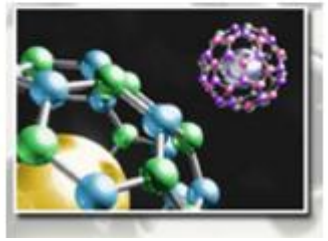
Scuola di Dottorato in Scienze della Natura e Tecnologie Innovative

Doctoral School of Sciences and Innovative Technologies

UNIVERSITÀ DEGLI STUDI DI TORINO

PHYSICS and ASTROPHYSICS



CHEMICAL and MATERIAL SCIENCES

Ion Beam Based Techniques for Materials Science

Teachers:
Paolo Olivero, Ettore Vittone
Physics Department, University of Torino
www.solid.unito.it

2 CFU : 8 h

Tuesday 2.5.2017, h. 16-18, Aula Verde, Physics Dept. - Ettore Vittone
Wednesday 3.5.2017, h. 16-18, Aula Wick, Physics Dept. - Ettore Vittone
Thursday 4.5.2017, h. 16-18, Aula D, Physics Dept. - Paolo Olivero
Friday 5.5.2017, h. 16-18, Aula Verde, Physics Dept. - Paolo Olivero

CAMPUSNET WEB SITE:
http://dott-scm.campusnet.unito.it/do/corsi.pl/Show?_id=j56m

Final exam:
Brief seminar (15 min) on a topic relevant to Ion Beam Based Techniques

IBA

Introduction

Instrumentation

- Accelerators
- Ion sources
- Detectors

Ion-Solid interaction

- Electronic energy loss
- Nuclear energy loss

IBA techniques

RBS	**Sample** (Ion,Ion) **Sample**	Structural/elemental analysis
ERDA	**Sample** (Ion,Ion') **Sample**	
PIXE	**Sample**(Ion, x ray) **Sample**	Structural analysis
IBIC	**Sample**(Ion, electron-hole) **Sample**	Functional analysis

IBA

Instrumentation

Accelerators

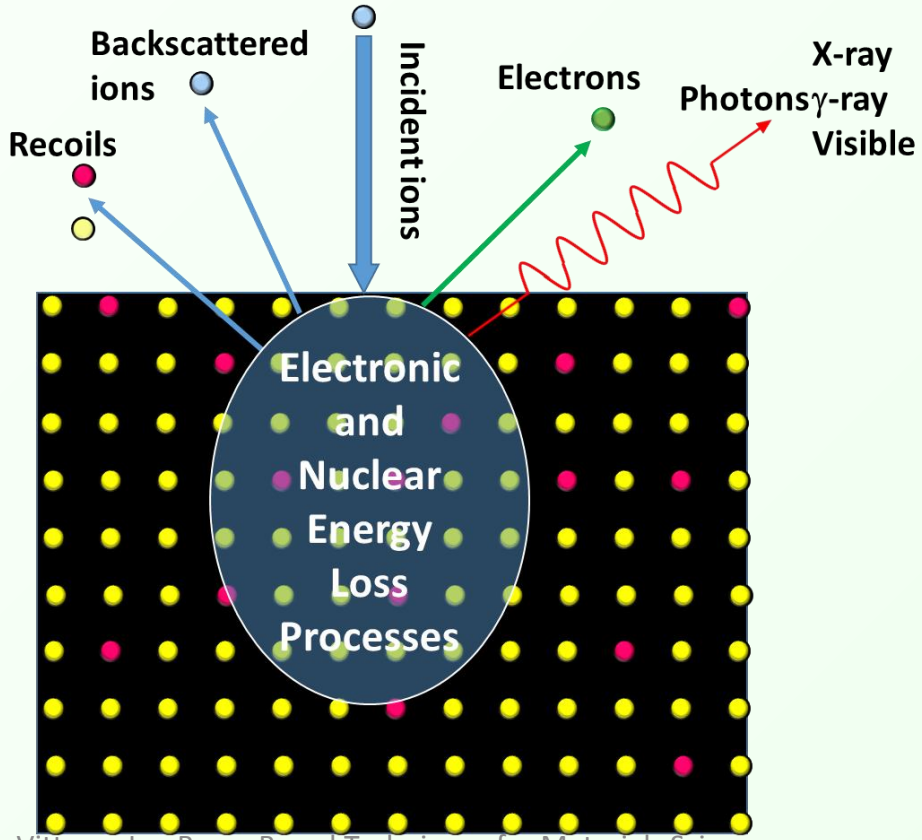
Ion sources

Detectors

Ion-Solid interaction

Electronic energy loss

Nuclear energy loss



IBA techniques

Compositional analysis

Structural analysis

Functional analysis

IBA

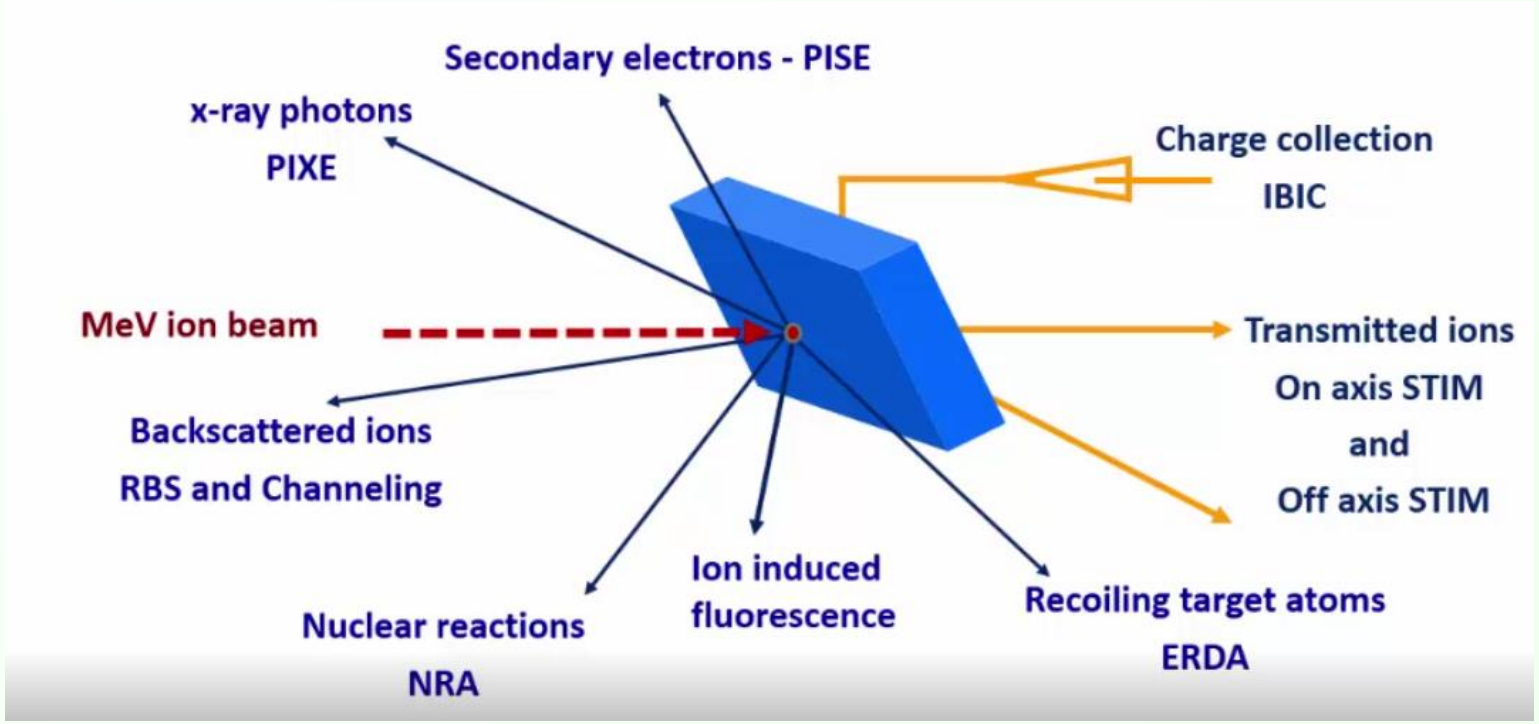
Instrumentation

- **Accelerators**
- **Ion sources**
- **Detectors**

Ion-Solid interaction

- **Electronic energy loss**
- **Nuclear energy loss**

IBA techniques



- **Compositional analysis**
- **Structural analysis**
- **Functional analysis**

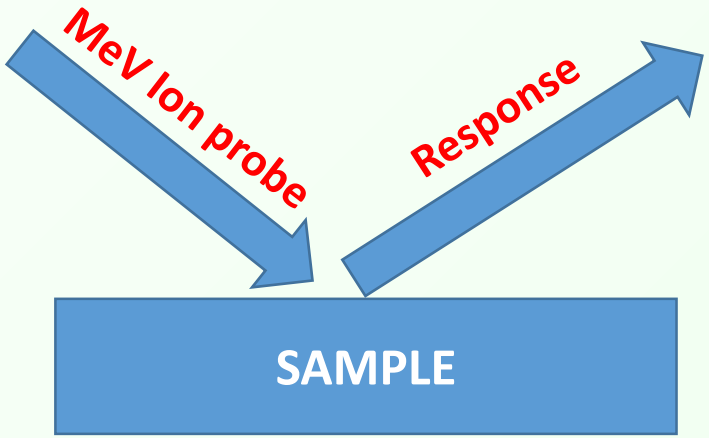
IBA

Ion Beam Analysis Techniques - IBA

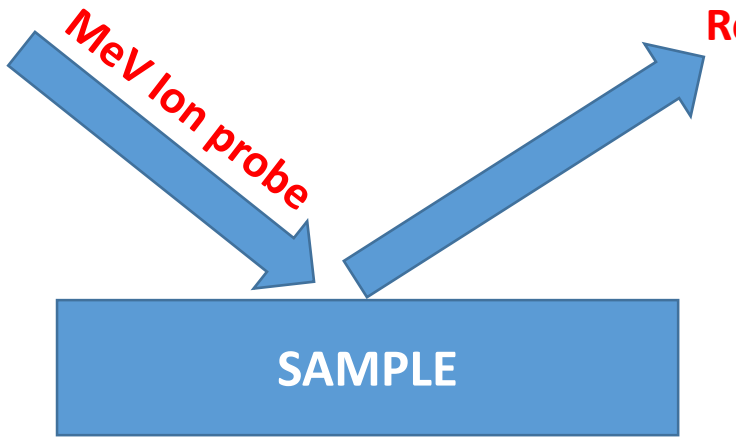
Main Features

- ✓ Quantitative multi-elemental analysis
- ✓ High sensitivity (1-100 ppm in at/cm^3)
- ✓ Depth profiling (1-10^4 nm)
- ✓ No invasive analysis
- ✓ No sample preparation
- ✓ Micro-spectroscopy (resolution μm)

- ✓ Compositional analysis
- ✓ Structural analysis
- ✓ Functional analysis (electronic devices)



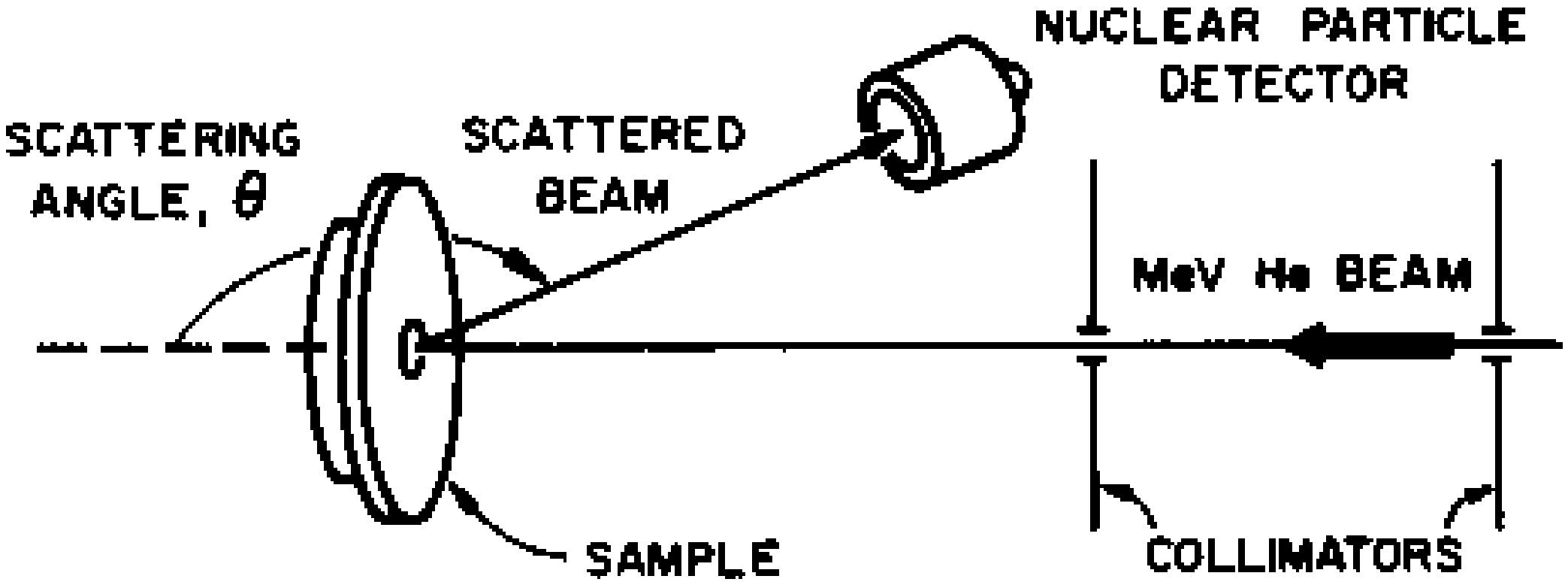
IBA-RBS



Rutherford Backscattering Spectrometry (RBS)

- RBS is an ion scattering technique that is used for the surface layer analysis of solids.
- A target is bombarded with ions at an energy in the MeV-range (0.5 – 4 MeV)
- The energy of the backscattered projectiles is recorded with an energy sensitive detector, typically a solid state detector.
- RBS allows the quantitative determination of the composition of a material and depth profiling of individual elements.
- quantitative without the need for reference samples,
- nondestructive,
- has a good depth resolution of the order of several nm,
- and a very good sensitivity for heavy elements of the order of parts-per-million (ppm).

