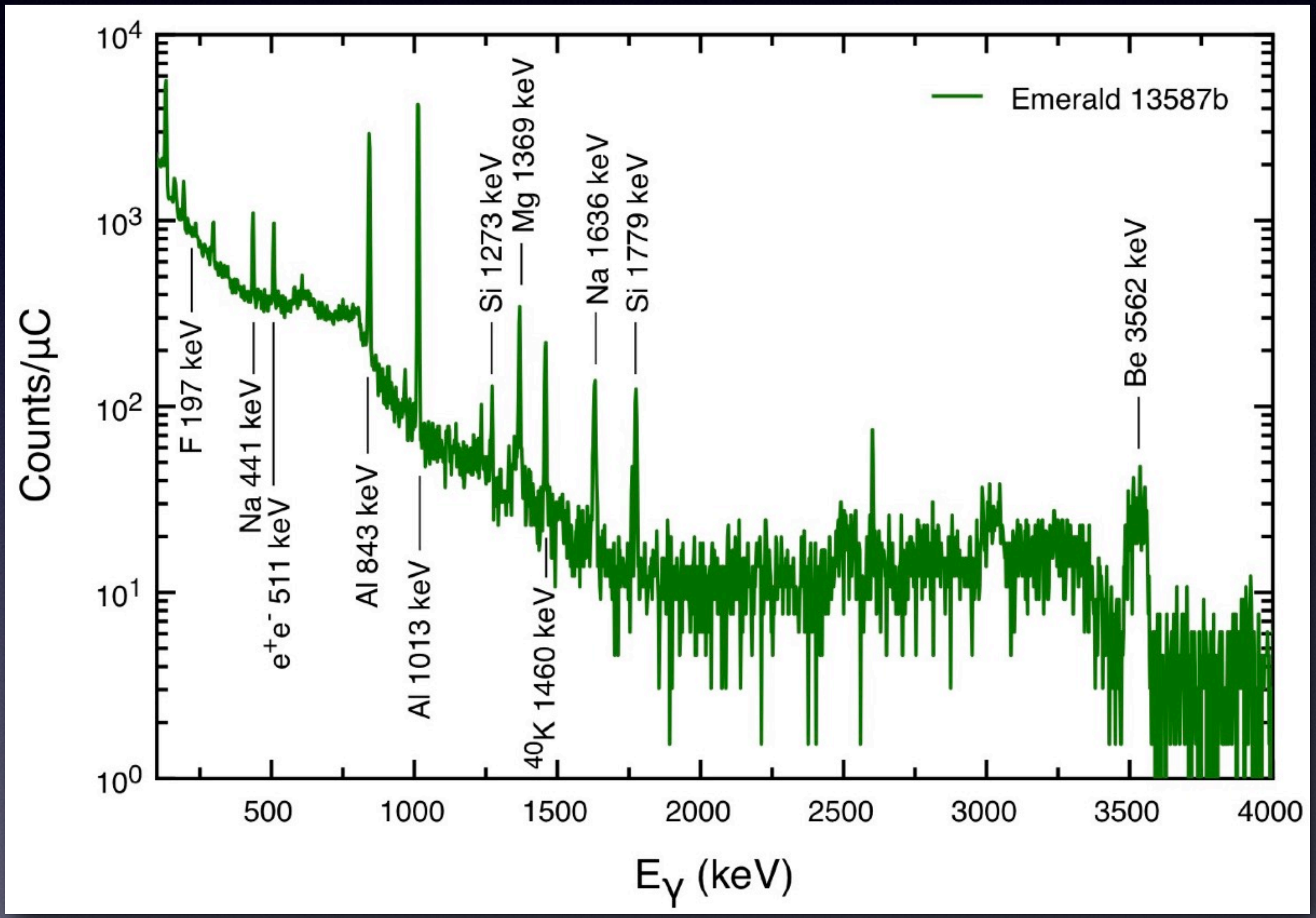
Element	Reaction	E_γ (keV)	Transition	Relative isotopic abundance
Li	^{7}Li(p,p'γ)^{7}Li	478	478 $\rightarrow$ 0	92.4%
Be	^{9}Be(p,$\alpha\gamma$)^{6}Li	3562	3562 $\rightarrow$ 0	100%
B	^{10}B(p,$\alpha\gamma$)^{7}Be	429	429 $\rightarrow$ 0	19.9%
F	^{19}F(p,p’γ)^{19}F	110	110 $\rightarrow$ 0	100%
	^{19}F(p,p’γ)^{19}F	197	197 $\rightarrow$ 0	100%
Na	^{23}Na(p,p'γ)^{23}Na	441	441 $\rightarrow$ 0	100%
Mg	^{25}Mg(p,p'γ)^{25}Mg	585	585 $\rightarrow$ 0	10.13%
Al	^{27}Al(p,p’γ)^{27}Al	843	843 $\rightarrow$ 0	100%
	^{27}Al(p,p’γ)^{27}Al	1013	1013 $\rightarrow$ 0	100%
Si	^{28}Si(p,p’γ)^{28}Si	1779	1779 $\rightarrow$ 0	92.23%
	^{29}Si(p,p’γ)^{29}Si	1273	1273 $\rightarrow$ 0	4.67%

PIGE cross sections

The cross sections are the superimposition of resonances (Breit-Wigner) on a continuum due to direct nuclear reactions



Example of PIGE spectrum



PIGE spectrum of an emerald (from Medici collection), using High-Purity Germanium (HPGe) detector

PIGE quantitative analysis of thick targets

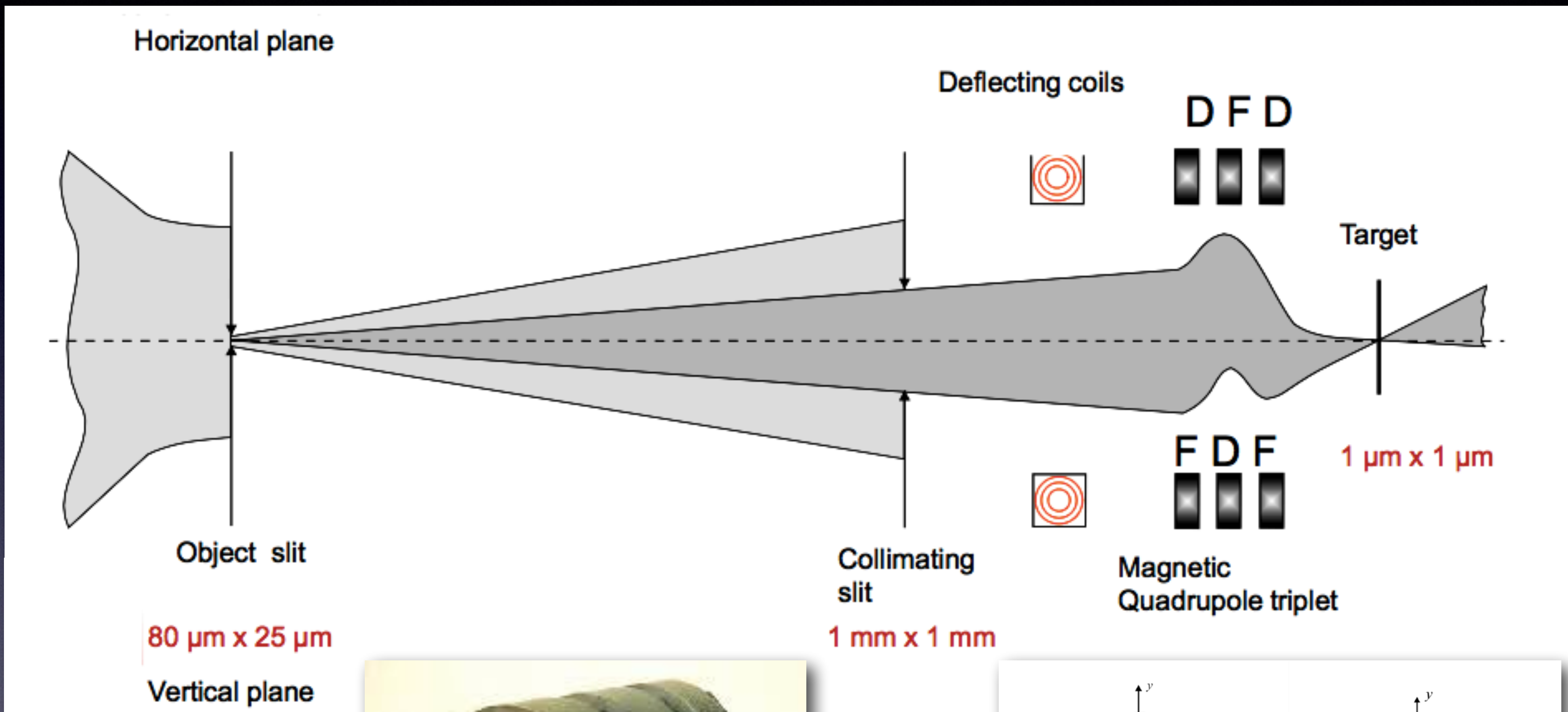
$$A_\gamma(E_0) = \varepsilon_{abs}(E_\gamma) \cdot N_p \cdot N_T \cdot \int_0^{E_0} \sigma(E) \cdot \frac{dE}{S(E)}$$

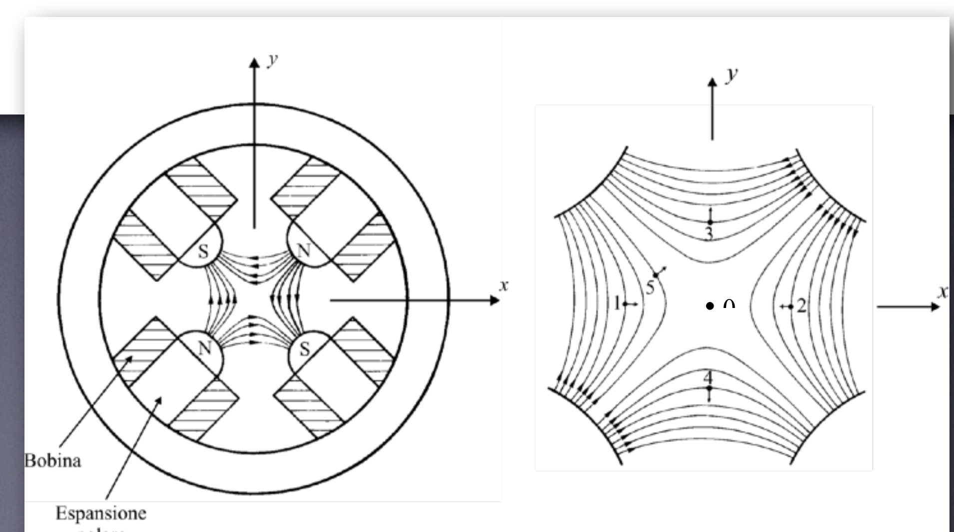
- A, area of the gamma-ray peak
- ε_{abs}, detector absolute efficiency at the gamma-ray energy
- N_p, number of impinging particles
- N_T, elemental concentration
- E_0, energy of the incident ion
- σ, differential reaction cross-section
- S, stopping power

Background in PIGE spectra and MDL

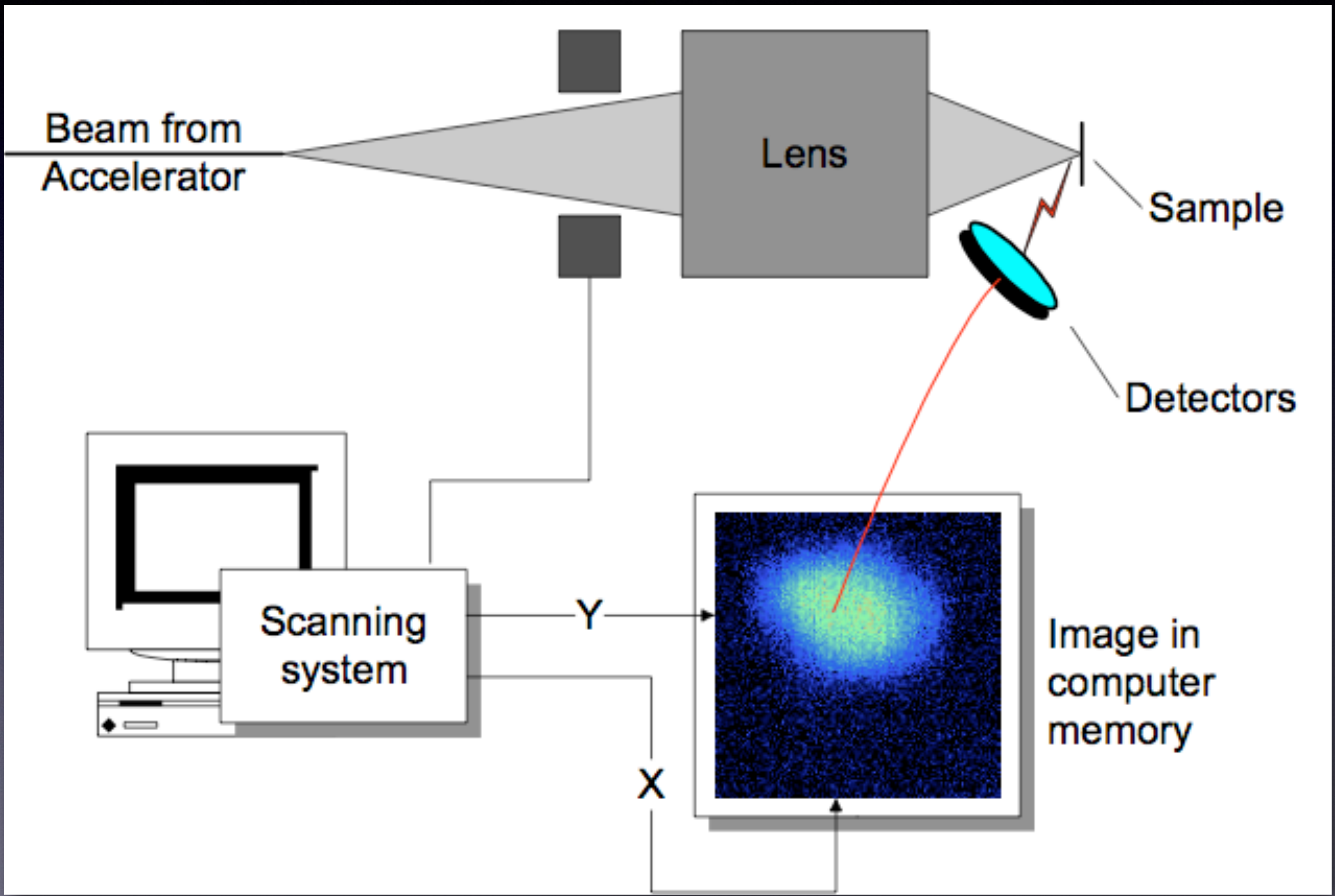
- The continuous background in PIGE spectra is mainly due to Compton interactions of the prompt gamma radiation from the beam bombarding the sample within the gamma-ray detector.
- Minimun Detection Limits (MDLs) in PIGE analysis can be calculated as for PIXE, e.g. assuming an equivalent area equal to three times the square root of the number of counts integrated in a region of the background under the peak as wide as the gamma-ray peak FWHM.