IBA-RBS


NUCLEAR PARTICLE
DETECTOR
SCATTERING
ANGLE, θ
SCATTERED
BEAM
MeV He BEAM
SAMPLE
COLLIMATORS

IBA-RBS

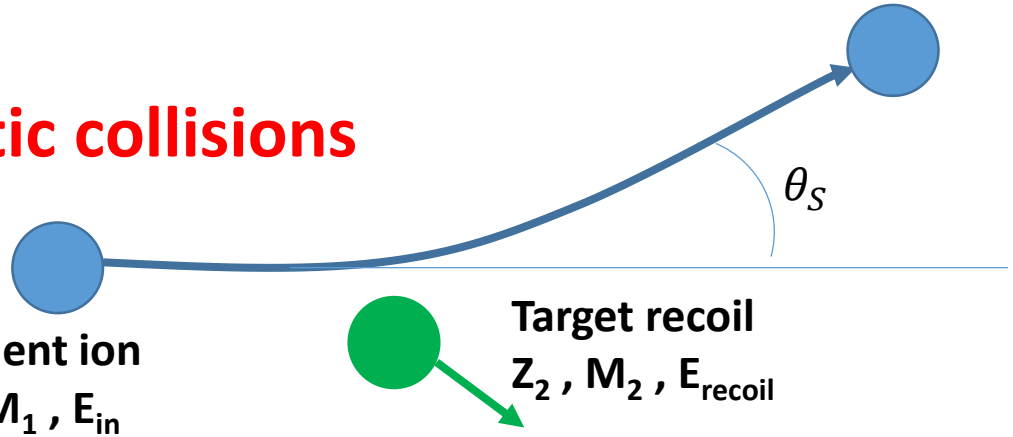
Classical Scattering theory

Fraction of the ion energy which remains with the ion after the collision; $E_{out} = E_{in} \cdot K(\theta_S)$

Kinematic factor $K(\theta_S)$; θ_S scattering angle.

Energy of the recoil nucleus: $E_{recoil}=(1-K(\theta_S)) \cdot E_{in}$

Elastic collisions



TARGET MASS DISCRIMINATION

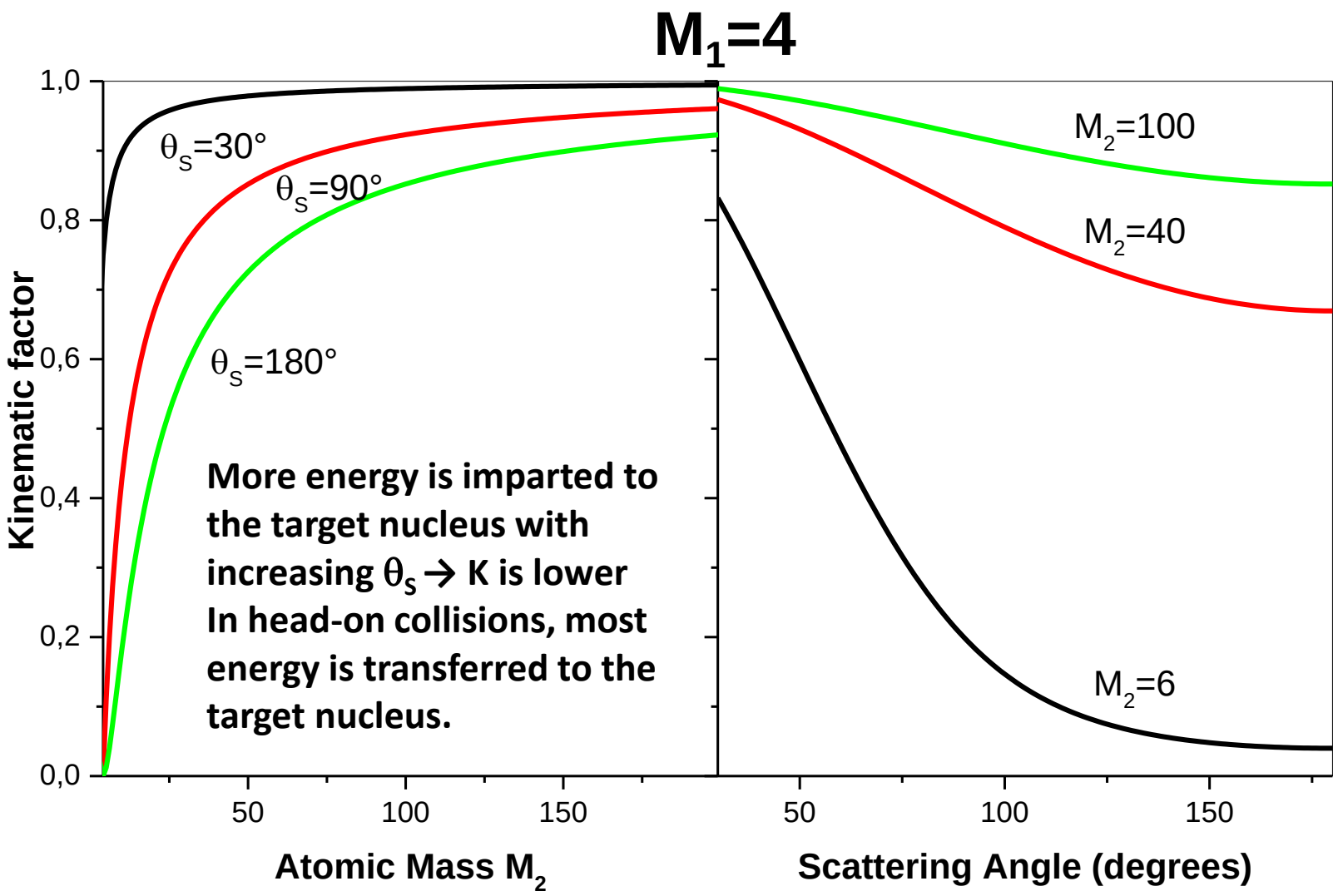
From the conservation of energy and momentum, in non-relativistic form and in the laboratory reference frame:

$$K(\theta_S) = \frac{E_{out}}{E_{in}} = \left\{ \frac{\sqrt{1 - \left(\frac{M_1}{M_2}\right)^2 \cdot \sin^2(\theta_S)} + \left(\frac{M_1}{M_2}\right) \cdot \cos(\theta_S)}{1 + \frac{M_1}{M_2}} \right\}^2$$

$K(\theta_S)$ depends only on the scattering angle and the ratio of masses of the ion and the atomic nucleus.