Ion microbeam

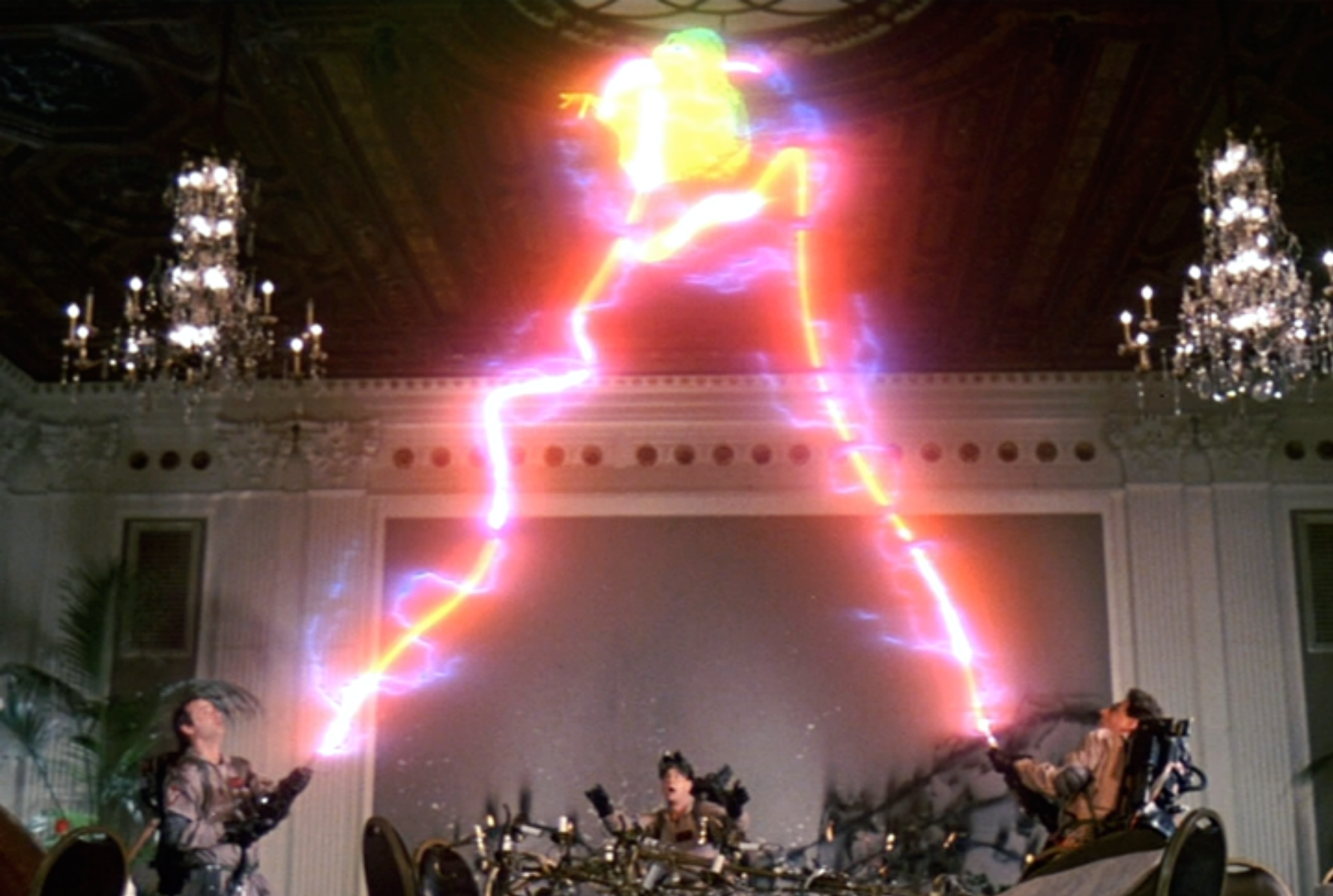




Ion microscopy

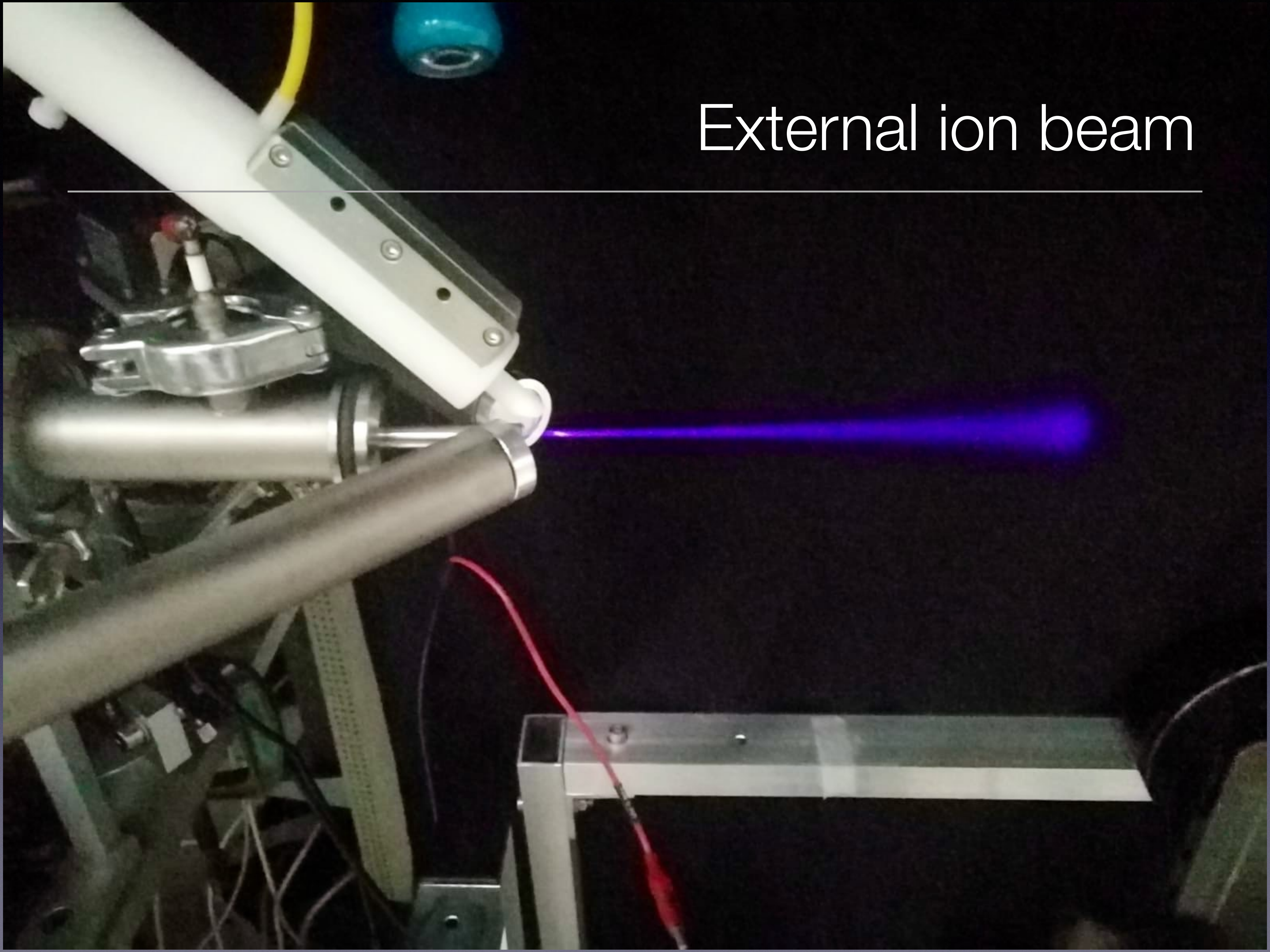


External beams

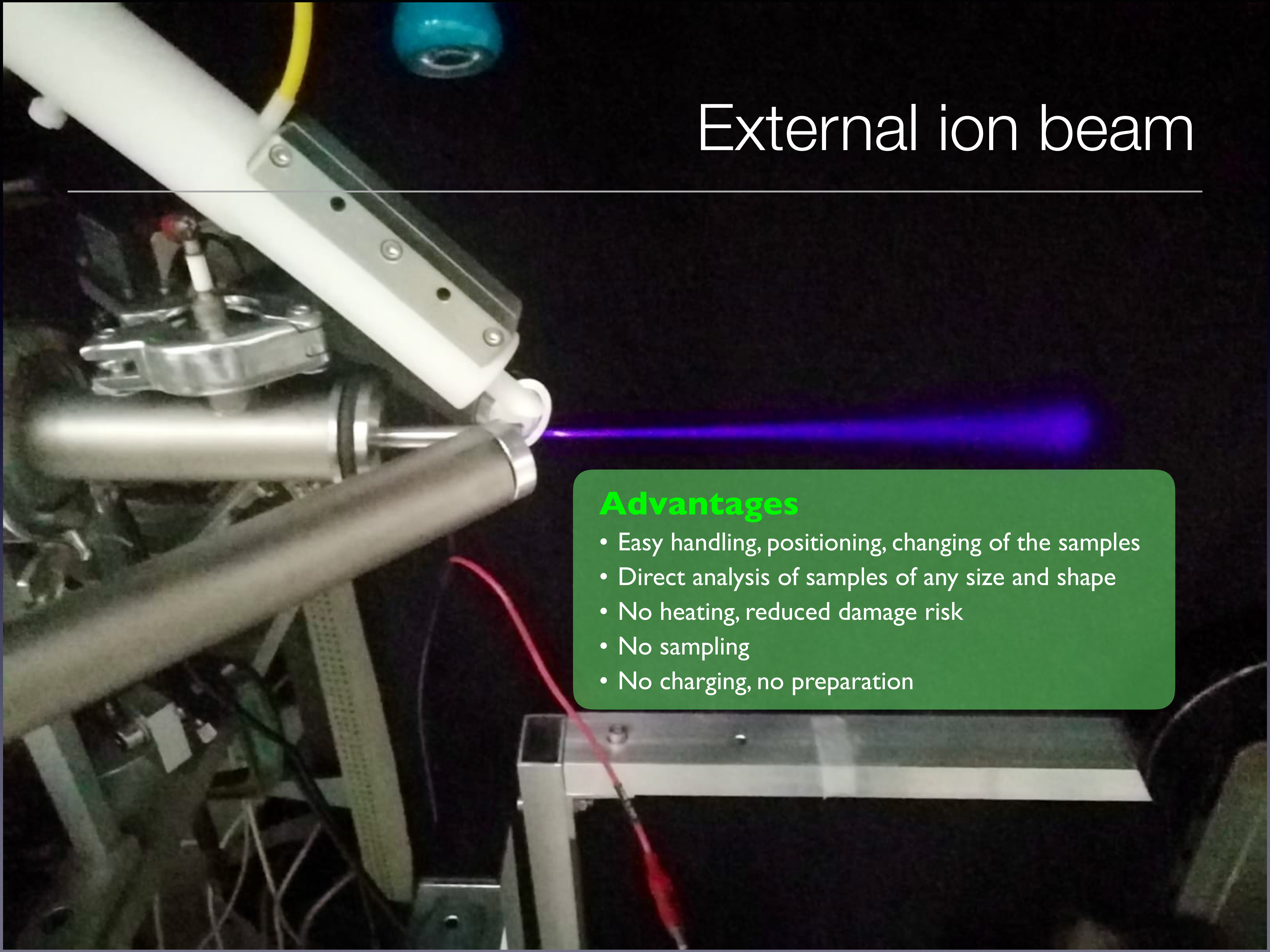


Do extracted ion beams look like these?

External ion beam



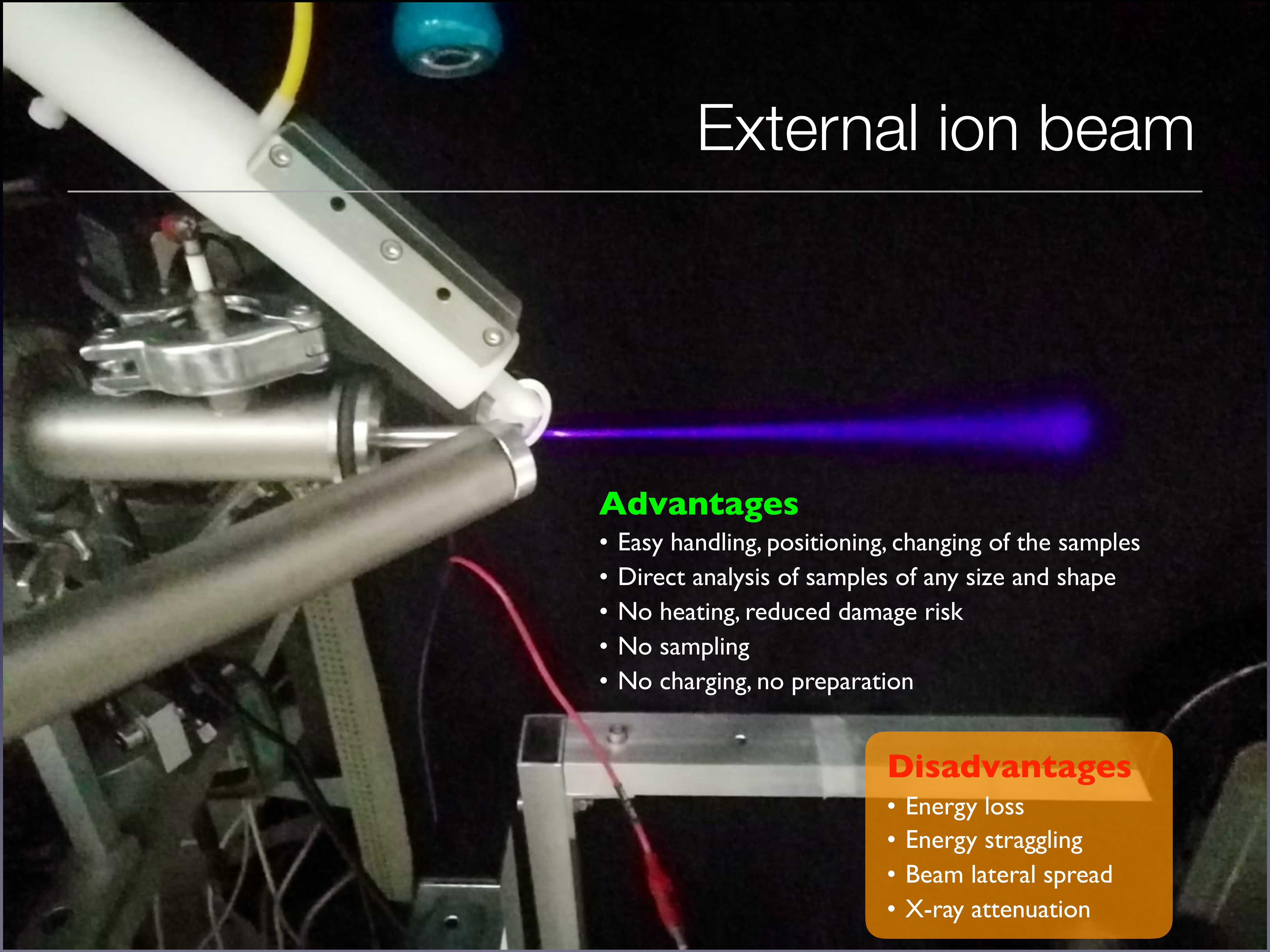
External ion beam



Advantages

- Easy handling, positioning, changing of the samples
- Direct analysis of samples of any size and shape
- No heating, reduced damage risk
- No sampling
- No charging, no preparation