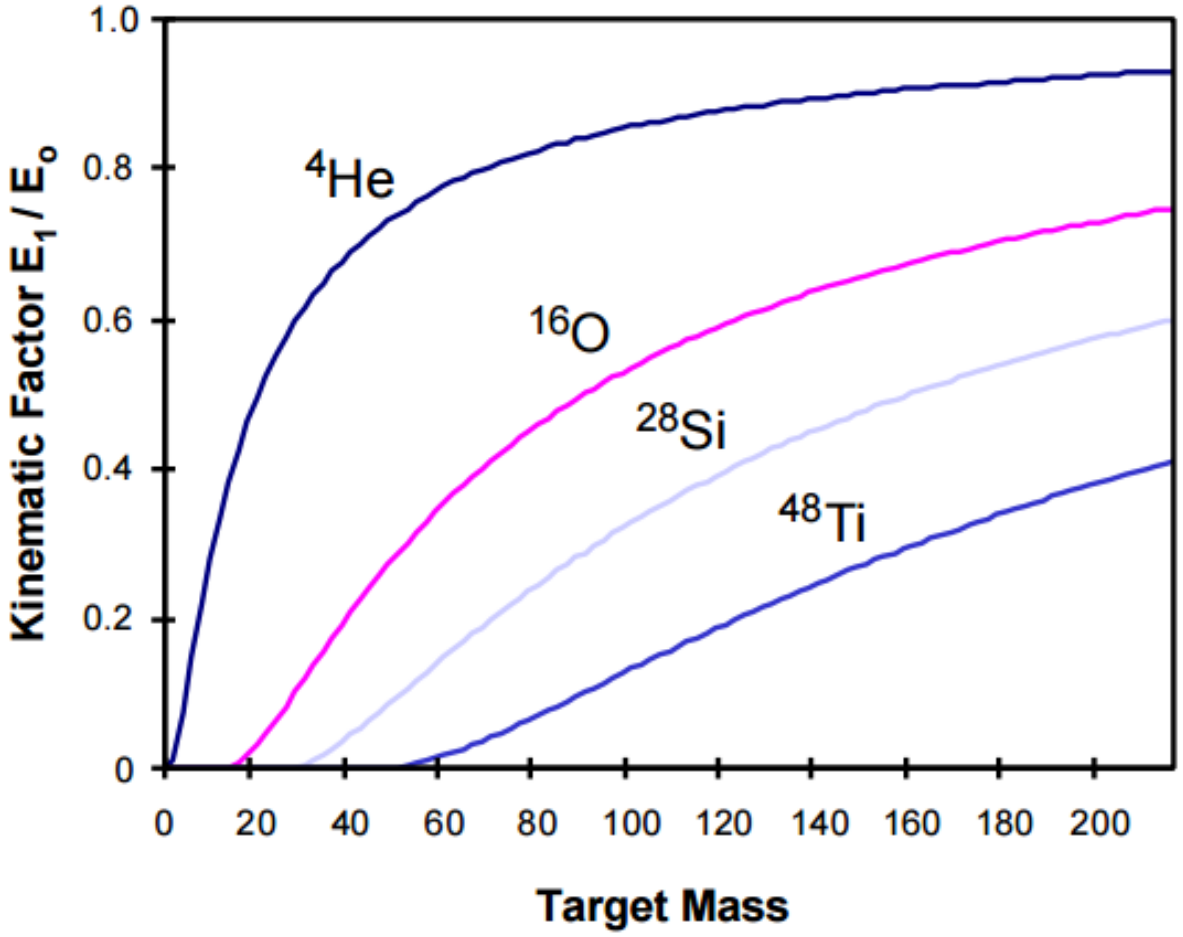
It does not depend on the ion energy

IBA-RBS



TARGET MASS DISCRIMINATION

θ_s=180°



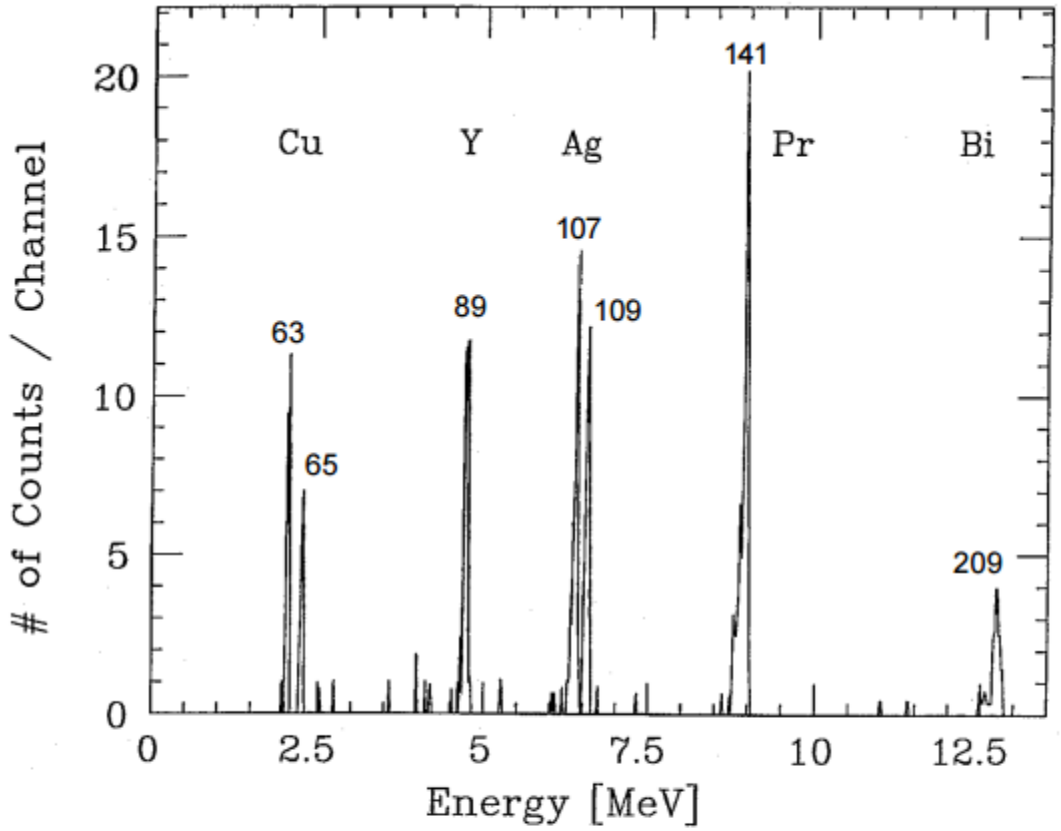
Kinematic factor as a function of Target Mass for a number of projectile types

TARGET MASS DISCRIMINATION

IBA-RBS

The signal from an atom at the sample surface will appear in the energy spectrum at a position $E_{out}=K\cdot E_{in}$

TARGET MASS DISCRIMINATION



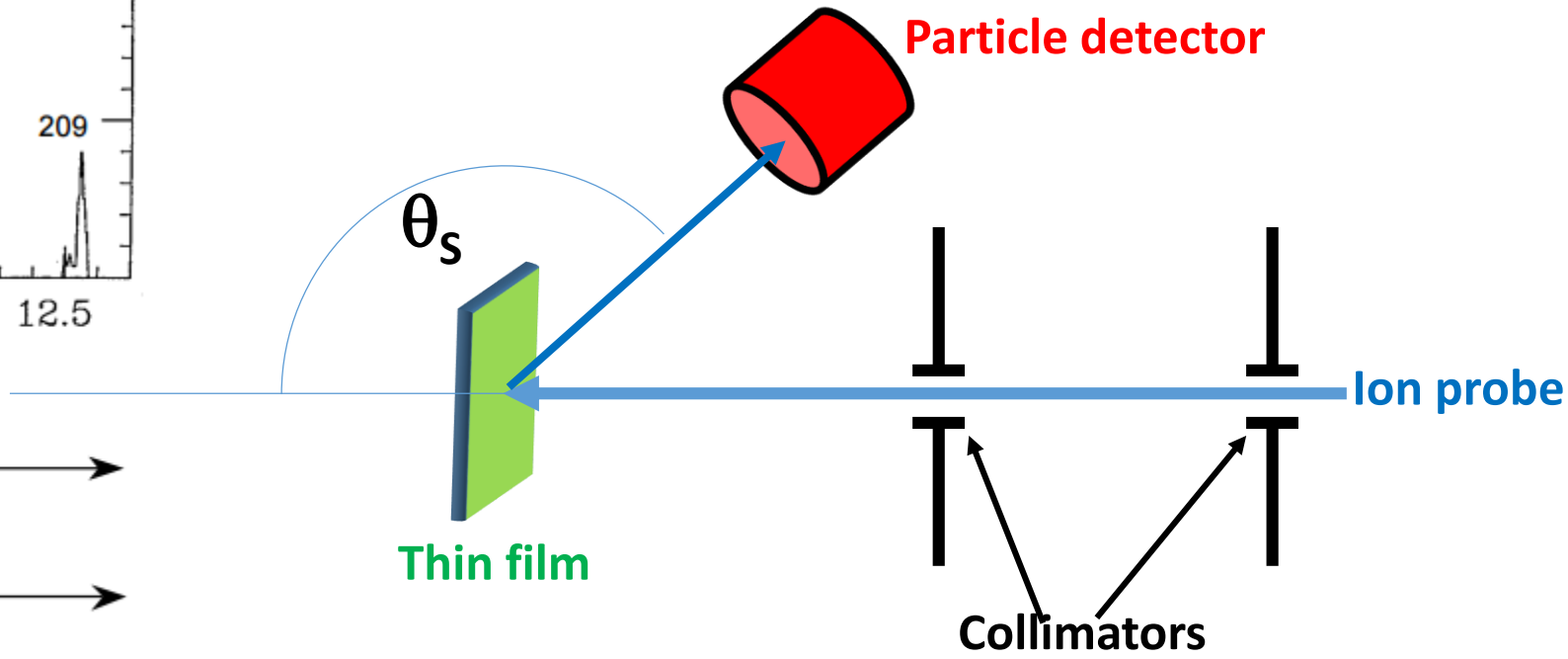
kinematic factor

mass scale!

Ion probe:^{35}Cl

Target: thin layer of Cu, Y, Ag, Pr, Bi

Isotopes of Cu and Ag are resolved



IBA-RBS

DEPTH SCALE

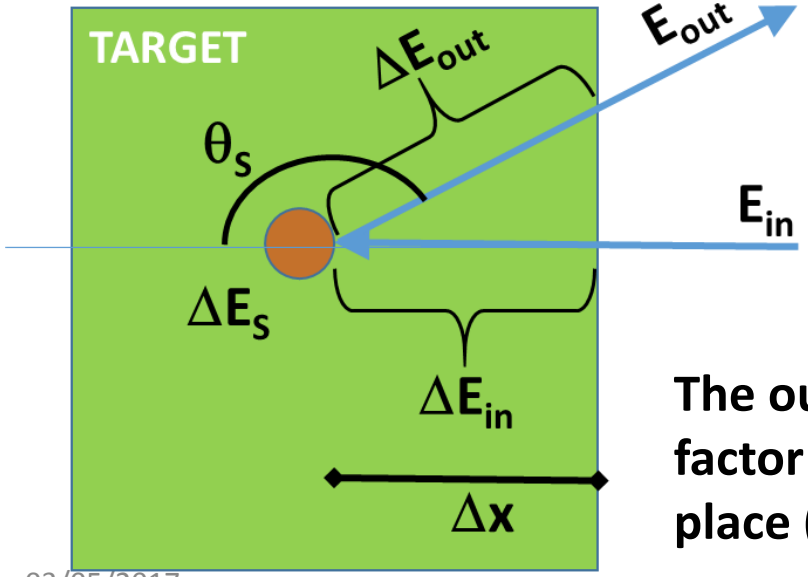
The signal from atoms of the same mass below the sample surface will be shifted by the amount of energy lost while the projectiles pass through the sample, both before ΔE_{in} and after ΔE_{out} collision

$$Entry\ ion\ energy = E_{in}$$

$$Energy\ loss\ before\ scattering = \Delta E_{in} = \left(\frac{dE}{dx}\right)_{in} \cdot \Delta x \Rightarrow Energy\ before\ scattering = E_x = E_{in} - \left(\frac{dE}{dx}\right) \cdot \Delta x$$

$$Kinematic\ loss = \Delta E_S = (1 - K) \cdot E_x \Rightarrow Energy\ after\ scattering = K \cdot E_x$$

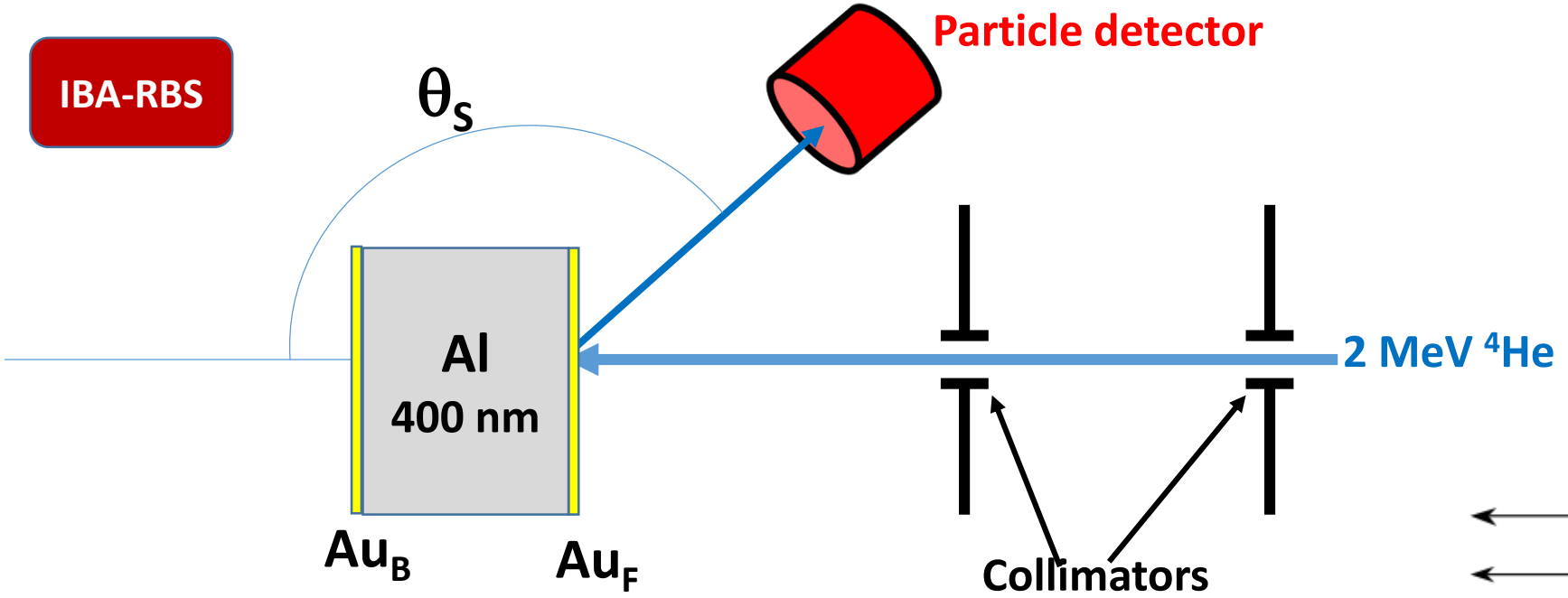
$$Energy\ loss\ after\ scattering = E_{out} = \left(\frac{dE}{dx}\right)_{out} \cdot \frac{\Delta x}{\cos(\vartheta_S)} \Rightarrow Output\ energy = E_{out} = K \cdot E_x - \left(\frac{dE}{dx}\right)_S \cdot \frac{\Delta x}{\cos(\vartheta_S)}$$