External ion beam



Advantages

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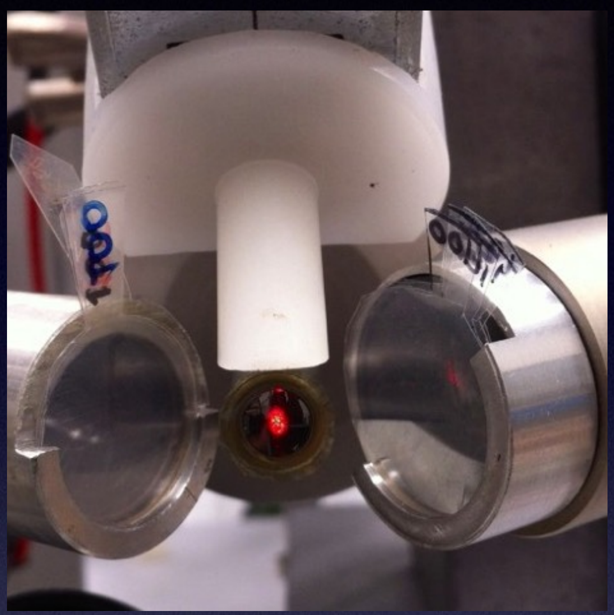
Disadvantages

- Energy loss
- Energy straggling
- Beam lateral spread
- X-ray attenuation

Typical extraction windows

0.5 µm Si_3N_4



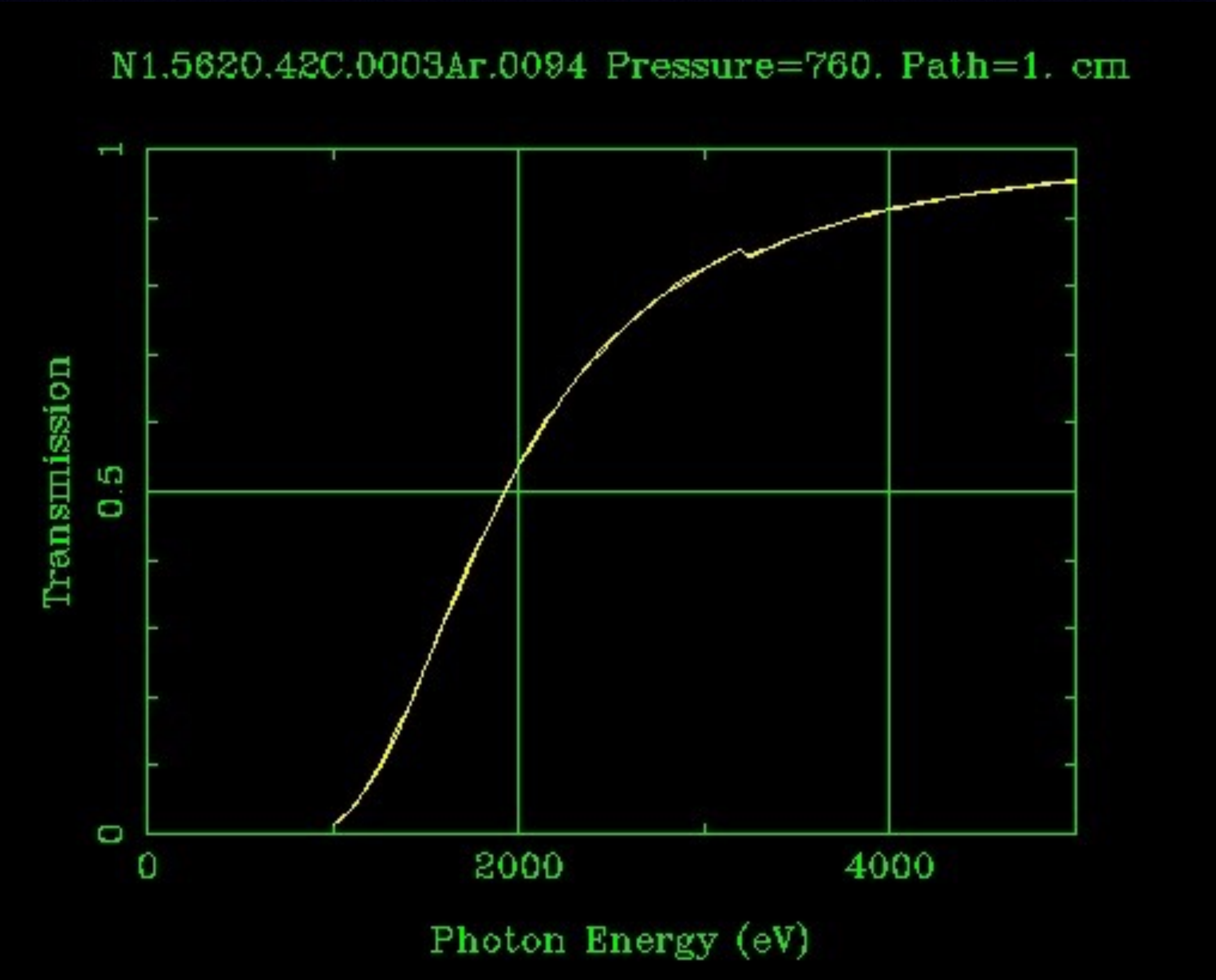
7.5 µm Upilex

For 3 MeV protons…

Material	Thickness (µm)	ΔE (keV)	σ_E (keV)	σ_θ (µm/mm)
Kapton	8	130	9	6
Si_3N_4	0.1	8	5	< 1
	0.5	40	9	< 2

Choice of external atmosphere

Air



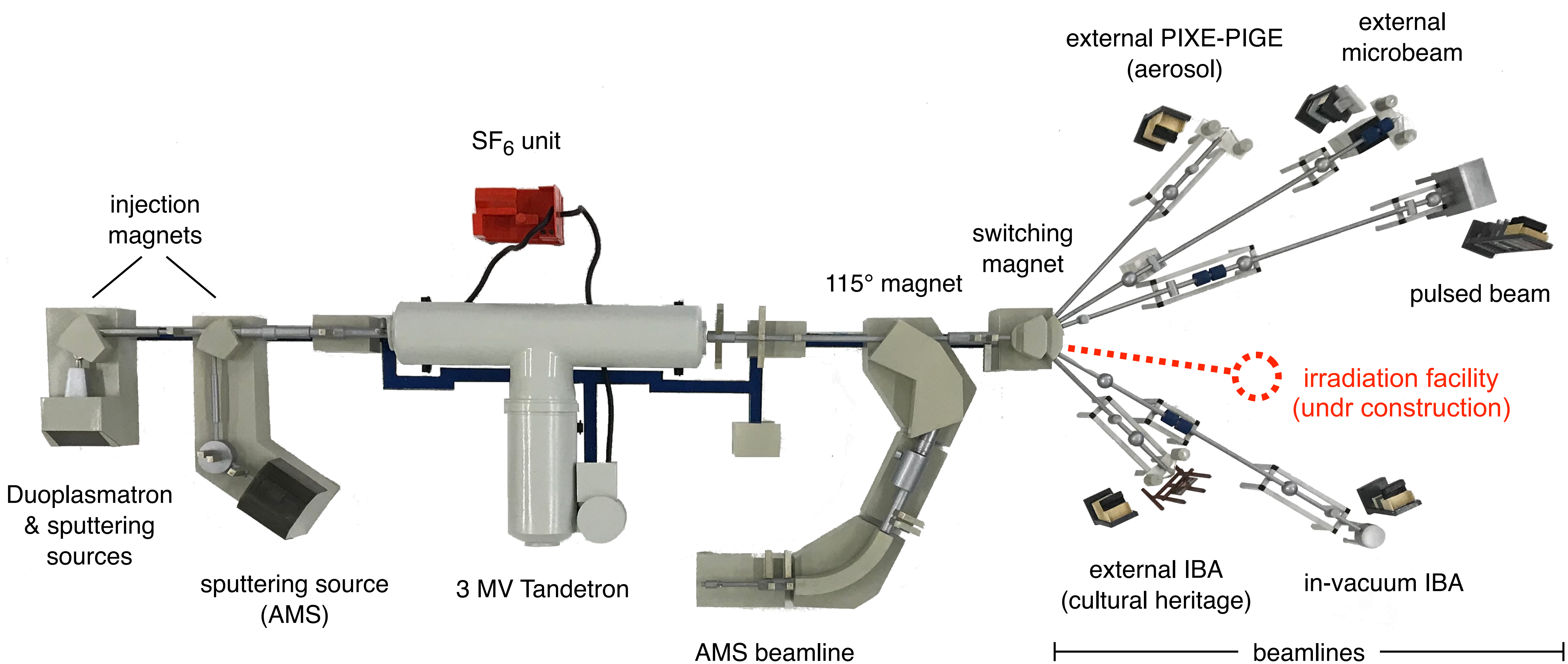
Helium

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

Applications

The LABEC laboratory in Florence

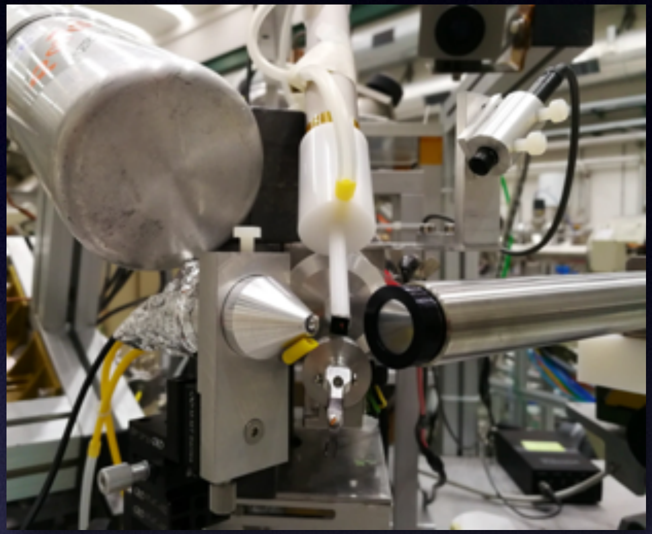
The LABEC laboratory in Florence



- 3 MV HVEE Tandetron accelerator
- 3 independent ion sources
- 5 beamlines for IBA (3 external-beamlines)
- 1 beamline for AMS

- XRF laboratories (Epsilon 5, custom portable XRF scanners)
- AMS sample prep labs

IBA set-ups

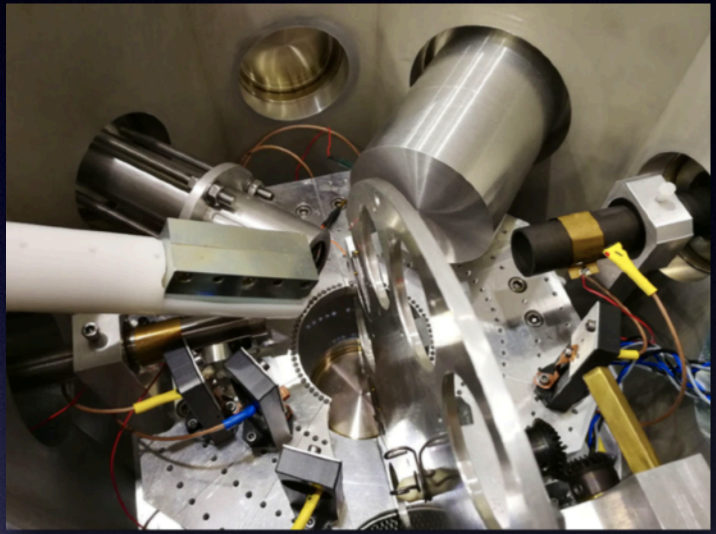


Cultural Heritage
-45° beamline

- PIXE (x2)
- PIGE
- RBS

Atmospheric aerosol
+45° beamline

- PIXE (x3)
- PIGE



Multipurpose IBA scattering chamber
+30° beamline

- PIXE (x2)
- PIGE
- RBS (x3)
- PESA/ERDA

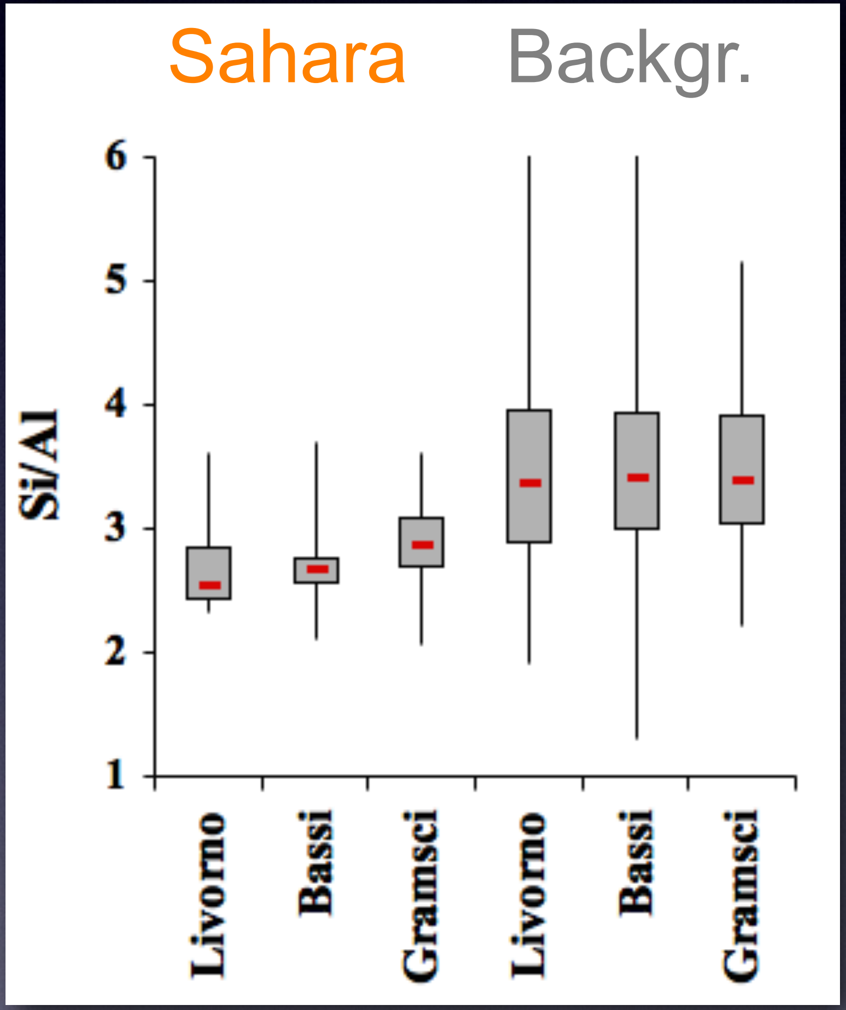
Elemental composition of aerosol samples

- Atmospheric aerosols are solid and liquid particles suspended in the air, with diameters up to ~100 µm.
- They have important impact on both human health, climate and environments.
- The elemental composition of aerosol samples gives important information about their emission sources.