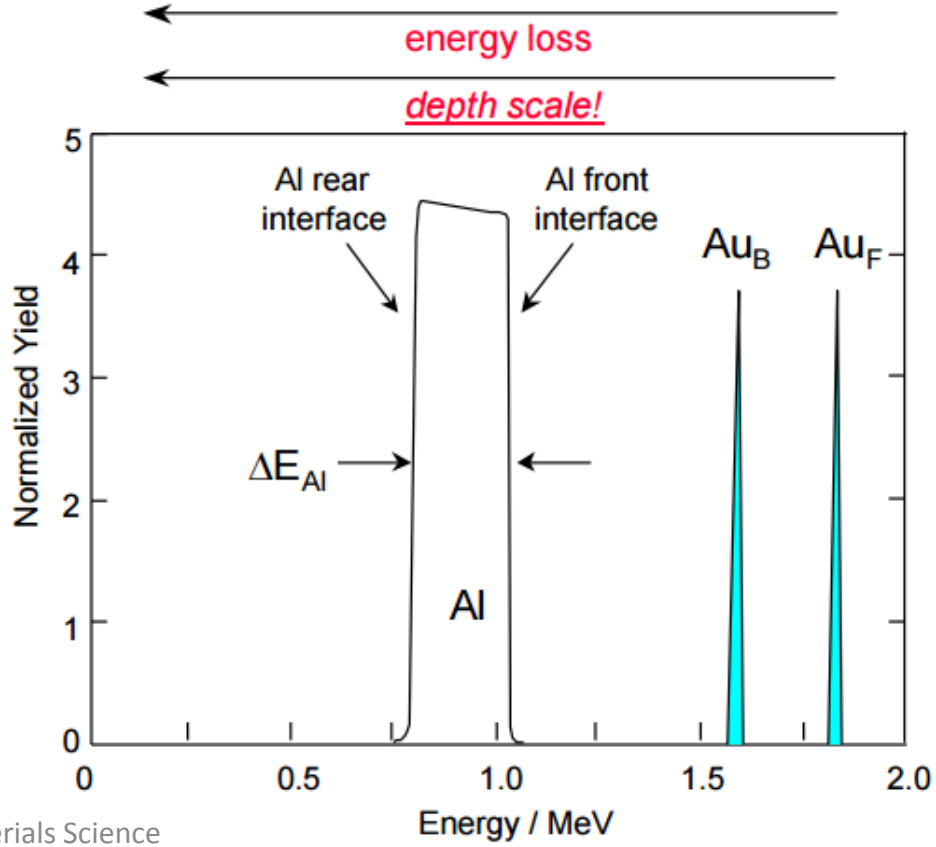


$$E_{out} = K \cdot E_{in} - \left[K \cdot \left(\frac{dE}{dx}\right) + \frac{\left(\frac{dE}{dx}\right)_S}{\cos(\vartheta_S)}\right] \cdot \Delta x$$

The output energy depends on the nuclear scattering through the kinematic factor K (Mass Discrimination) and on the depth at which the scattering took place (Depth Profile).

IBA-RBS

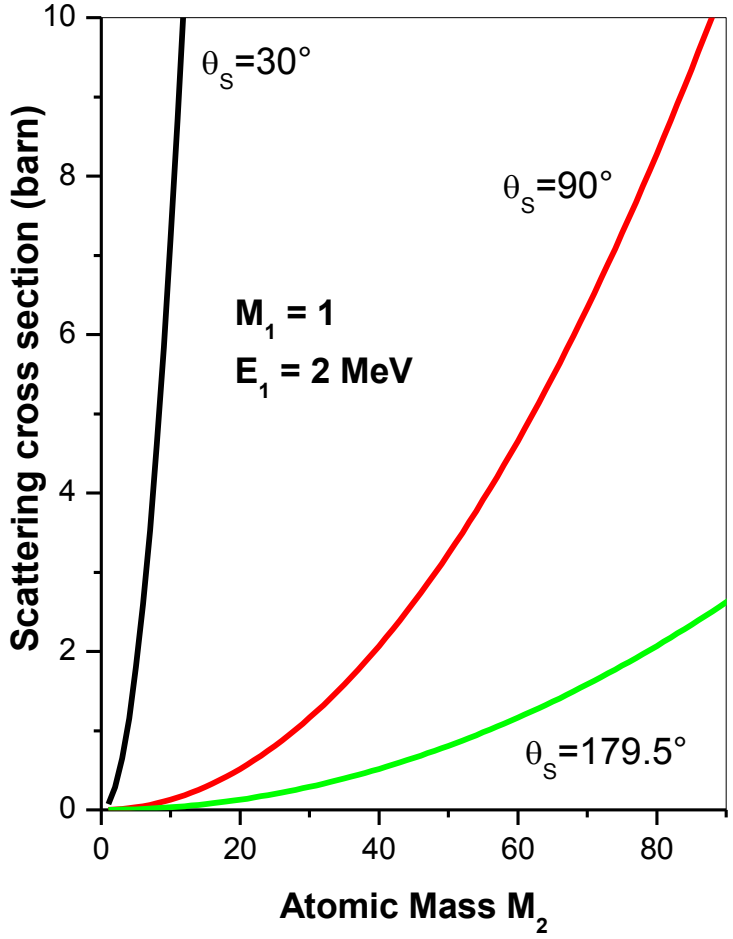

Particle detector
θS
Al
400 nm
AuB
AuF
2 MeV 4He
Collimators

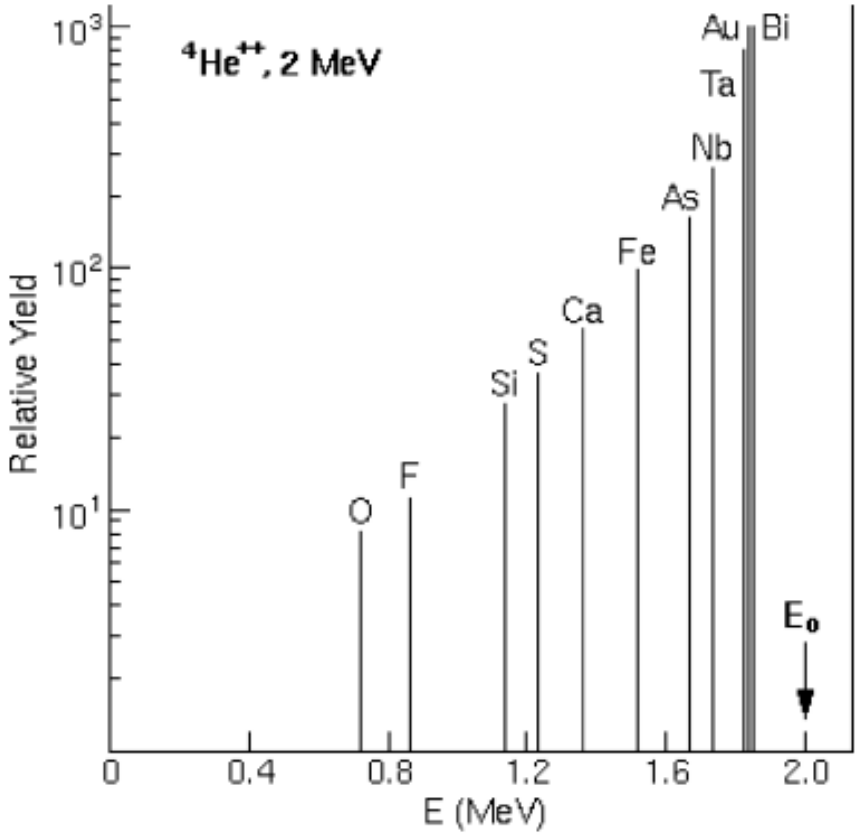

energy loss
depth scale!
Al rear interface
Al front interface
AuB
AuF
ΔEAl
Al
Normalized Yield
Energy / MeV
0
1
2
3
4
5
0
0.5
1.0
1.5
2.0

Scattering cross section

The yield of scattered particle is calculated using the differential scattering cross section which is given by Rutherford's formula:

$$\sigma(\theta_S) = \left[\frac{e^2}{4 \cdot \epsilon_0} \cdot \frac{Z_1 \cdot Z_2}{4 \cdot E_{in}}\right]^2 \cdot \left\{\frac{1}{\sin^4\left(\frac{\theta_s}{2}\right)} - 2\left(\frac{M_1}{M_2}\right)^2\right\}$$

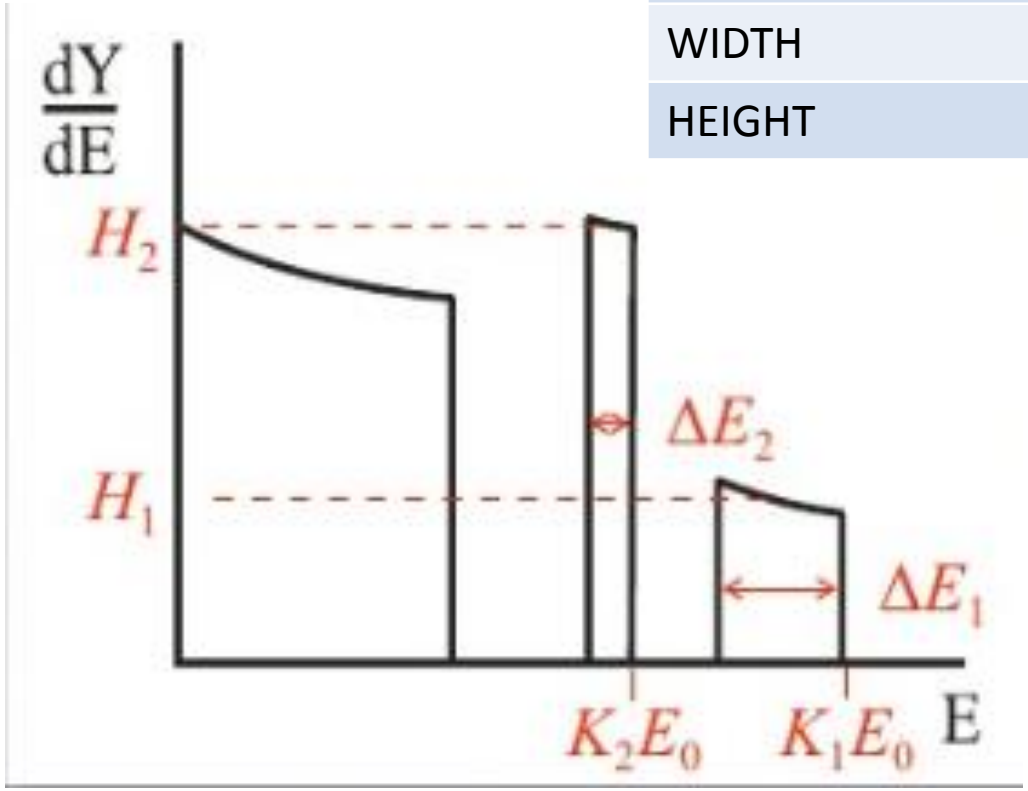




Scattering Yield as a function of the target atomic number

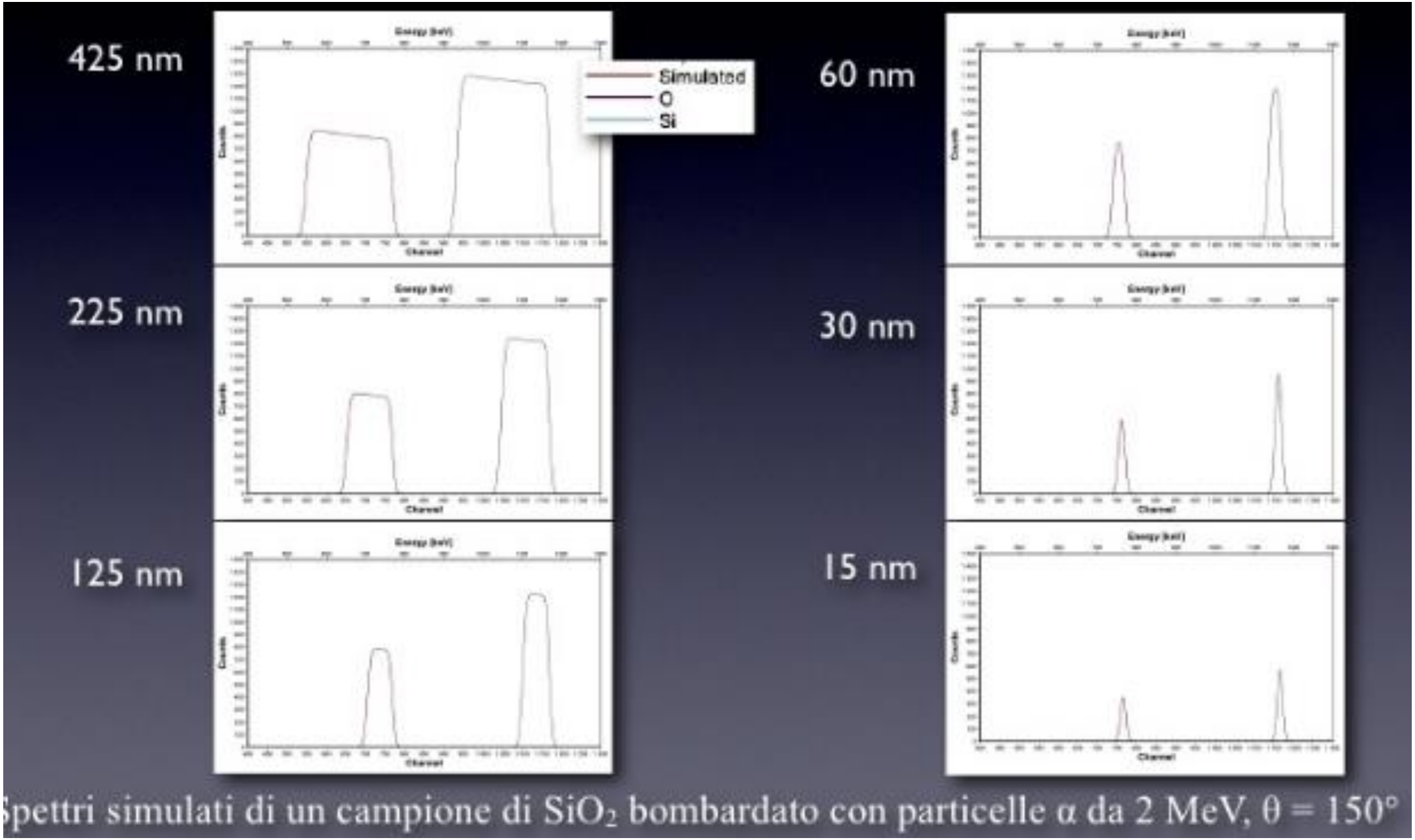
IBA-RBS

SEGNALE	INFORMAZIONE	
POSITION	MASS	Kinemati factor
WIDTH	THICKNESS/DEPTH	Stopping Power
HEIGHT	QUANTITY	Cross Section



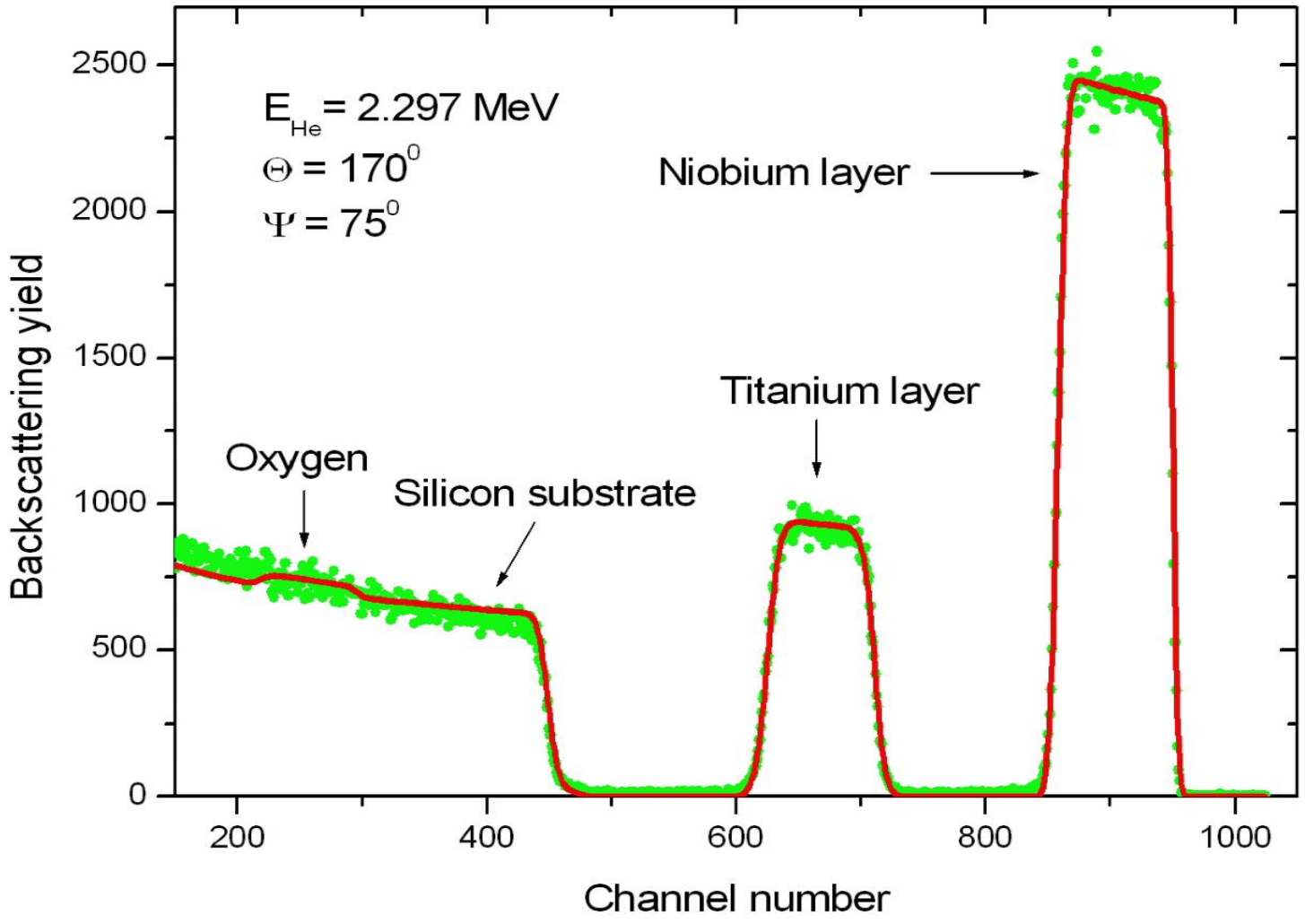
www.slideshare.net/max0068/chiari-lezione-su-rutherford-backscattering-spectrometry-rsb-2012

IBA-RBS

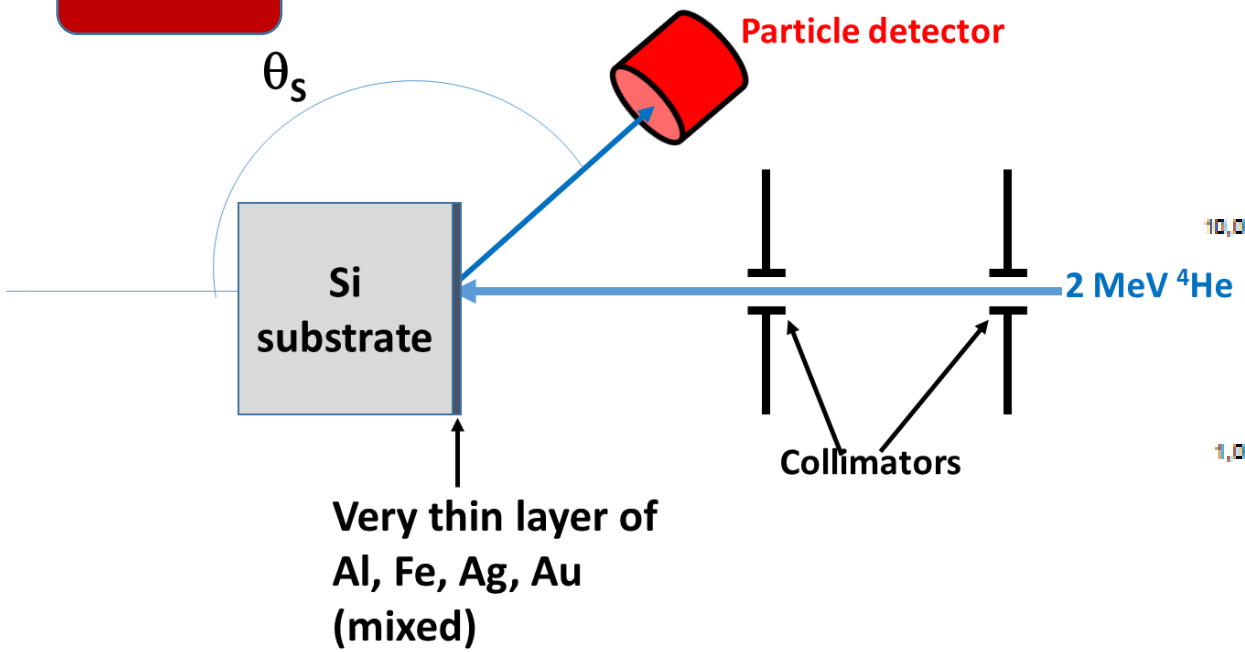


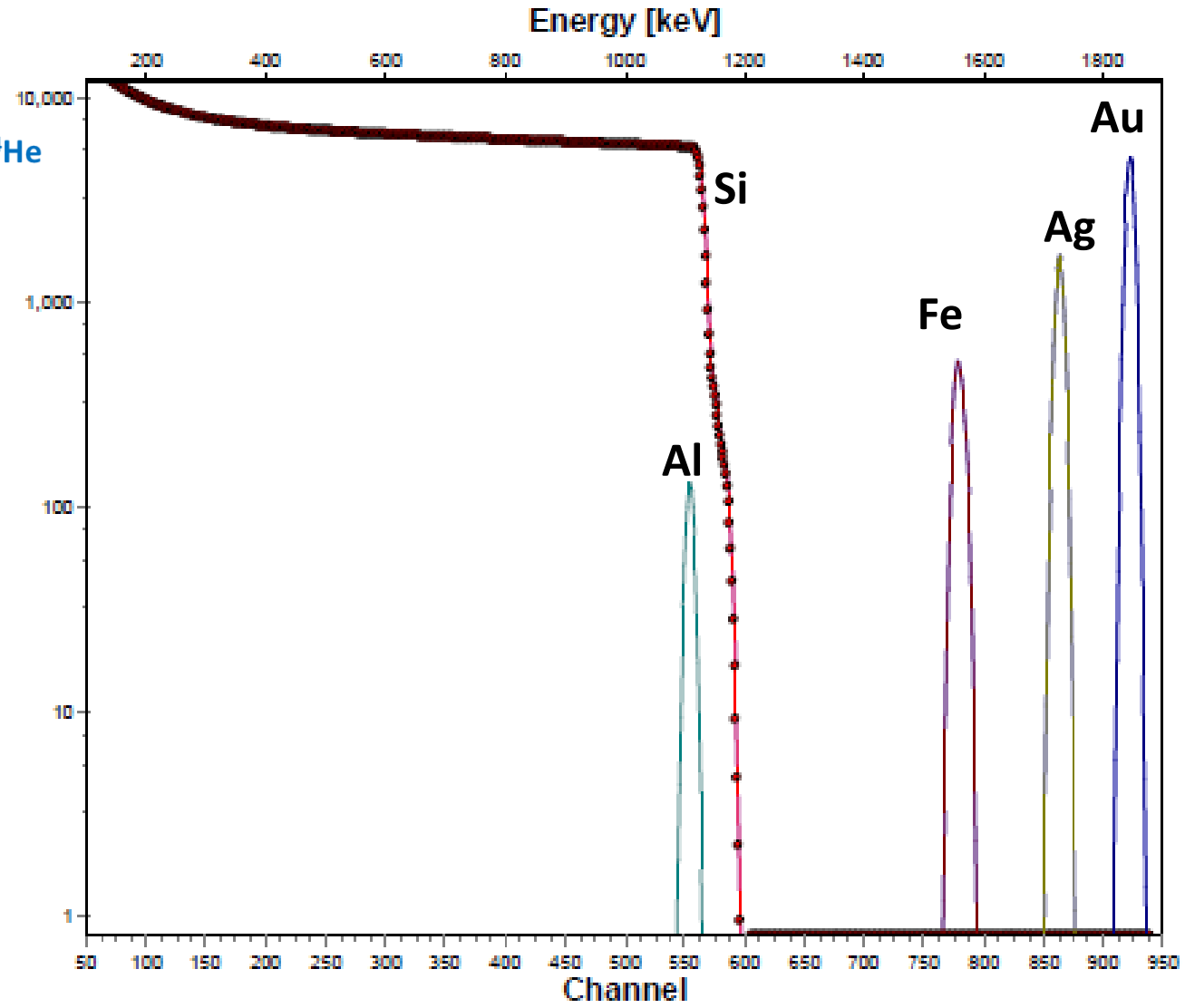
Spettri simulati di un campione di SiO_2 bombardato con particelle α da 2 MeV, θ = 150°

IBA-RBS


E_{He} = 2.297 MeV
Θ = 170°
Ψ = 75°
Niobium layer
Titanium layer
Oxygen
Silicon substrate
Backscattering yield
Channel number
2500
2000
1500
1000
500
0
200
400
600
800
1000