PIXE analysis of aerosol mineral dust

- Study of the desert aerosol which is one of the major component of the aerosol on global scale

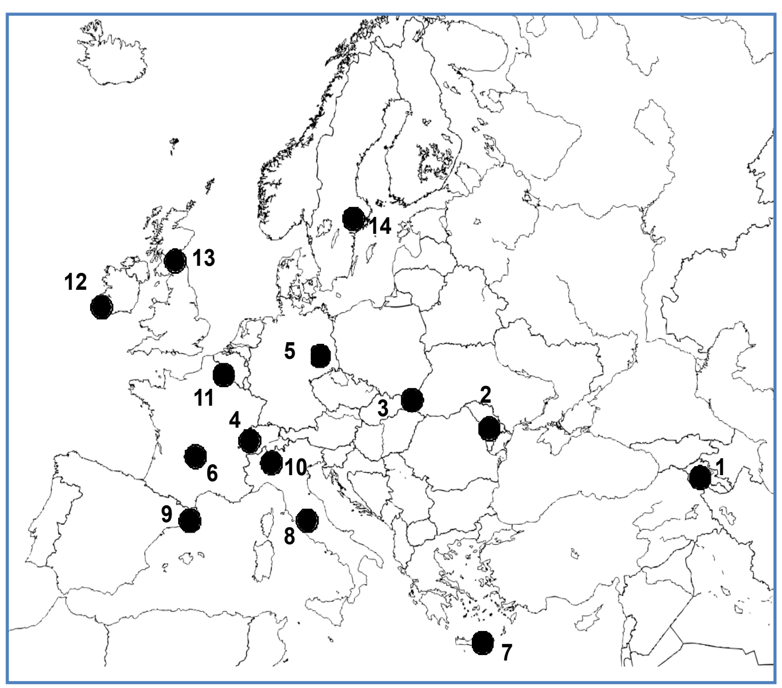
		Si/Al	Al/Ca	Si/Ca	Al/Fe	Si/Fe
Rural site	Sahara	2.5	1.05	2.6	1.37	3.4
	Backgr.	*3.7*	*0.55*	*1.9*	*0.70*	*2.4*
Urban site	Sahara	2.6	0.71	1.8	0.91	2.4
	Backgr.	*3.5*	*0.36*	*1.2*	*0.43*	*1.3*
Traffic site	Sahara	2.7	0.60	1.5	0.42	1.1
	Backgr.	*3.5*	*0.27*	*0.9*	*0.16*	*0.5*

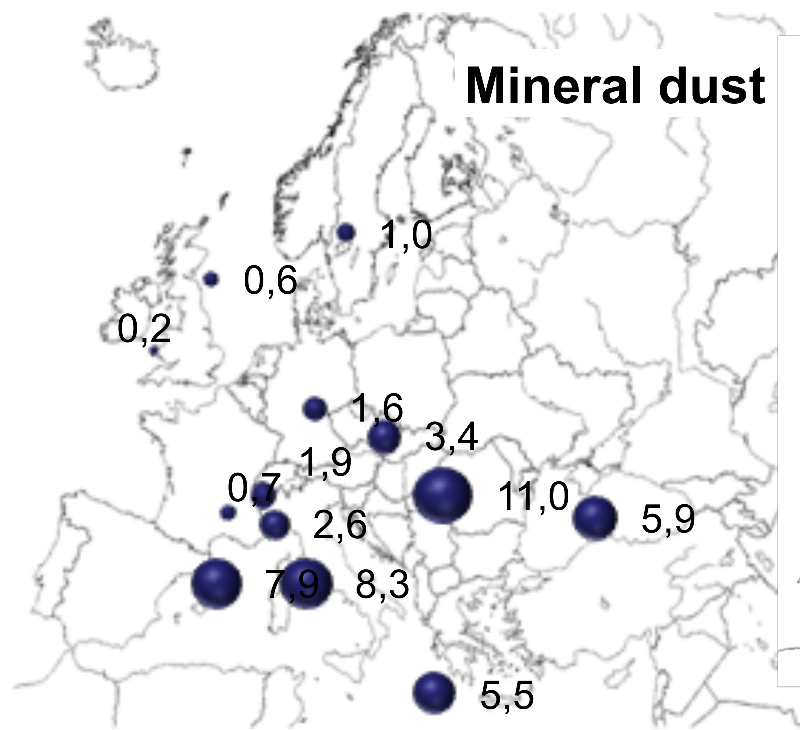


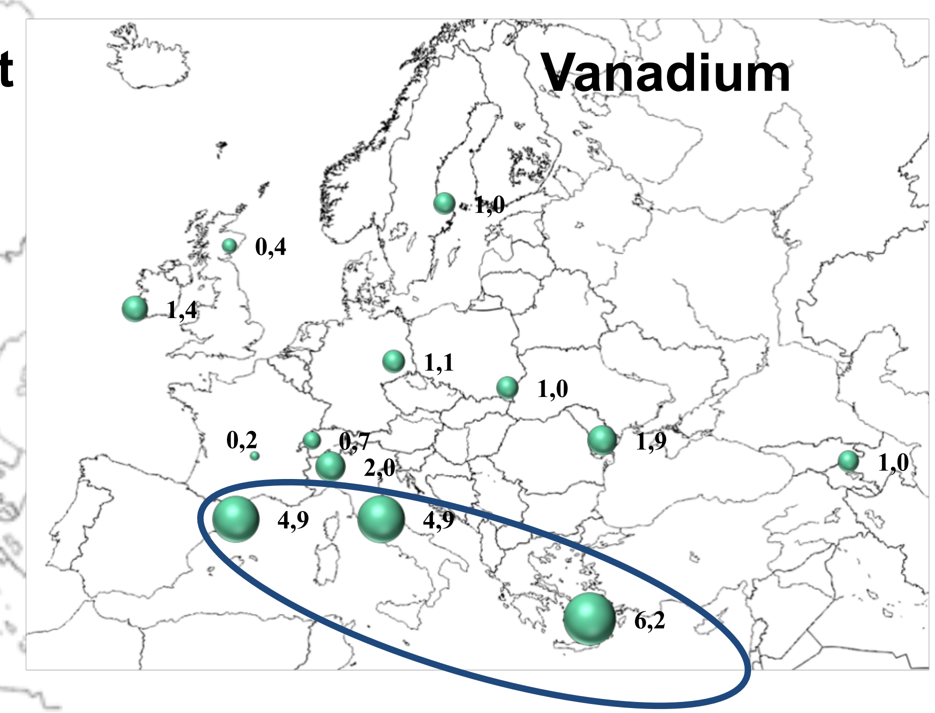
- Si/Al lower in desert dust (with very similar values in the 3 sampling sites)
- Ratios to Ca and Fe higher in desert dust, due to Ca and Fe enrichment in local soil dust (more site-dependent)

Elemental composition of aerosol samples

- EMEP (European Monitoring and Evaluation Programme) is a scientifically based and policy driven programme under the Convention on Long-range Transboundary Air Pollution for international co-operation to solve transboundary air pollution problems.
- PIXE analysis of about 1000 PM10 aerosol samples, with special emphasis on mineral dust, with daily samplings for two one-month periods in 14 sites.







PIXE analysis of high-time resolution aerosol samples

New prototype of sampler

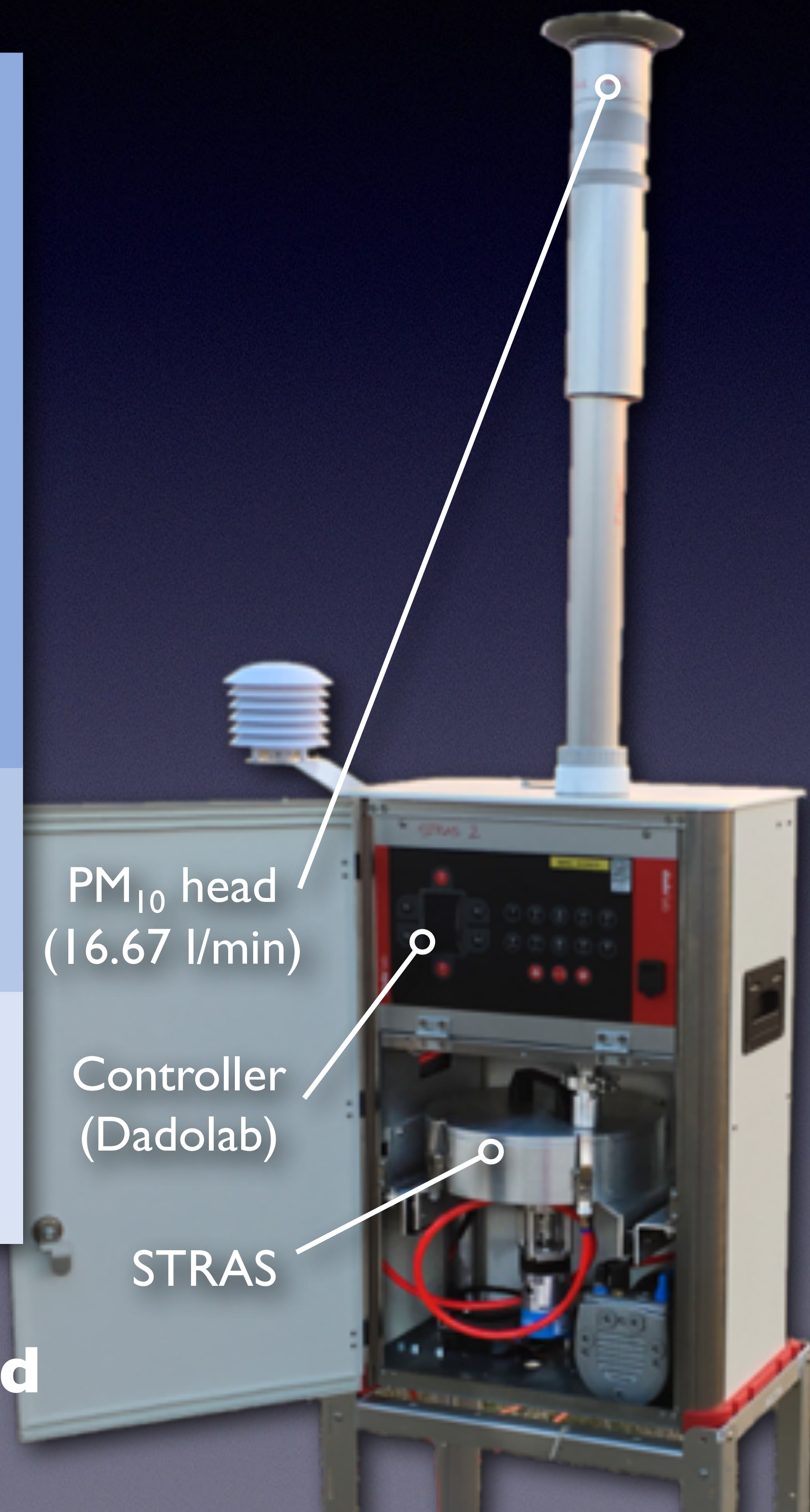
Aim of the project:

- Separate two fractions
  - Fine: < 2.5 μm
  - Coarse: 2.5 - 10 μm
- Collect each sample in a stripe
- Collect samples with a high temporal resolution (e.g. 1 hour)
- Use a commercial controller and an EPA standard head
- Record time and position

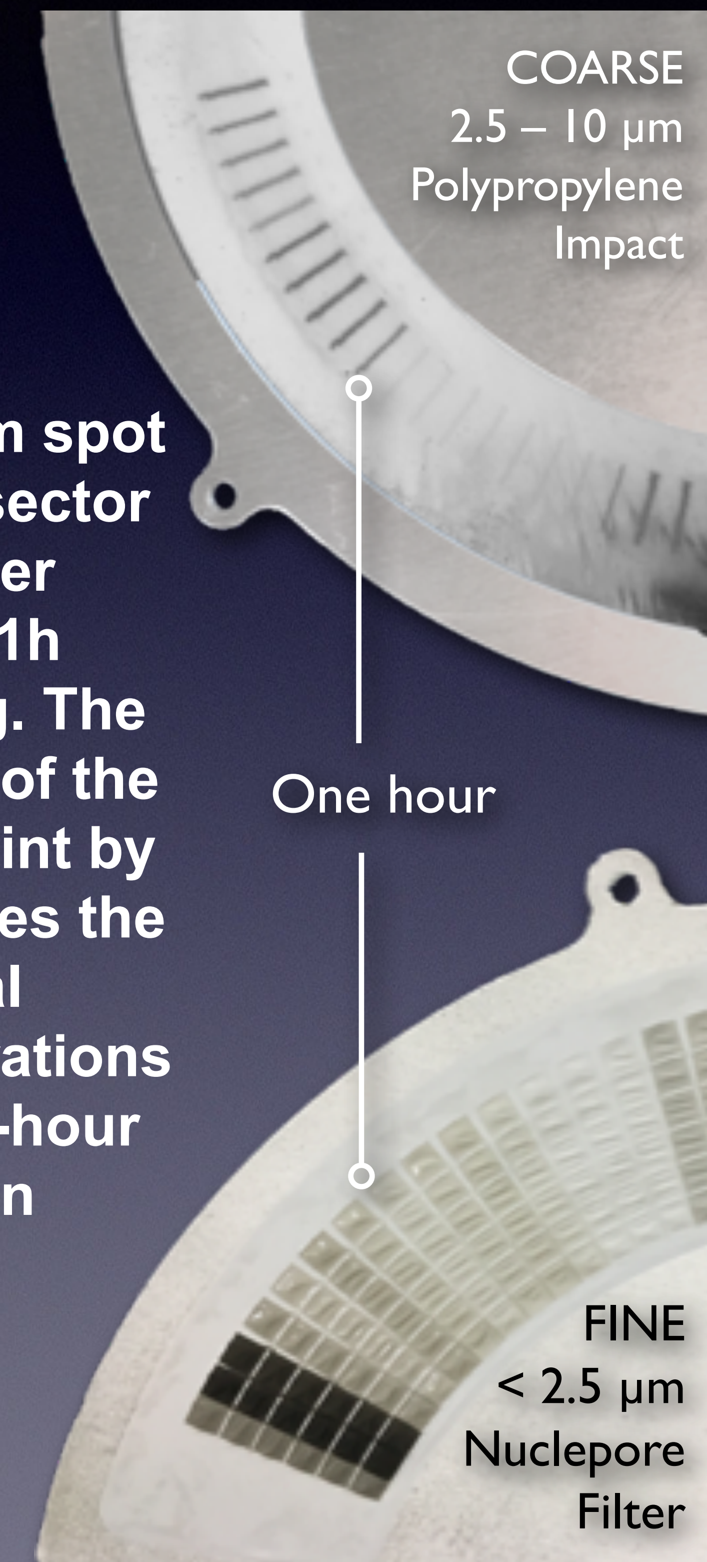
High surface density excellent for **Ion Beam Analysis** techniques (PIXE)

Hourly chemical composition useful for **source apportionment** with receptor models

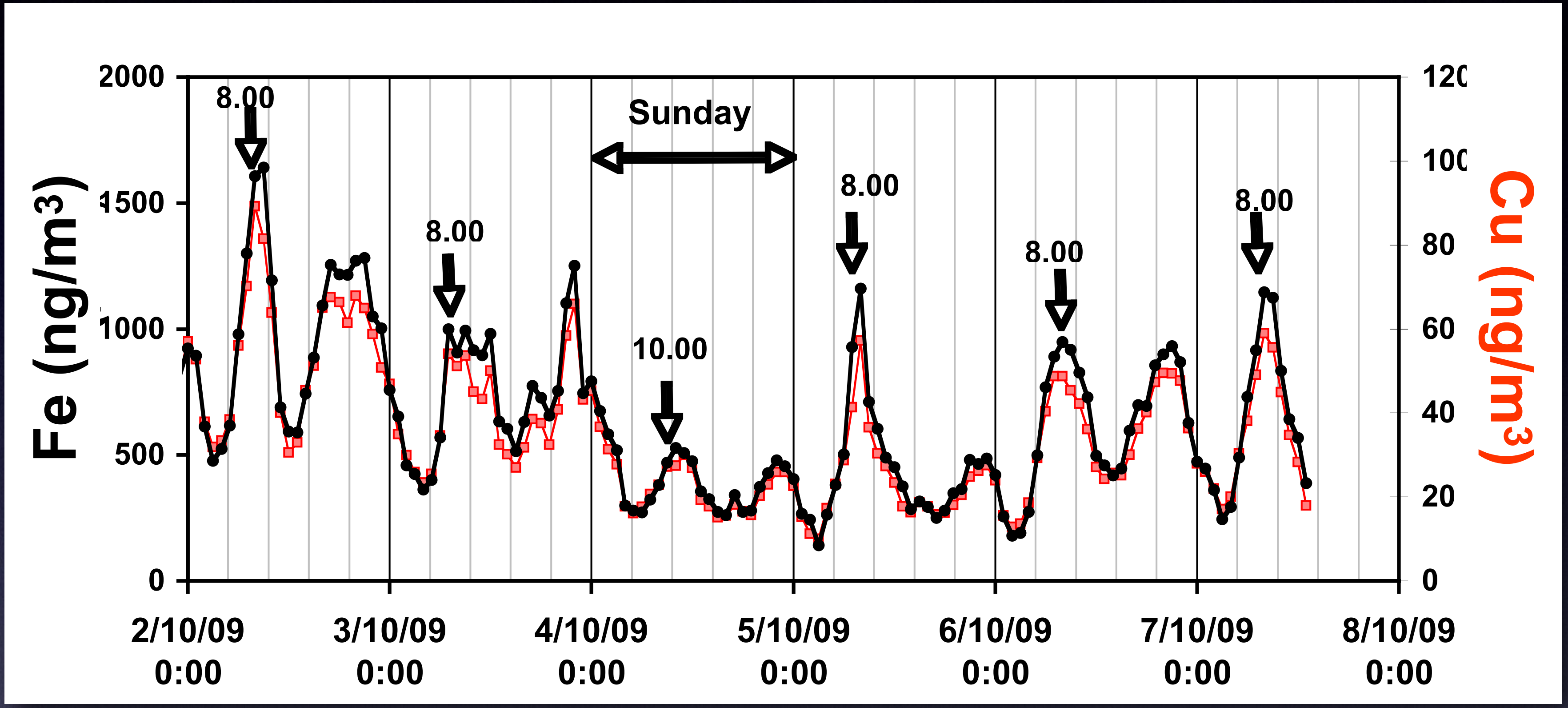
STRAS (Size and Time Resolved Aerosol Sampler)



The beam spot cover a sector of the filter equal to 1h sampling. The analysis of the stripe point by point gives the elemental concentrations with one-hour resolution

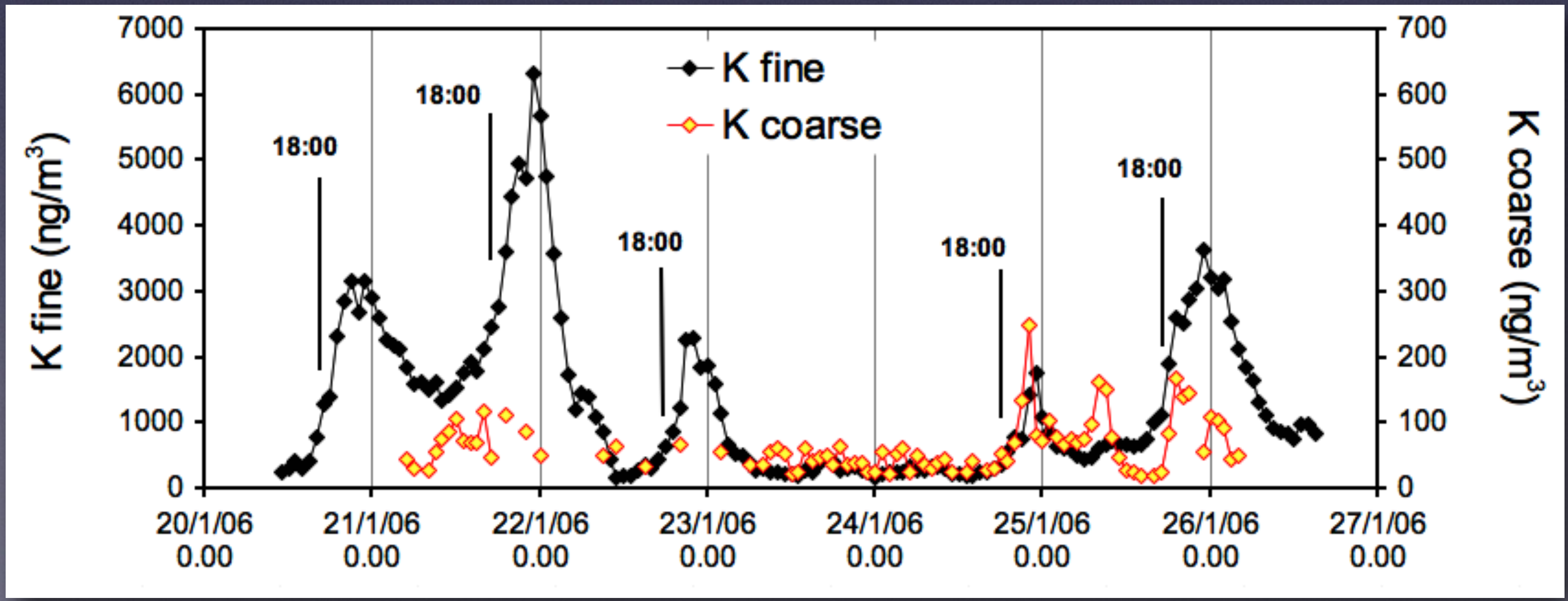


PIXE analysis of high-time resolution aerosol samples



Periodic time pattern with peaks during traffic rush hours and lower concentrations on Sunday

Periodic time pattern with peaks during the evening-night hours in the fine fraction, suggesting the use of biomass burning for domestic heating



What IBA can do for cultural heritage?

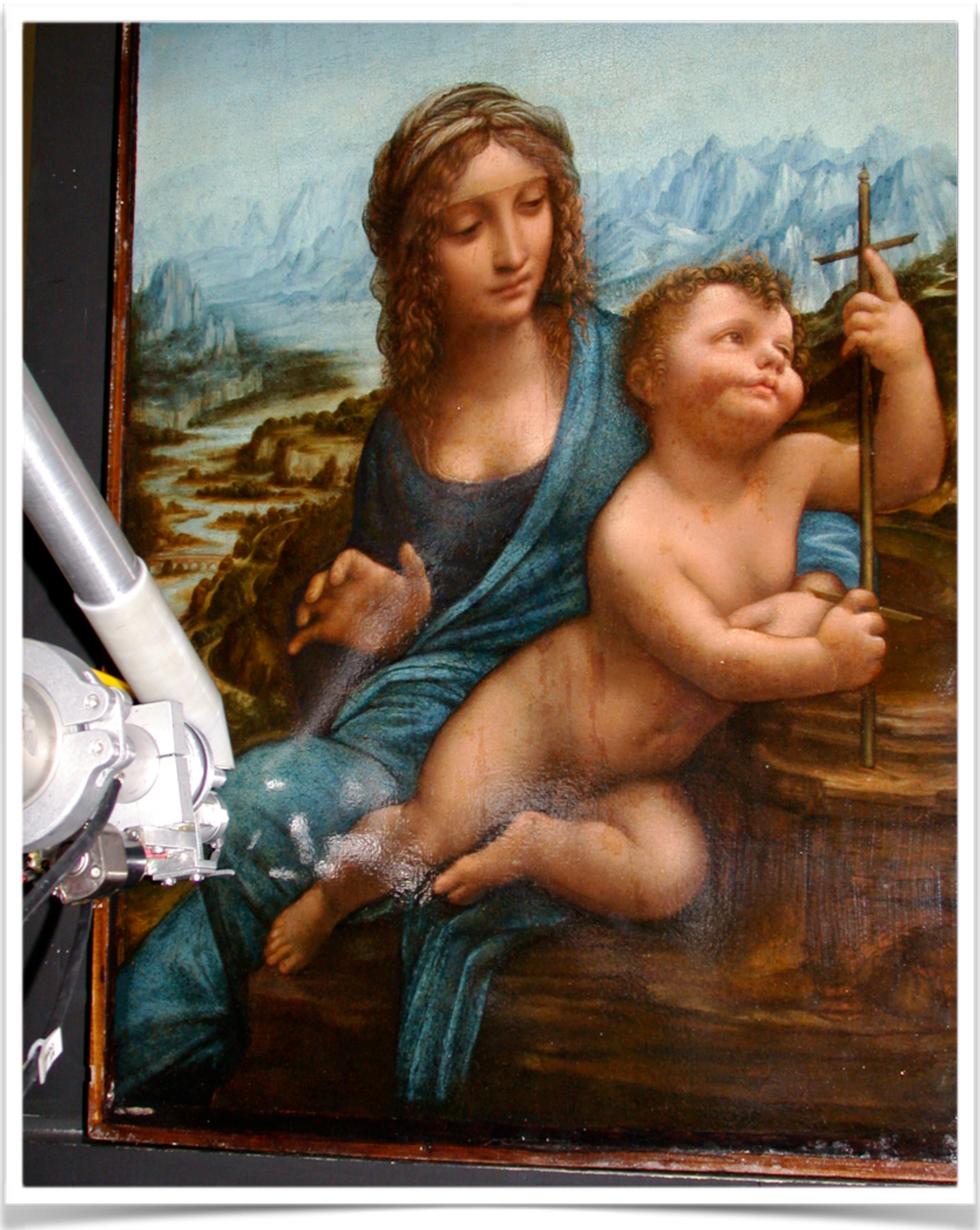
- Materials identification
  - *analysis of major elements by PIXE (and PIGE)*

- 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)*

- Among IBA techniques, PIXE is a “killer application” for the non-destructive analysis of cultural heritage objects 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, thus reducing the risk of damaging the object (truly “not deliberatively destructive”).

PIXE-PIGE analysis of paint layers: identification of lapis-lazuli pigment



“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*

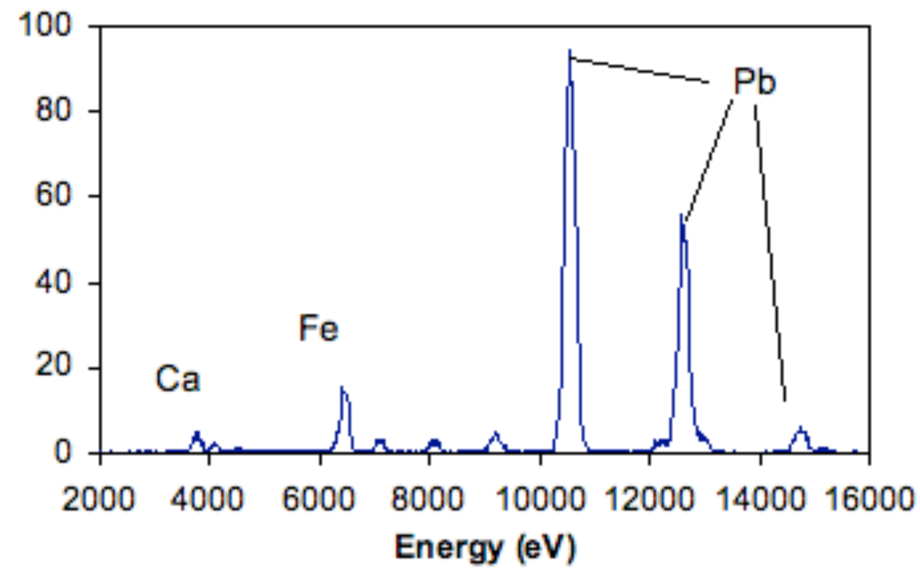
PIXE-PIGE analysis of paint layers: identification of lapis-lazuli pigment

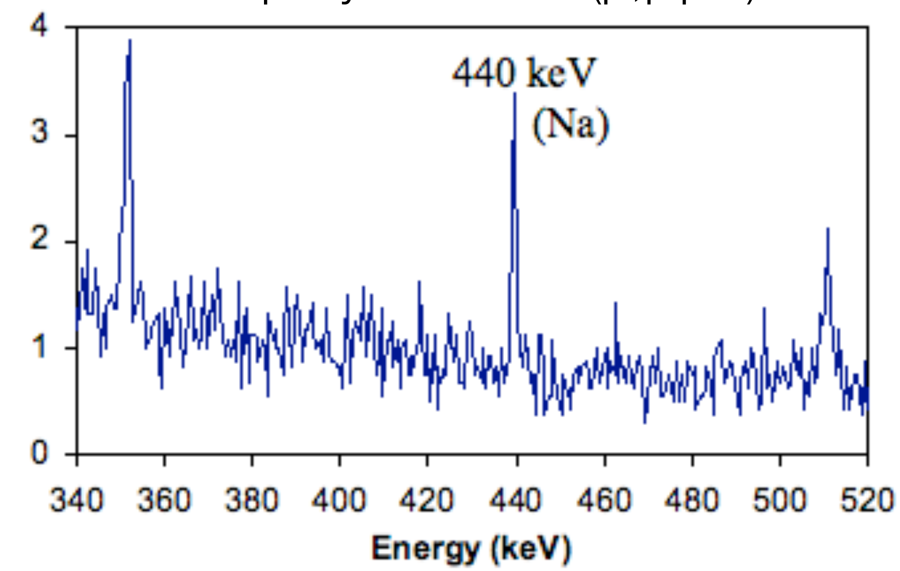
PIXE spectra

PIGE spectra

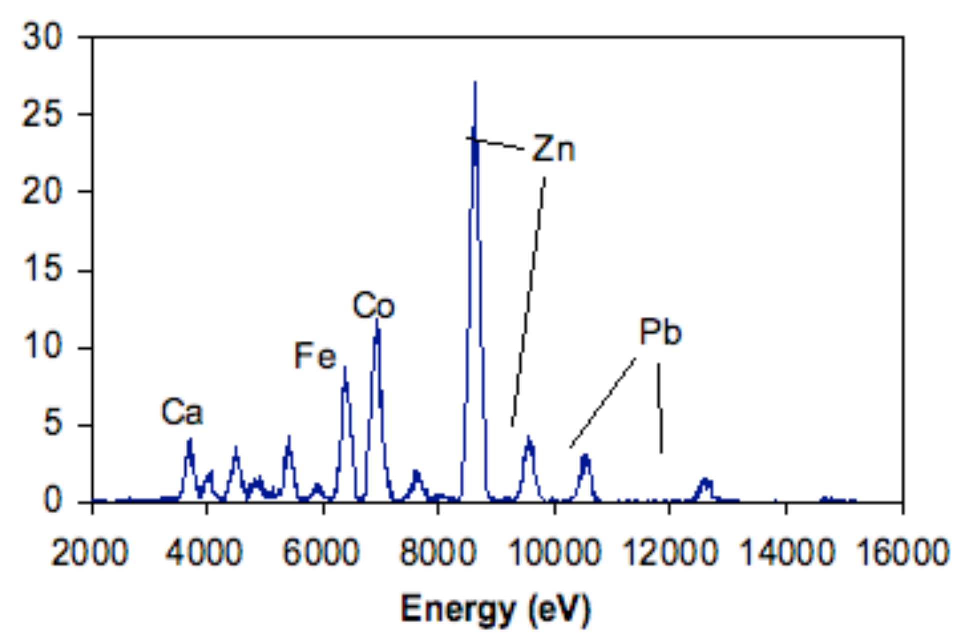
441 keV γ-ray from $^{23}Na(p,p\gamma_{1\text{-}0})^{23}Na$