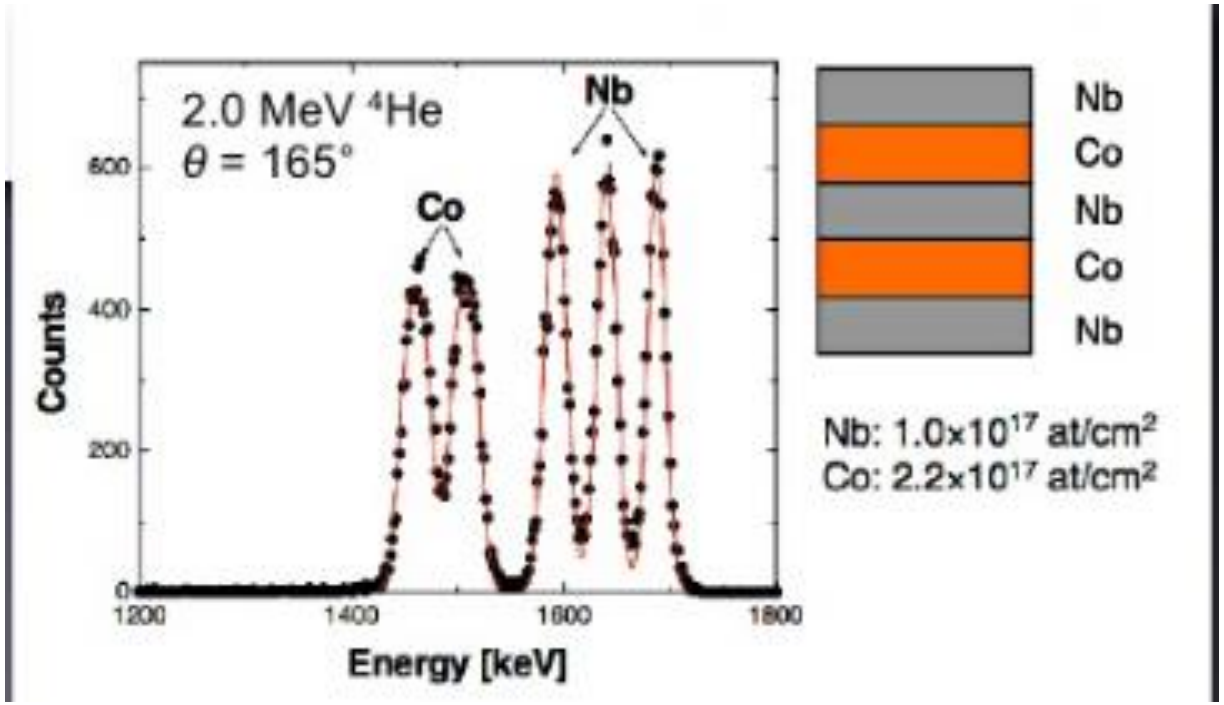
IBA-RBS





Bad choice of the substrate

IBA-RBS

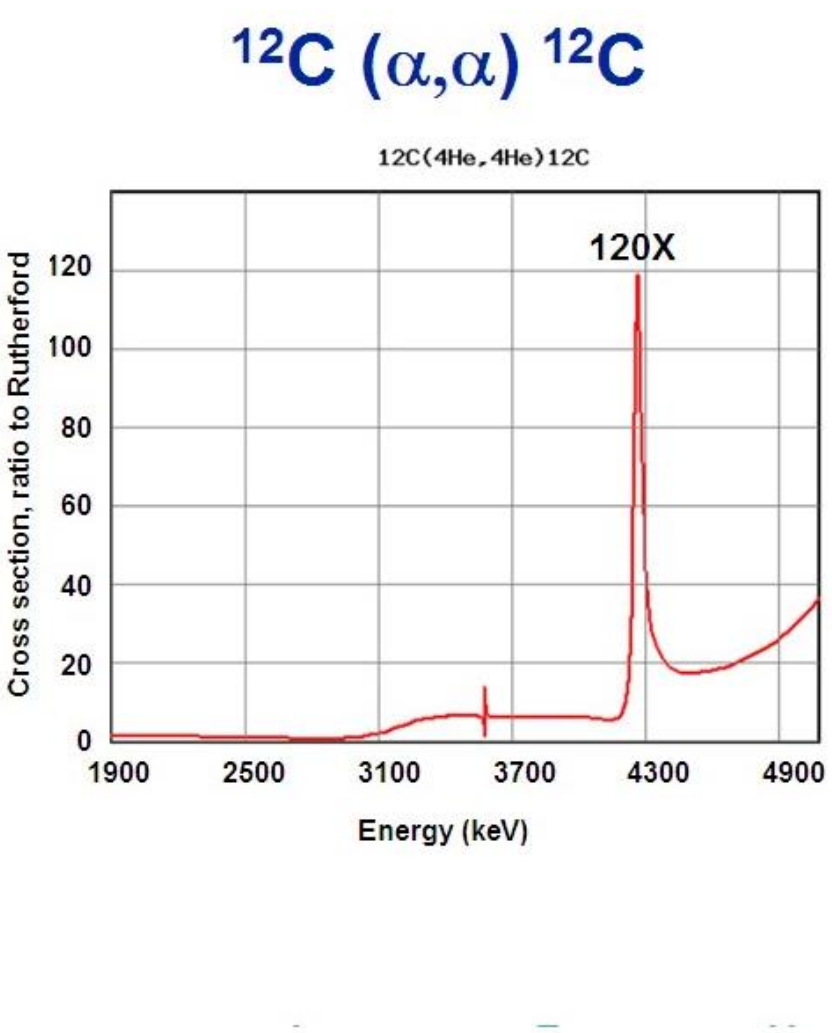

2.0 MeV ⁴He
θ = 165°
Nb
Co
Counts
600
400
200
0
1200
1400
1600
1800
Energy [keV]
Nb
Co
Nb
Co
Nb
Nb: 1.0×10¹⁷ at/cm²
Co: 2.2×10¹⁷ at/cm²

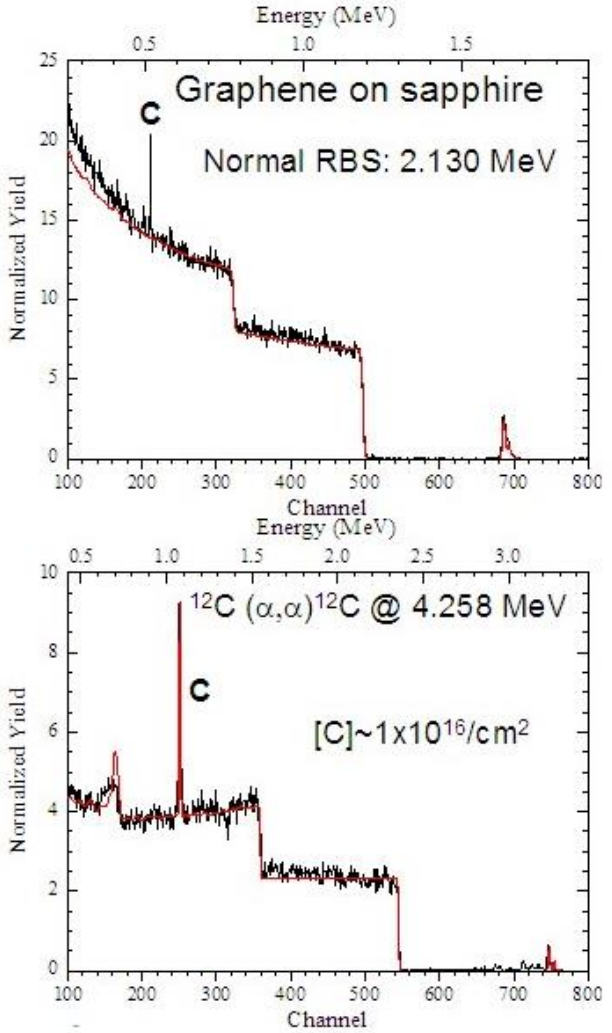
IBA-RBS

Non Rutherford Cross Section

When the collision diameter is very small and becomes comparable to the sum of the nuclear radii of the projectile and the target atom, the finite sizes of the nuclei and the nuclear force interactions lead to **deviations from the Rutherford scattering cross section**.

For MeV ion beams, this phenomenon can be observed in low Z projectile/target system where the Coulomb barrier is small.





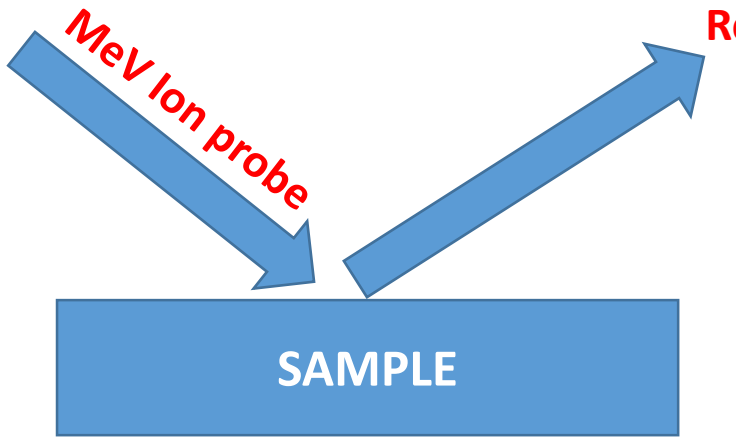
IBA-RBS

Main features of RBS

Elements	Be - U
Standard Conditions	2 Mev ^{4}He beam Silicon detector 10 minutes per sample
Precision	Stoichiometry: < 1% relative Thickness: < 5%
Sensitivity	Bulk: % to 10^{-4} , depending on Z Surface: 1 to 10^{-4} Monolayers
Depth Resolution	1 to 10 nm
Data analysis	e.g. by RUMP software: http://www.genplot.com/
Remarks	Accessible depth range ~ 1μm No light elements detectable on heavy substrates

http://cas.web.cern.ch/cas/Pruhonice/PDF/Doebeli.pdf

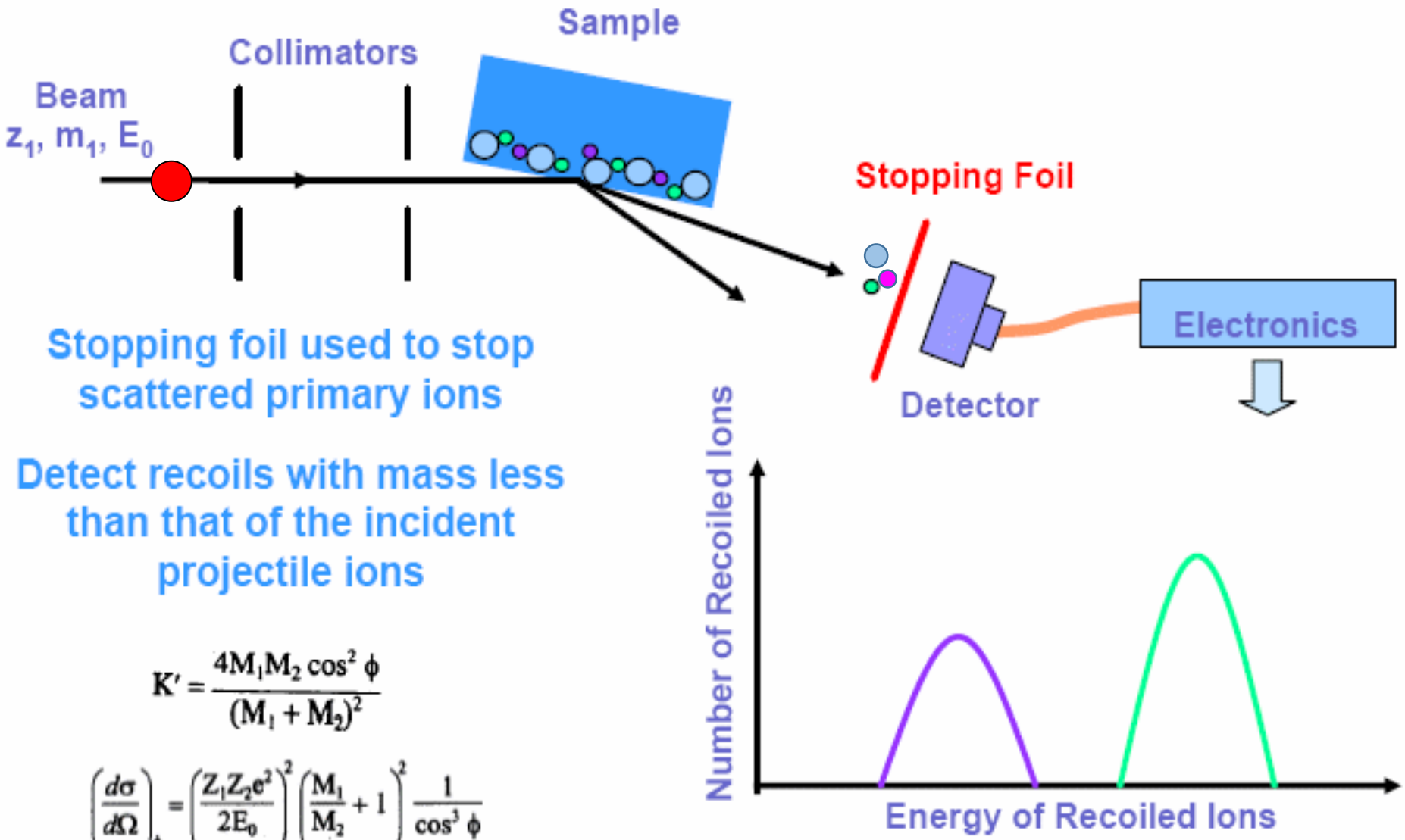
IBA-ERD



Elastic Recoil Detection Analysis

If light elements in heavy substrates or elements lighter than the incident beam particles have to be analysed (e.g. hydrogen profiling) the recoiling target atoms can be detected in a grazing angle geometry

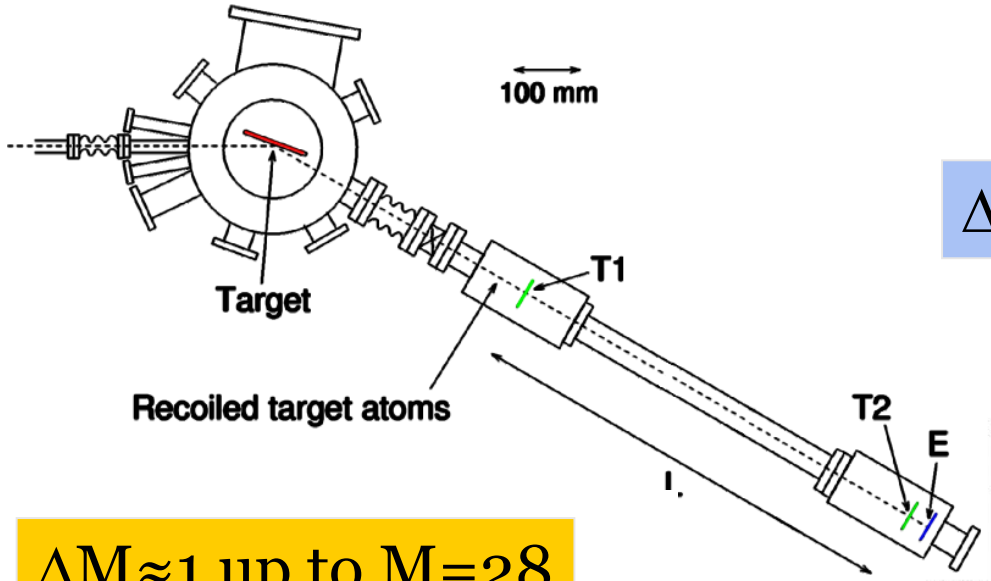
IBA-ERD



Iva Bogranovic, NIS Colloquium, Torino, 22 December, 2008

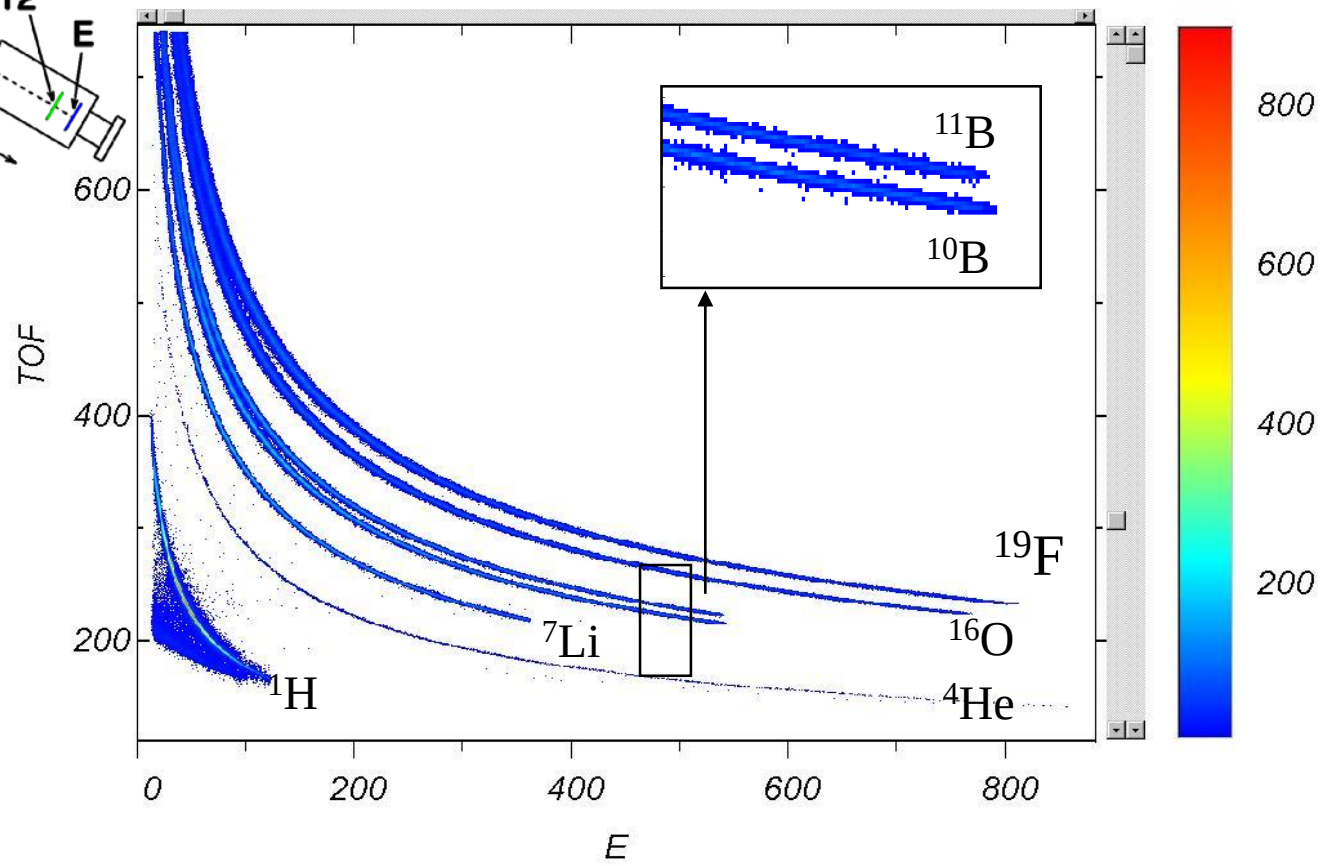
IBA-ERD

Time-of-flight ERDA



$$\Delta T = T_2 - T_1 = L(M_2/2E_r)^{1/2}$$

$\Delta M \approx 1$ up to M=28

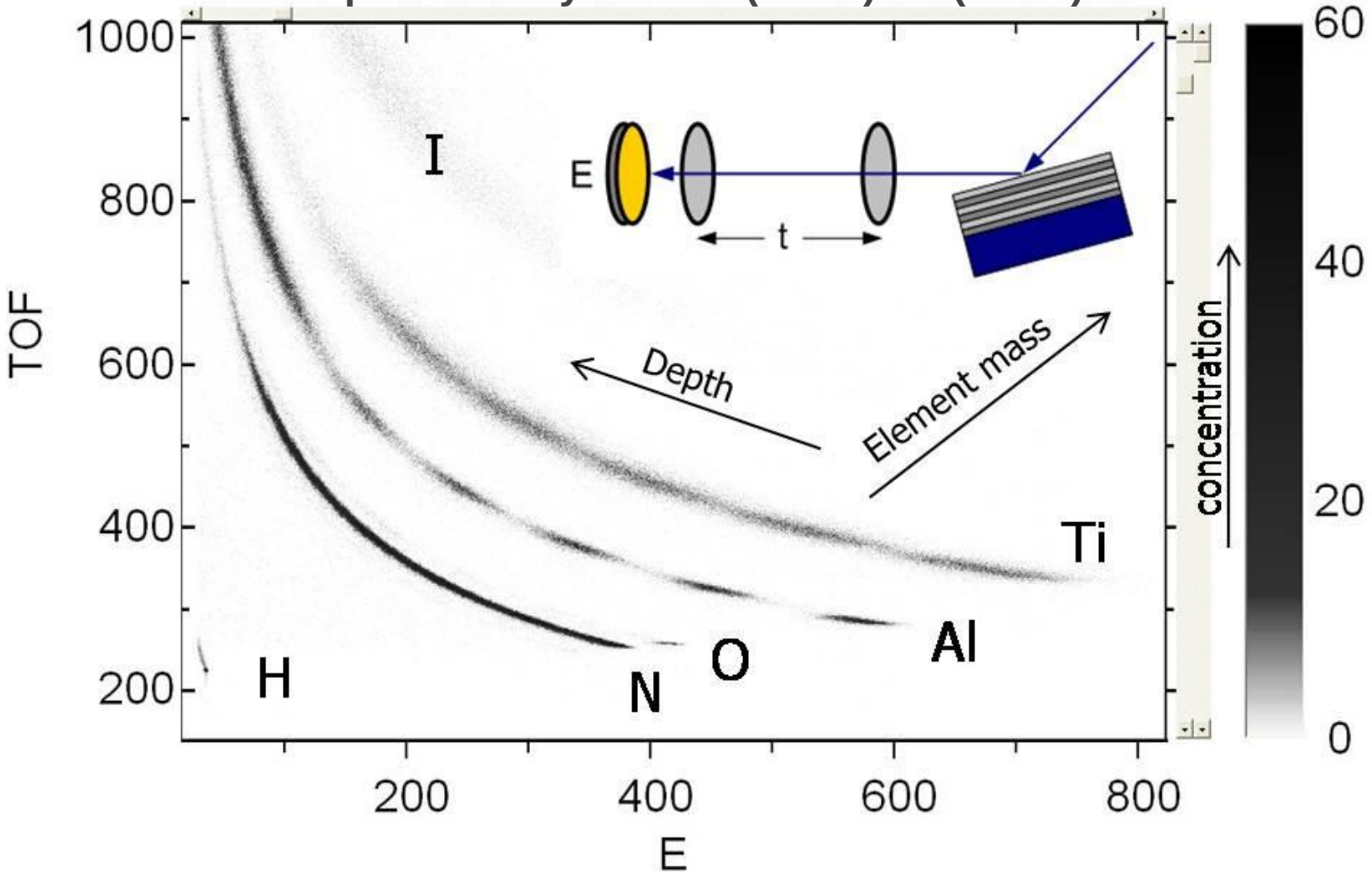


Overlapped TOF – ERDA coincidence maps: ^{1}H, ^{4}He, ^{7}Li, ^{10}B, ^{11}B, ^{16}O and ^{19}F ions elastically scattered from the thick Au target.