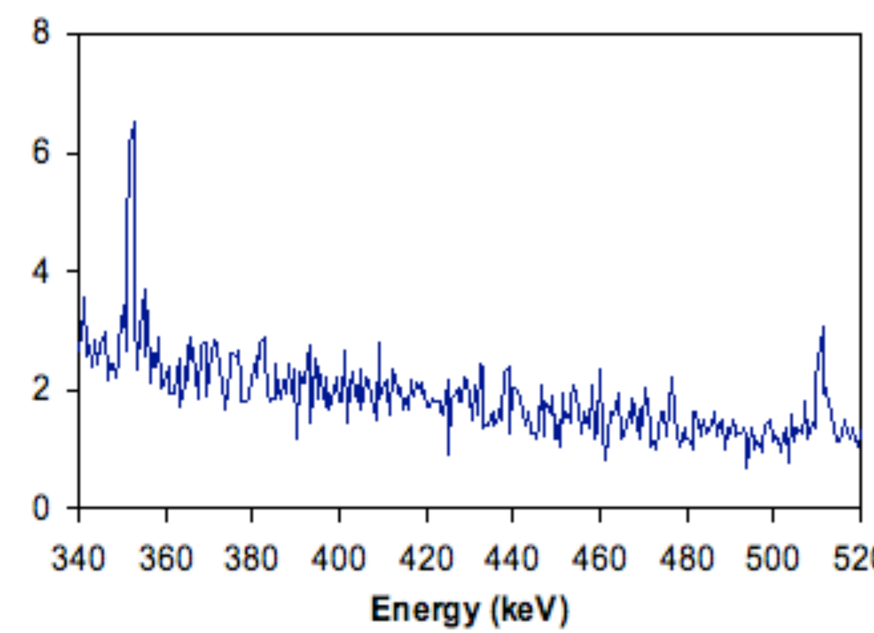
- Original
  - *Blue pigment mixed with Lead white*
  - *Ca and Fe from the varnish*





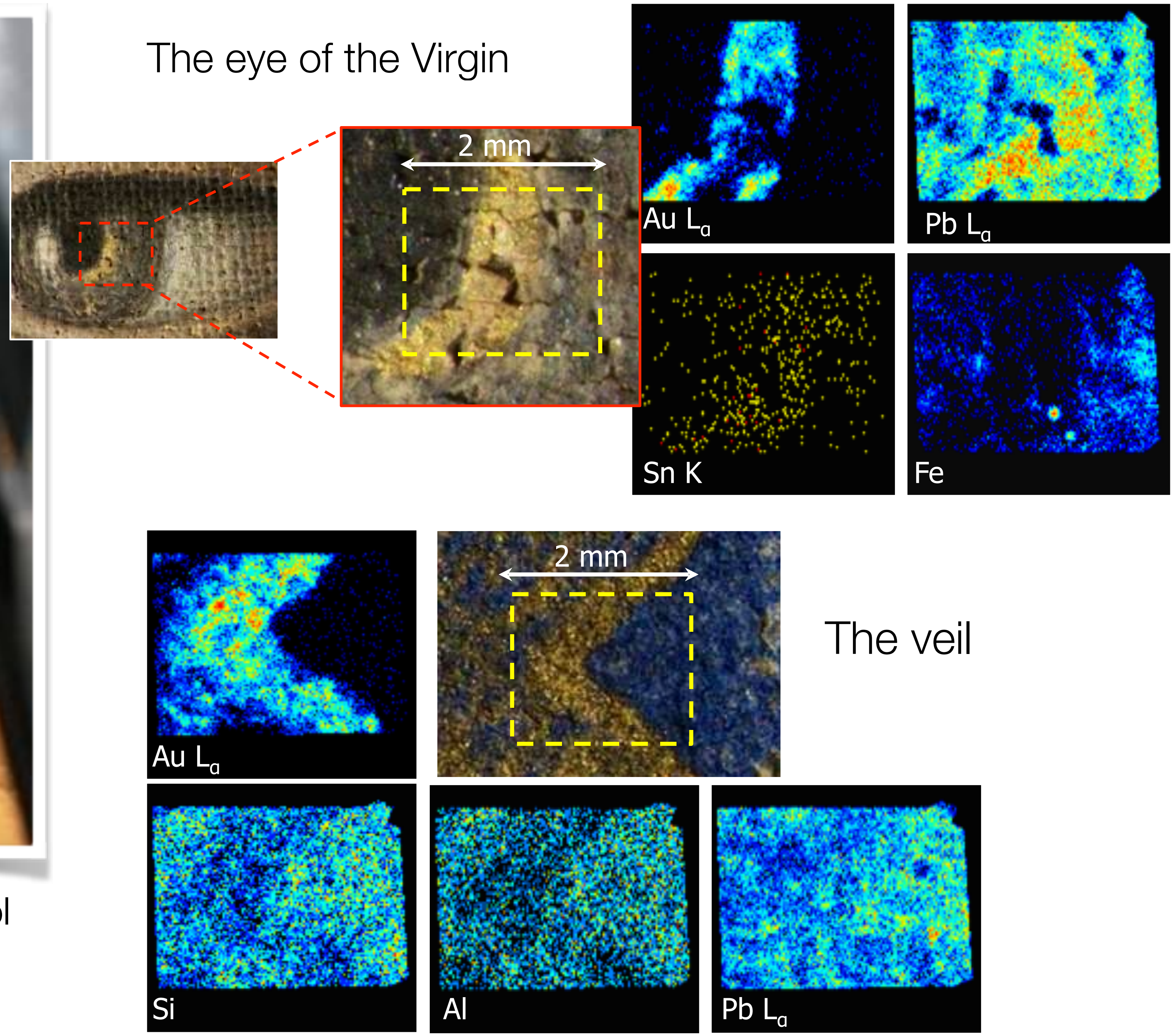
- Restored
  - *Cobalt blue and Zinc white*
  - *Used only from XIX century!*



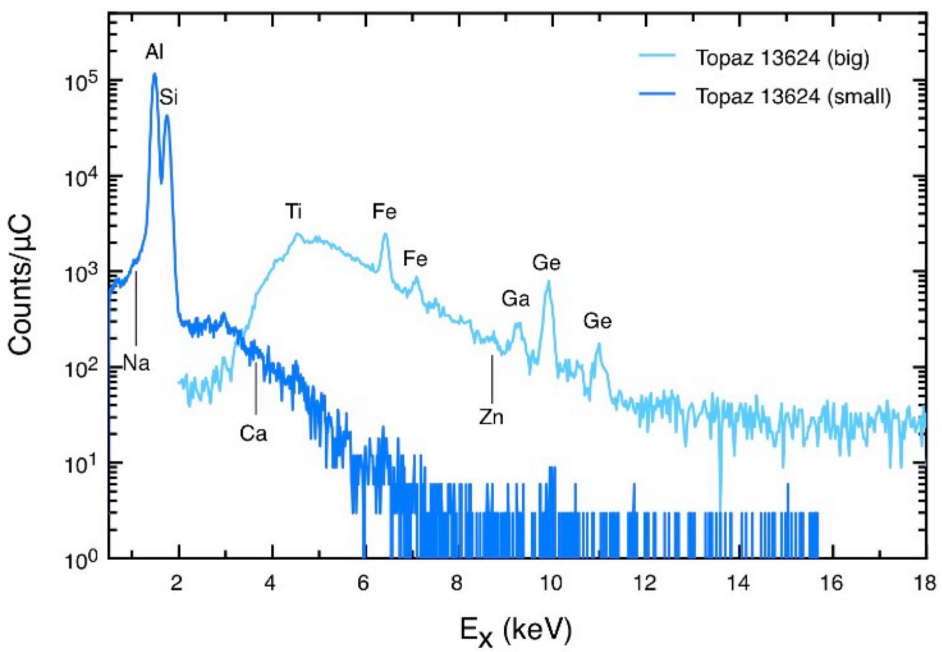


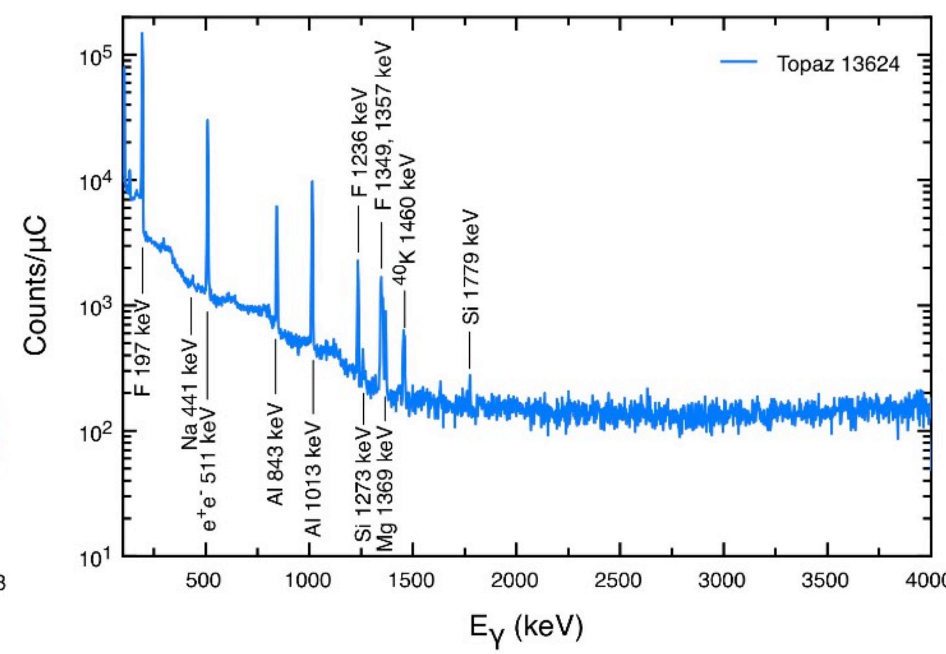
Elemental mapping with microPIXE

Andrea Mantegna, “Madonna col Bambino”, oil on canvas, Bergamo, Italy



PIXE-PIGE study of gems





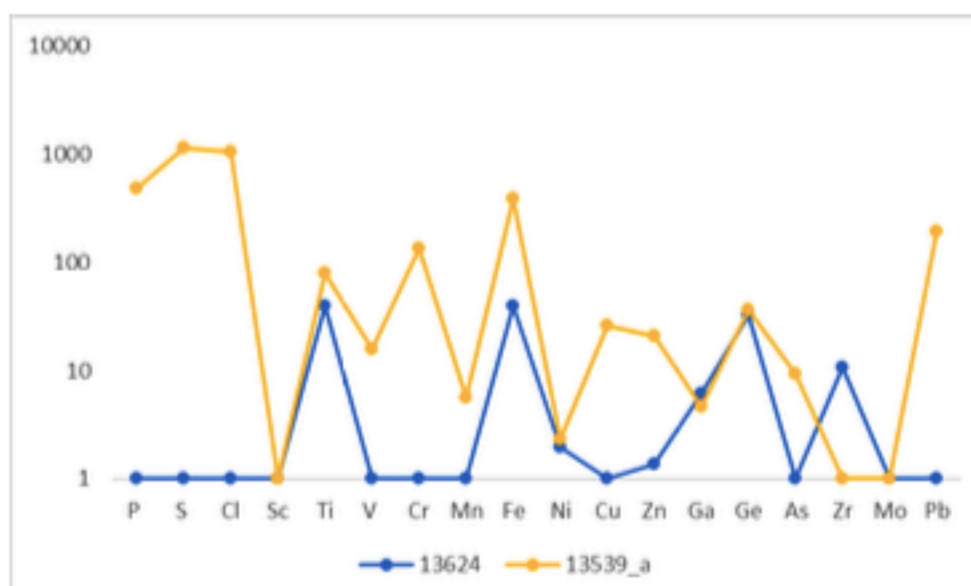
F= 20.7wt% the OH-free end-member (F-topaz)

13624: 16.5 wt% of F

F = 13.12 wt%, minimum fluorine for natural topaz in near-surface environments

13539_a: 12.7 wt% of F

F=0 wt% synthetic hydroxyl end member (topaz-OH)

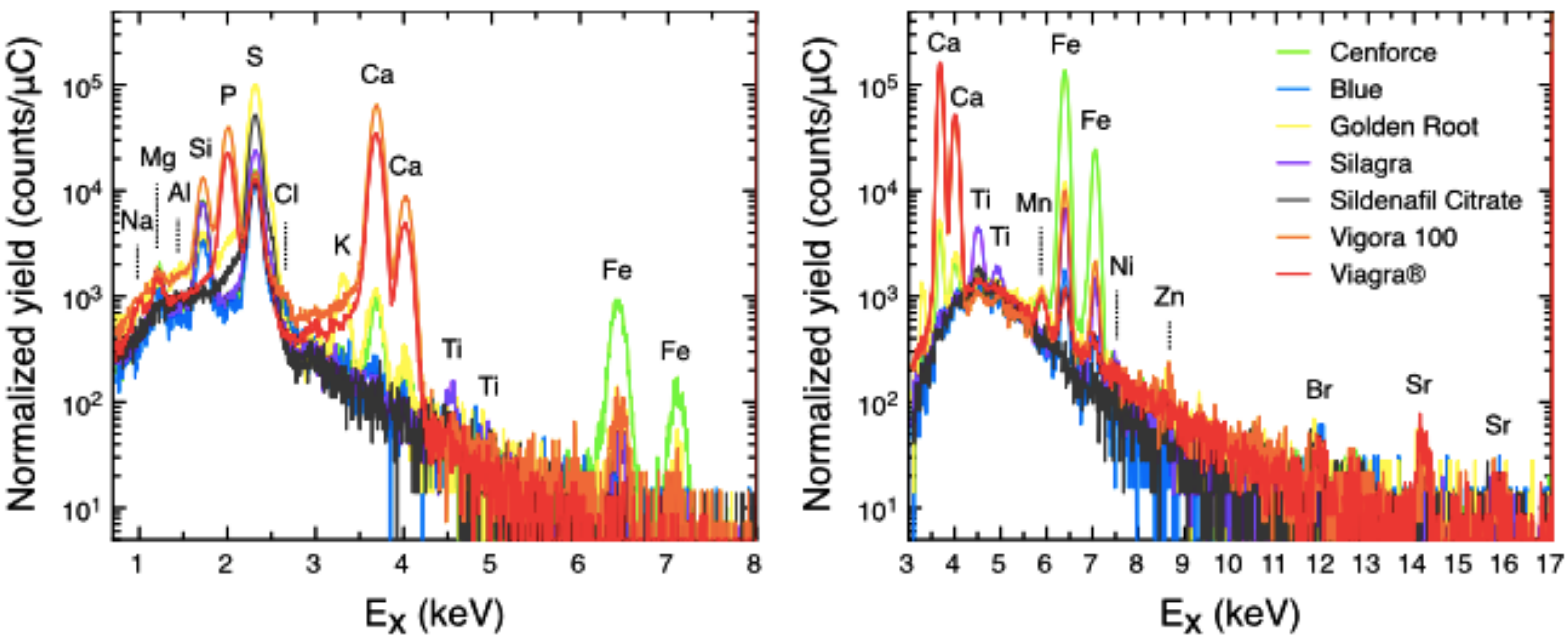


→ F content in topaz can give important information about genesis and origin of deposits

→ Completely different concentration in trace elements

Forensics: medical products

- Comparison of PIXE spectra obtained from some pure Sildenafil and from illegal products containing Sildenafil.
- Forensic examination of counterfeit products is based on the comparison with authentic versions of the product: it is a classification.



Study of dopants in inorganic scintillators

- PIXE is a useful tool to check the concentration of doping species and spurious contaminants dispersed in inorganic crystals.
- Although it cannot explore the whole bulk of the detectors, PIXE can readily be used for a quick check of the first tens of microns from crystal faces.

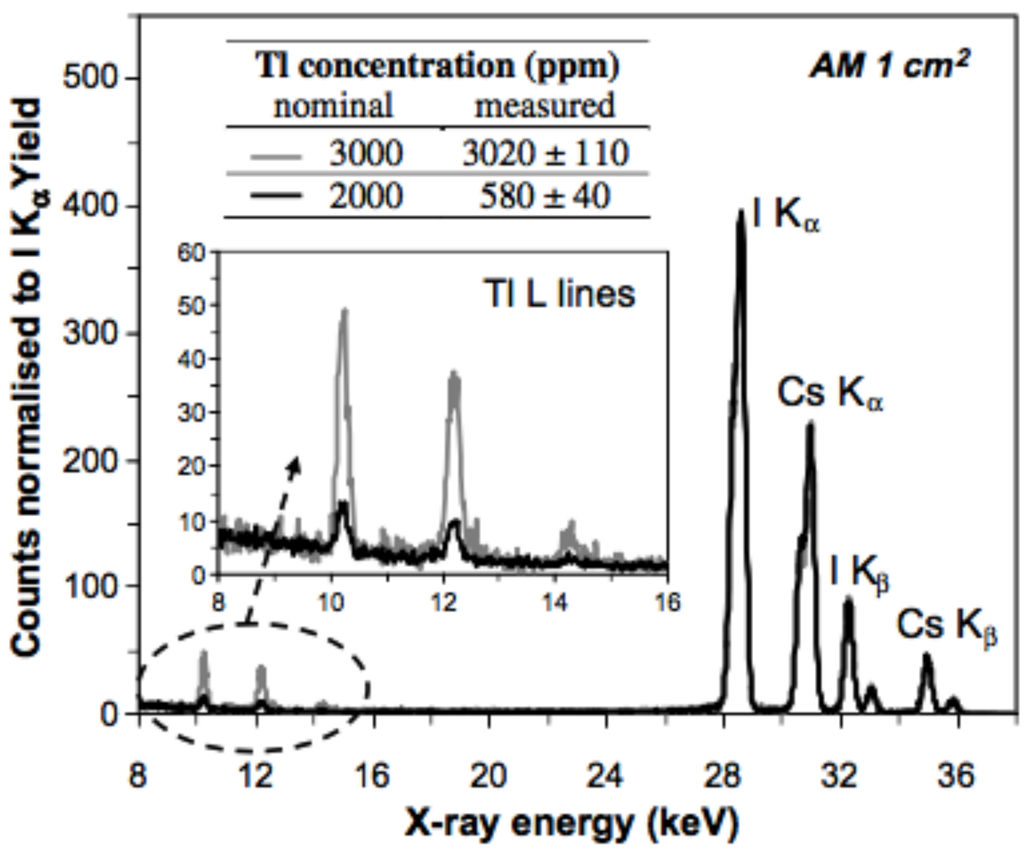


Fig. 2. PIXE spectra (normalized to iodine K_α peak area) for two crystals with different Tl concentration. For one of them the actual Tl content is largely different from the nominal value. The spectra refer to average measurements (AMs), performed by scanning a 1 cm^2 area.

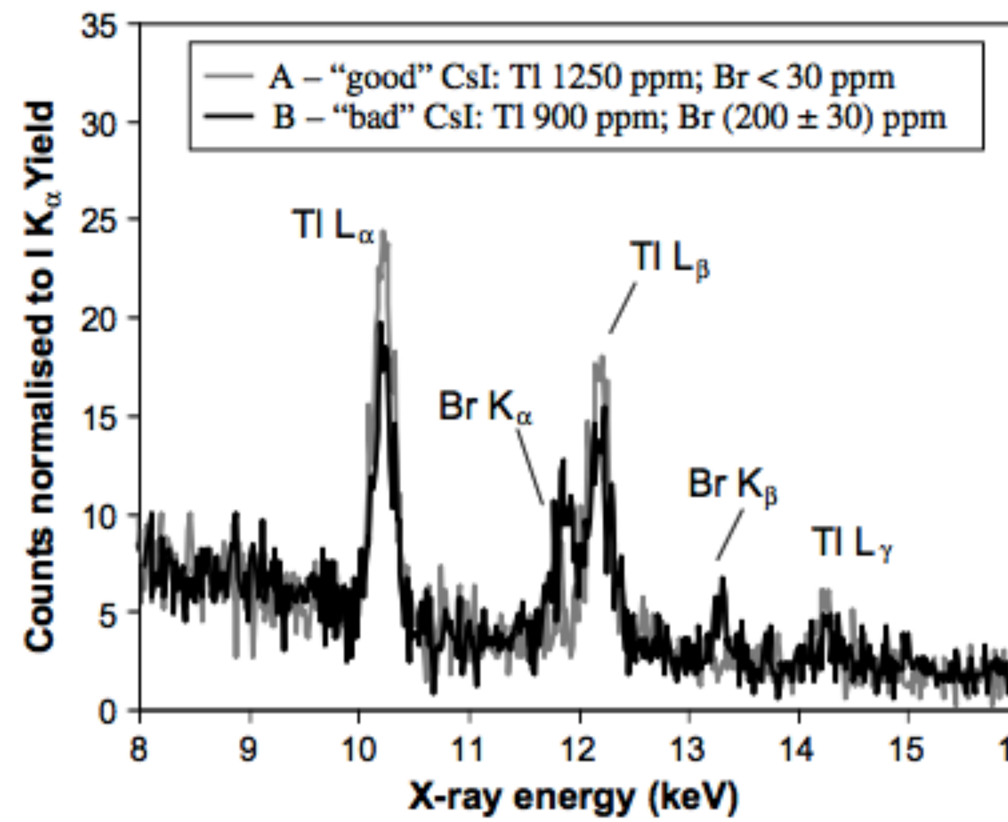
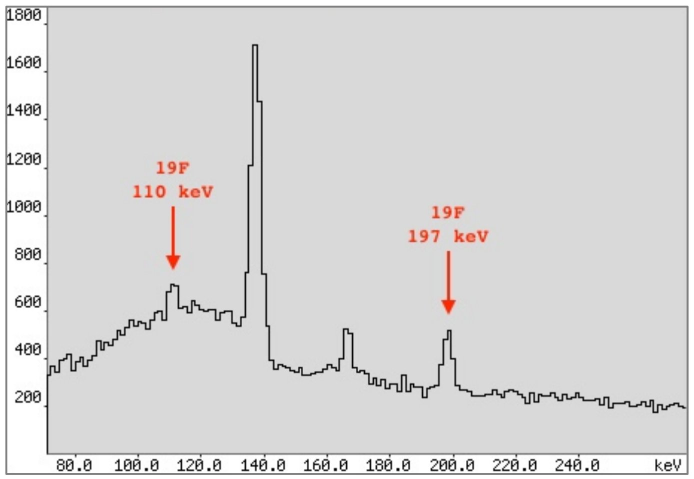


Fig. 5. PIXE spectra for two crystals (Tl 1000 ppm nominal): scintillator (A) had shown good energy resolution, while (B) a very bad one. In sample (B) the presence of bromine can be observed as a contaminant.

PIGE analysis of Fluorine in food containers



- External-beam PIGE can be very useful for rapidly measuring total fluorine in as-is solid samples, without any pre-treatment .
- The discovery of fluorinated chemicals in food containers demonstrates their potentially significant contribution to dietary PFAS exposure.

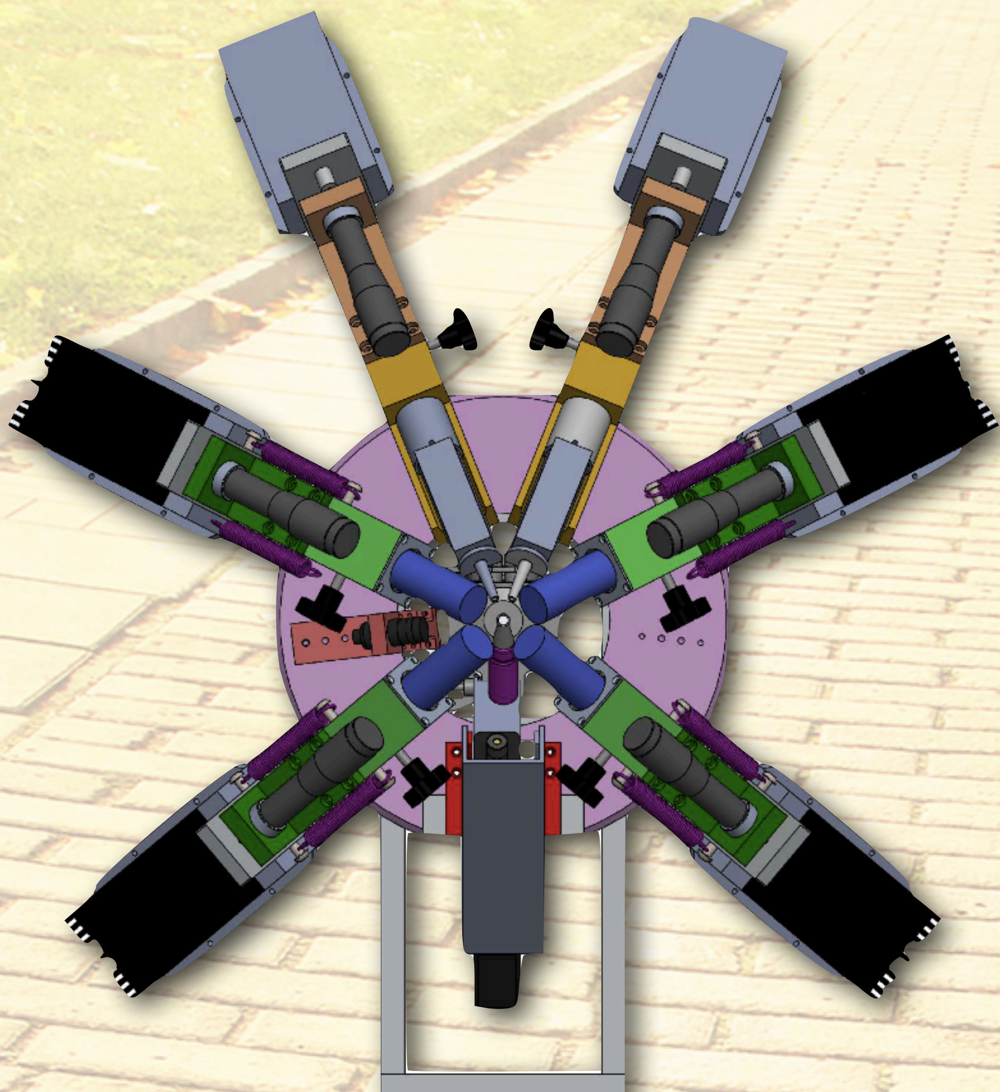
Source	Sample type	# samples	F concentraion (ppm)
Supermarket in Rome	Plate	15	990 ± 200
Cafeteria in Bologna	Bowl Cup	1 4	830 ± 200 470 ± 120
Cafeteria in Rome (1)	Plate	1	1130 ± 240
Cafeteria in Rome (2)	Plate Lid	1 1	840 ± 190 <LOD
Cafeteria in Milan	Plate Bowl Cup Food container w/lid	3 3 4 1	850 ± 210 620 ± 165 <LOD 550 ± 140
Cafeteria in Rome (3)	Bowl	1	410 ± 110
Cafeteria in Ferrara	Plate	1	2030 ± 710

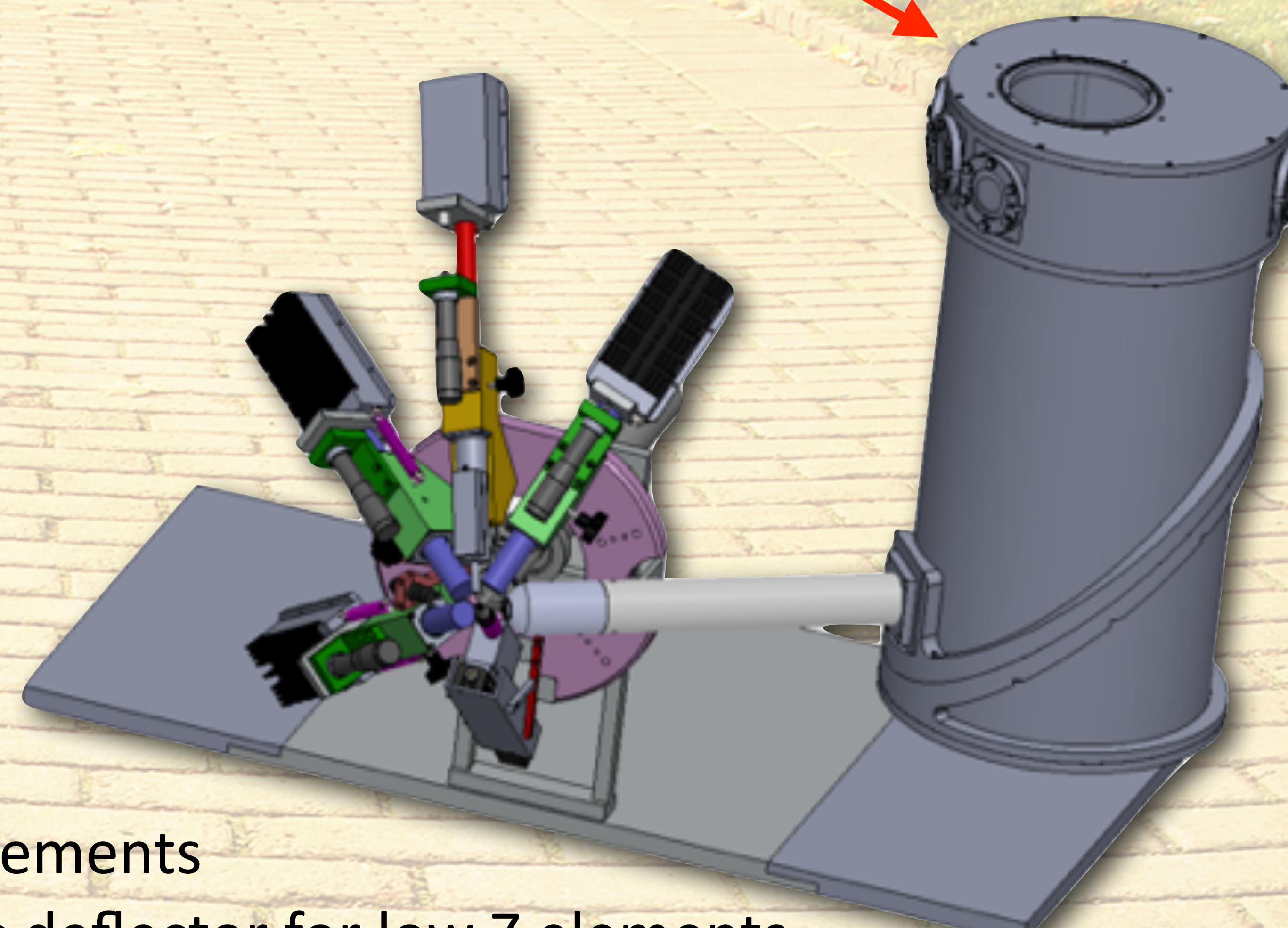
LOD were in the 200-300 ppm range, varying mainly with the beam intensity


Where advanced techniques
might lead ?

Where are they leading?

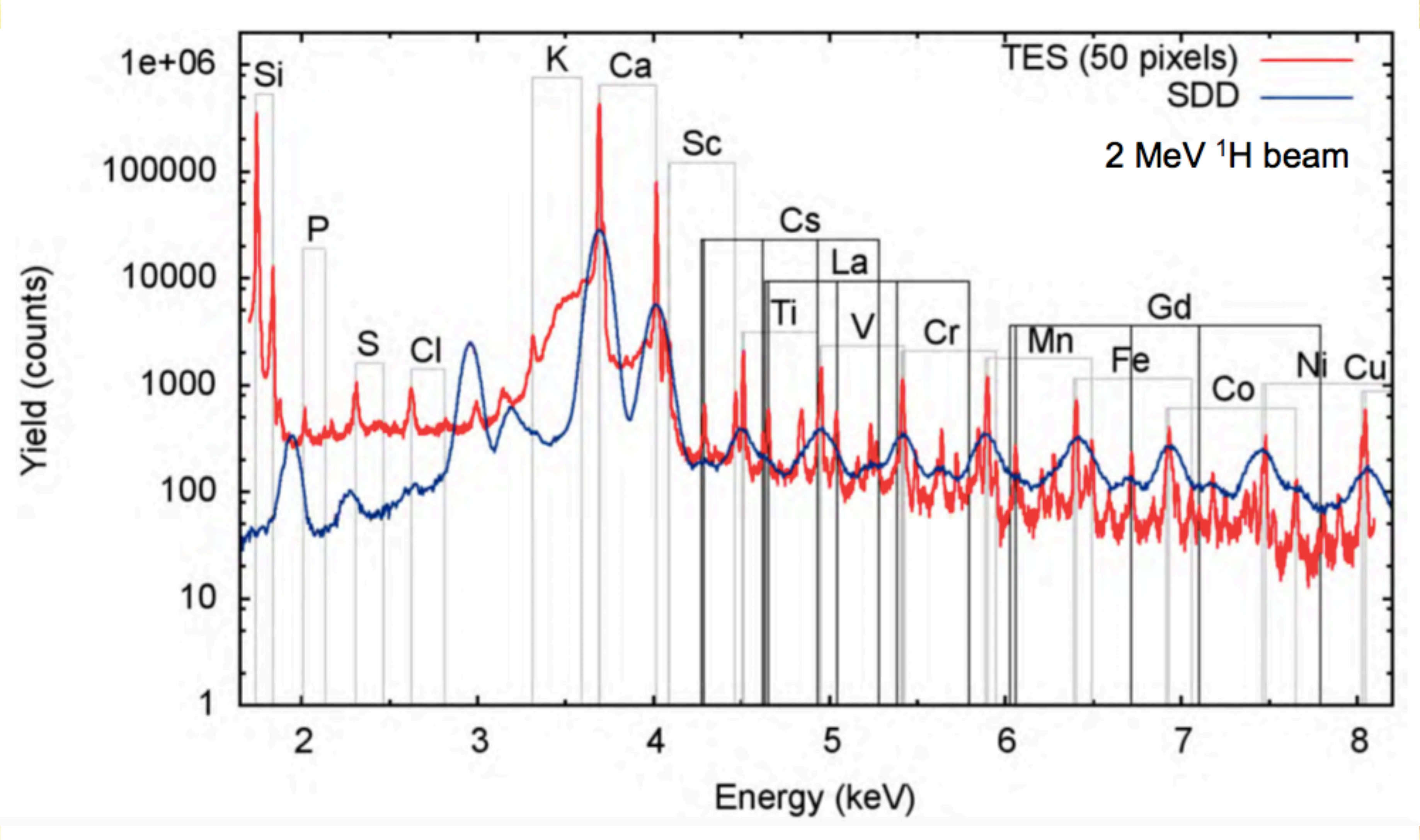
High-resolution PIXE spectrometer (TES) for chemical speciation from **AHEAD2020** EU H2020 project





- Four 80 mm^2 SDDs for medium-high Z elements
- Two 30 mm^2 SDDs with proton magnetic deflector for low Z elements
- Total subtended solid angle: 0.45 sr

They are leading to chemical speciation

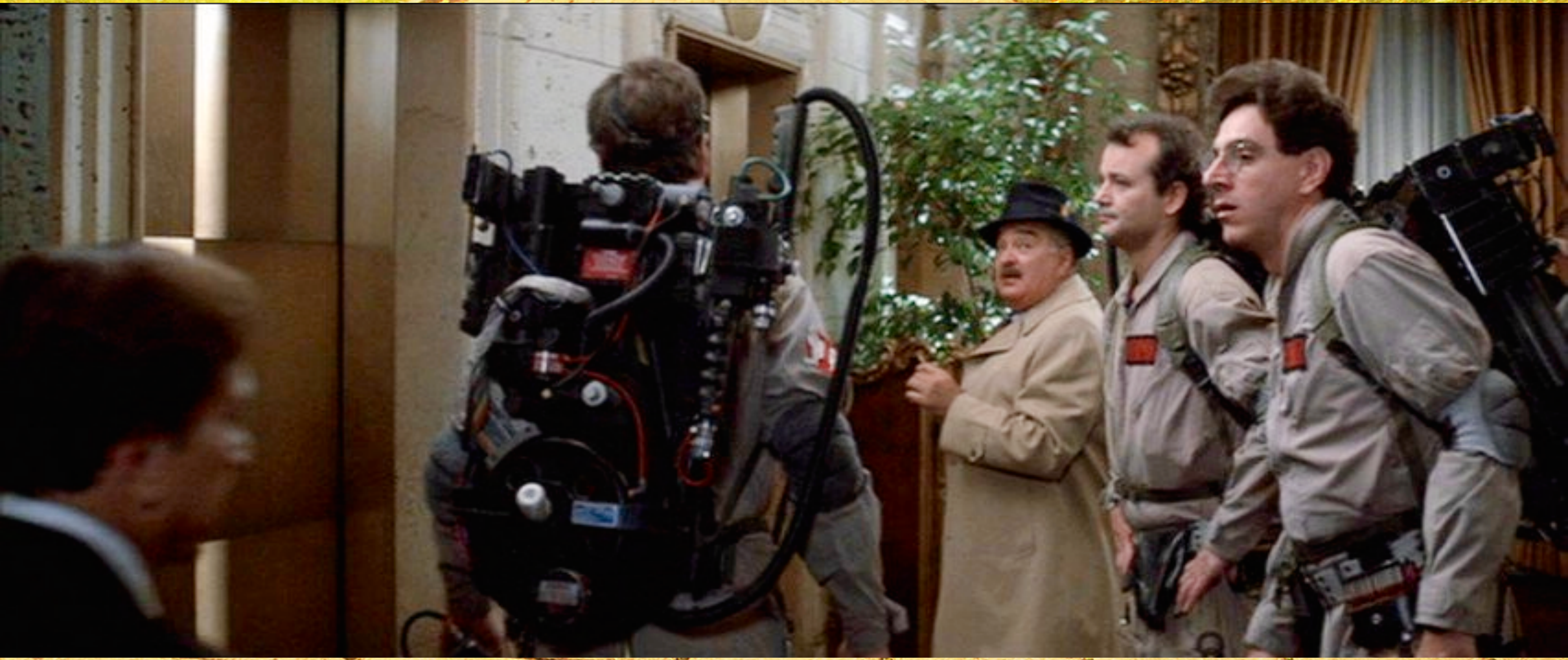


Comparison of PIXE measurements with 2 MeV protons on a glass reference standard with a TES detector and with a traditional Silicon Drift Detector (SDD)

Where are they leading?

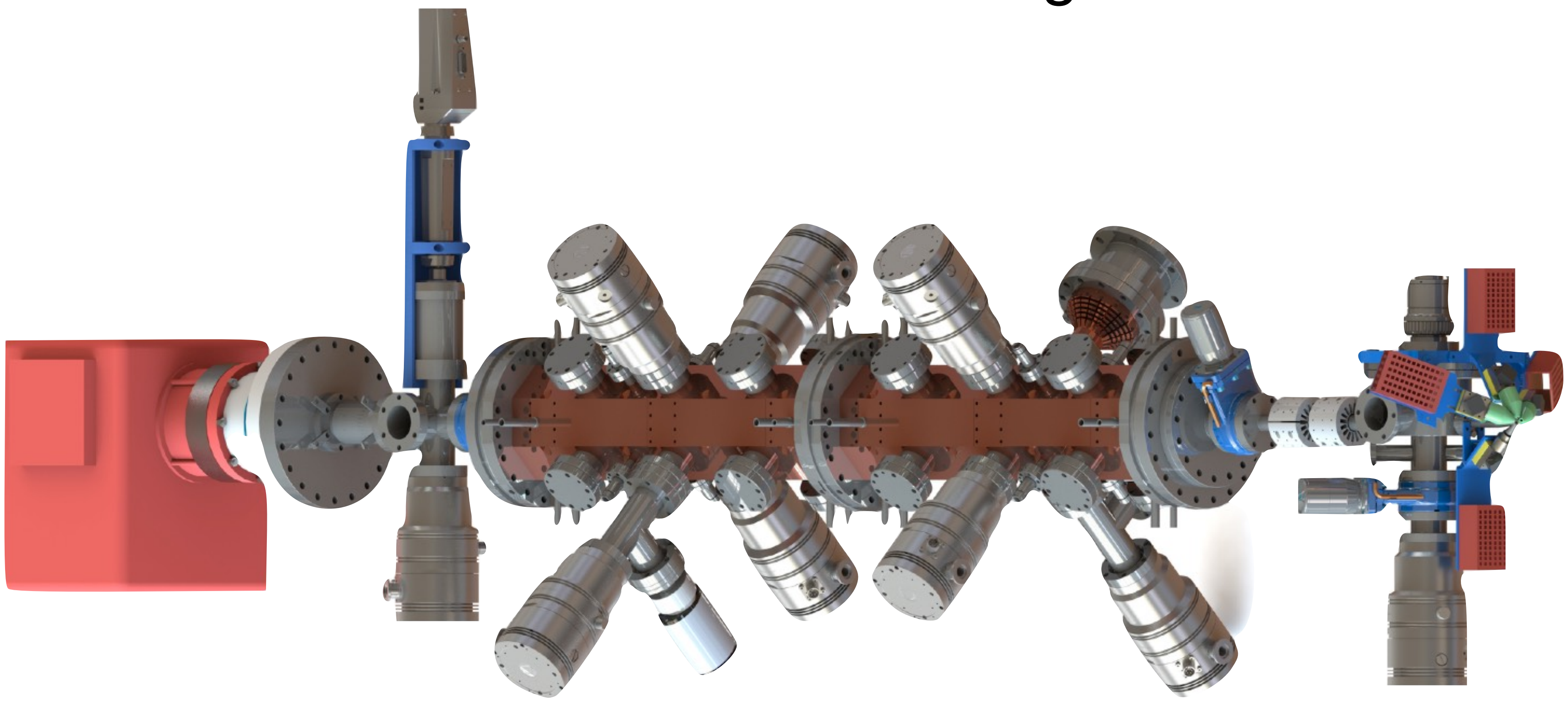
The development of **smaller transportable accelerators** would open new fields, in particular in those applications, as cultural heritage, where the vast majority of the world cultural heritage is immovable. The impact of laboratory based analytical techniques could diminish in the future with the advent of more and more performing ED-XRF systems for elemental analysis of cultural heritage objects

Could they lead to proton backpacks ?



They are leading to MACHINA…

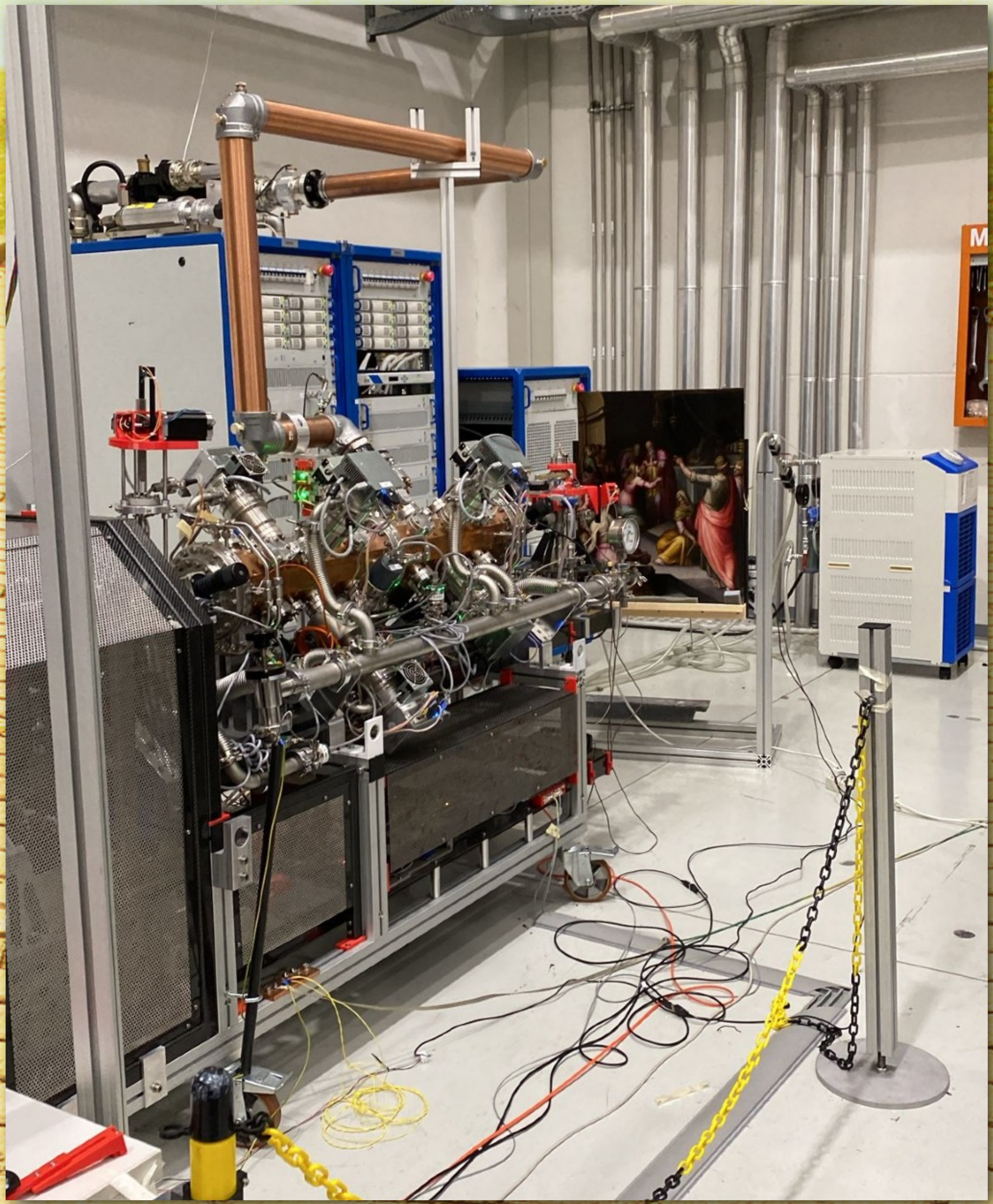
Movable Accelerator for Cultural Heritage In-situ non-Destructive Analysis



Istituto Nazionale di Fisica Nucleare

- 2 MeV proton PIXE RFQ
- Transportable (~200 kg)
- Low power consumption (few kW)
- Very small footprint (2.3 x 0.5 m^2 accelerator)
- Appealing for radiosafety (low energy proton beams)

Here it is MACHINA



Thanks for your attention!