IBA-ERD

Ruđer Bošković Institute

TOF-E map of multilayered AlN(20nm)/TiN(40nm) film



http://www.irb.hr/eng/Research/Divisions/Division-of-Experimental-Physics/Laboratory-for-ion-beam-interactions/TOF-ERDA

IBA-ERD

D. Gracin, Z. Siketić, K. Juraić, M. Čeh

Analysis of amorphous-nanocrystalline silicon thin films by time-of-flight elastic recoil detection analysis and high-resolution electron microscopy

Applied Surface Science, Volume 275, 2013, 19–22

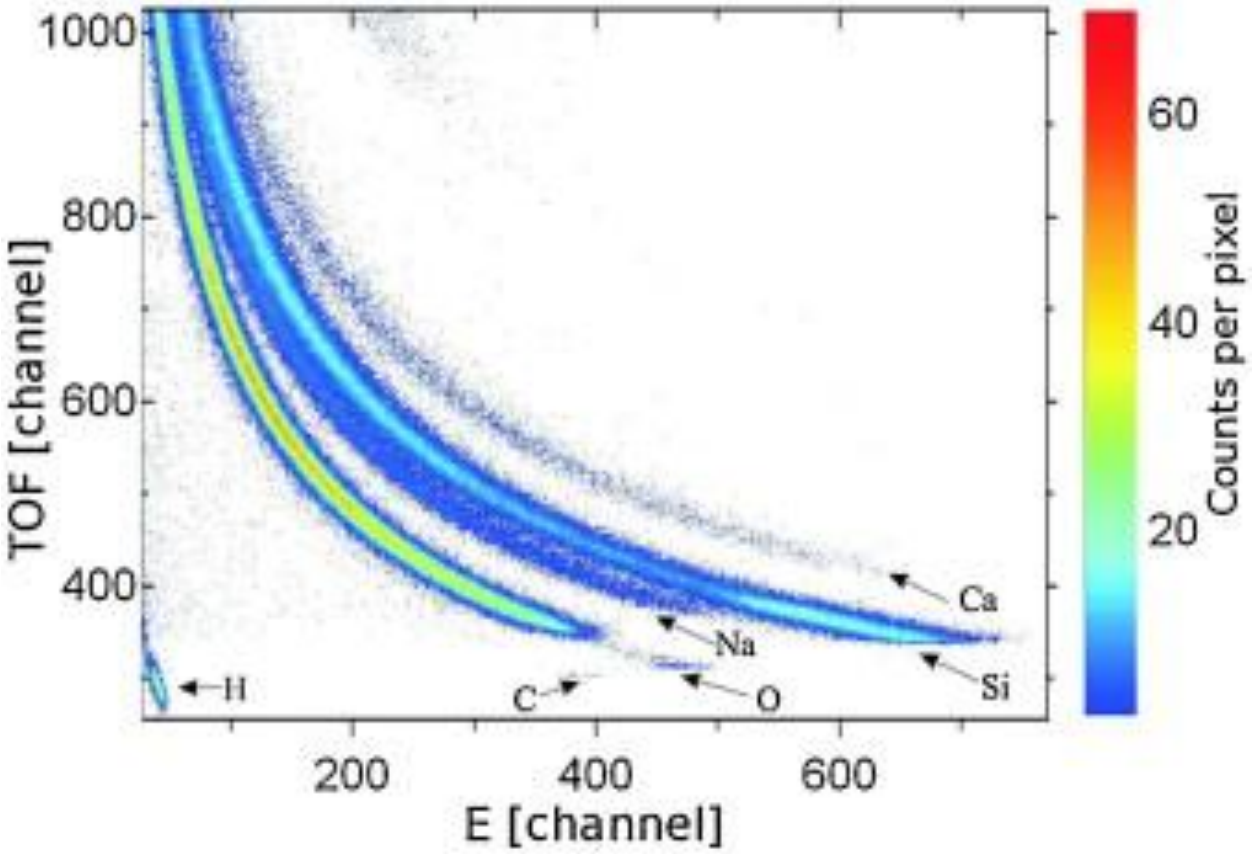


Fig. 6. TOF-ERDA coincidence map of the a-nc-Si:H sample (as deposited).

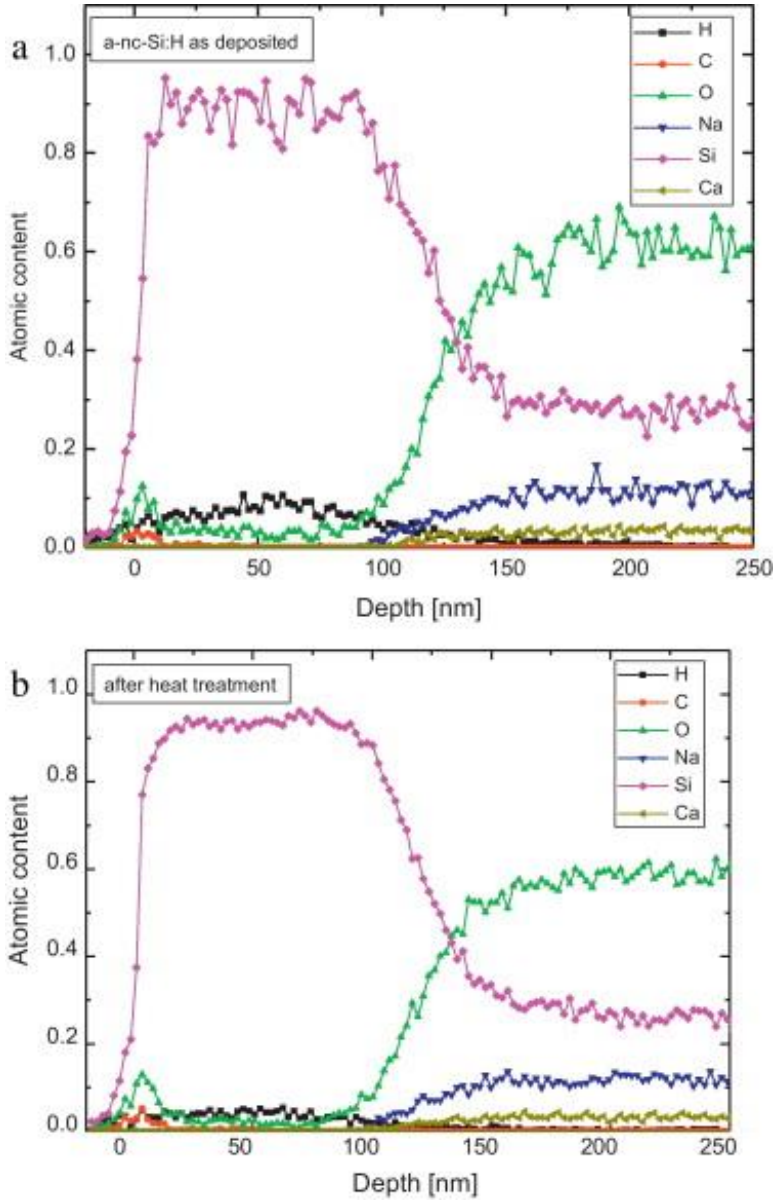
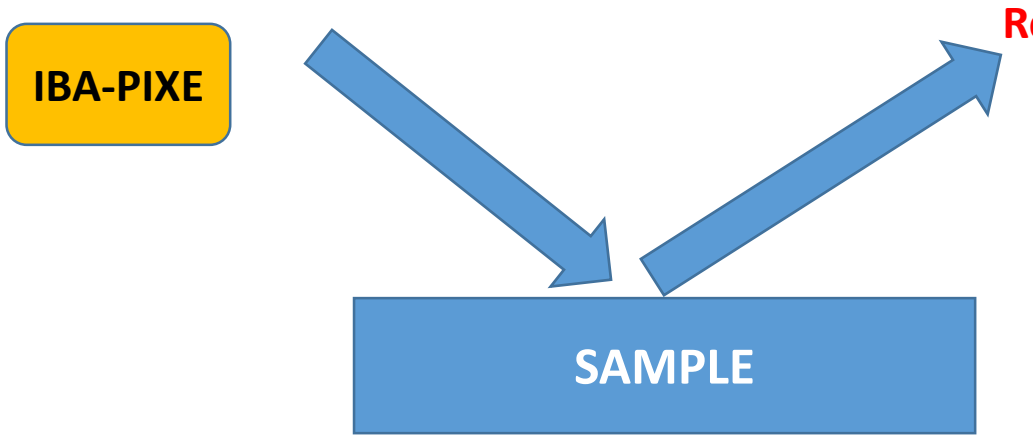


Fig. 7. Elemental analysis of the as-deposited sample (a) and the heat-treated sample (b).

IBA-ERD

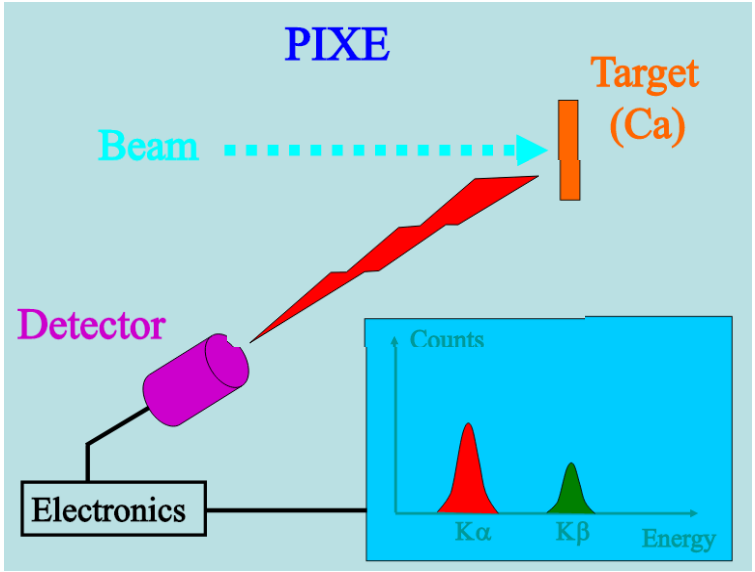
Main features of ERDA

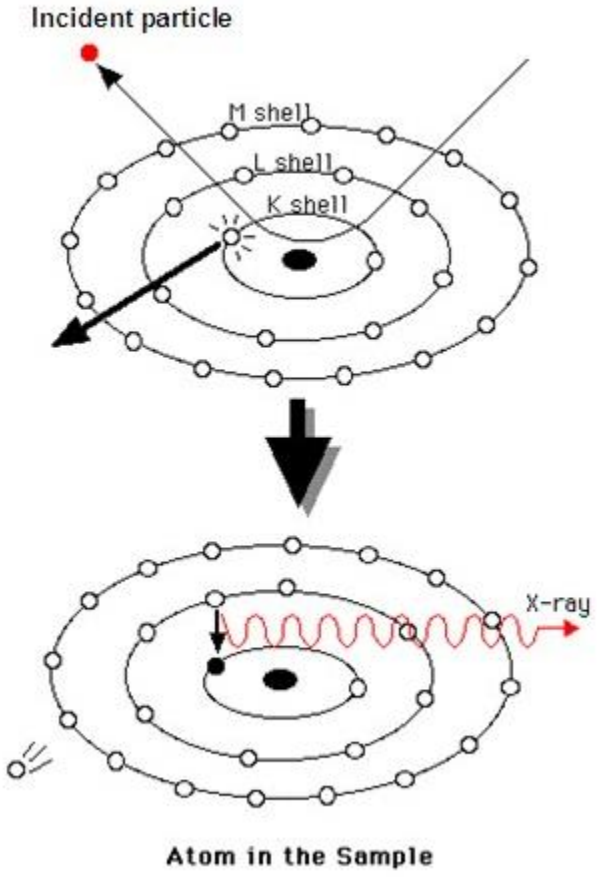
Elements	H – U (Mainly applied for hydrogen)
Standard Conditions	~100 MeV heavy ion beam (2 MeV ^{4}He beam for hydrogen detection) TOF, magnetic, gas ionisation detector 10 minutes per sample
Precision	Stoichiometry: 1% relative Thickness: < 5%
Sensitivity	Bulk: % to 10^{-5}, depending on Z
Depth Resolution	1 to 10 nm
Remarks	Simultaneous profiles of all elements Accessible depth range ~ 1μm Light elements detectable on heavy substrates



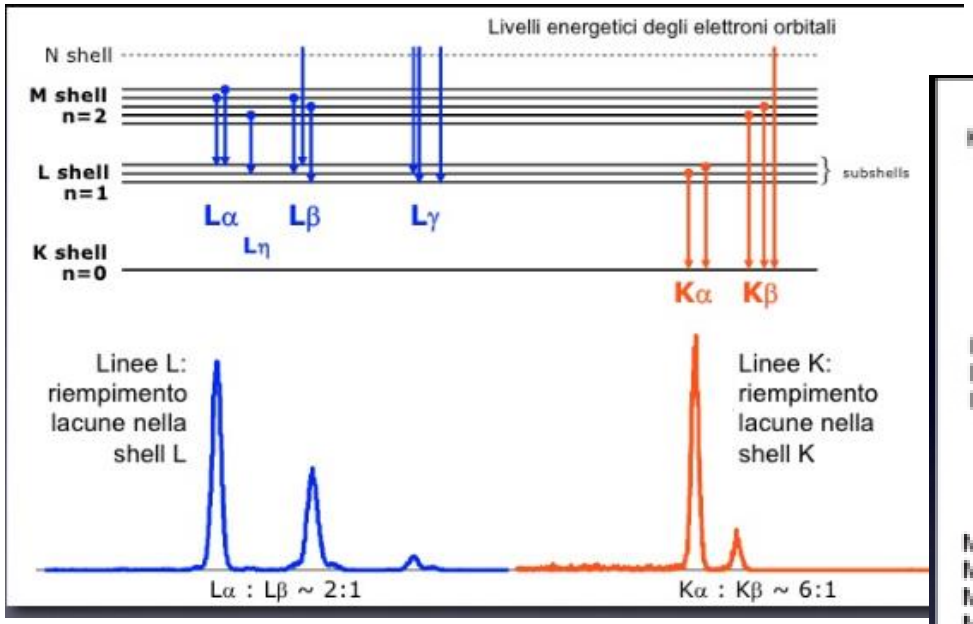
Particle (proton) induced x-ray emission

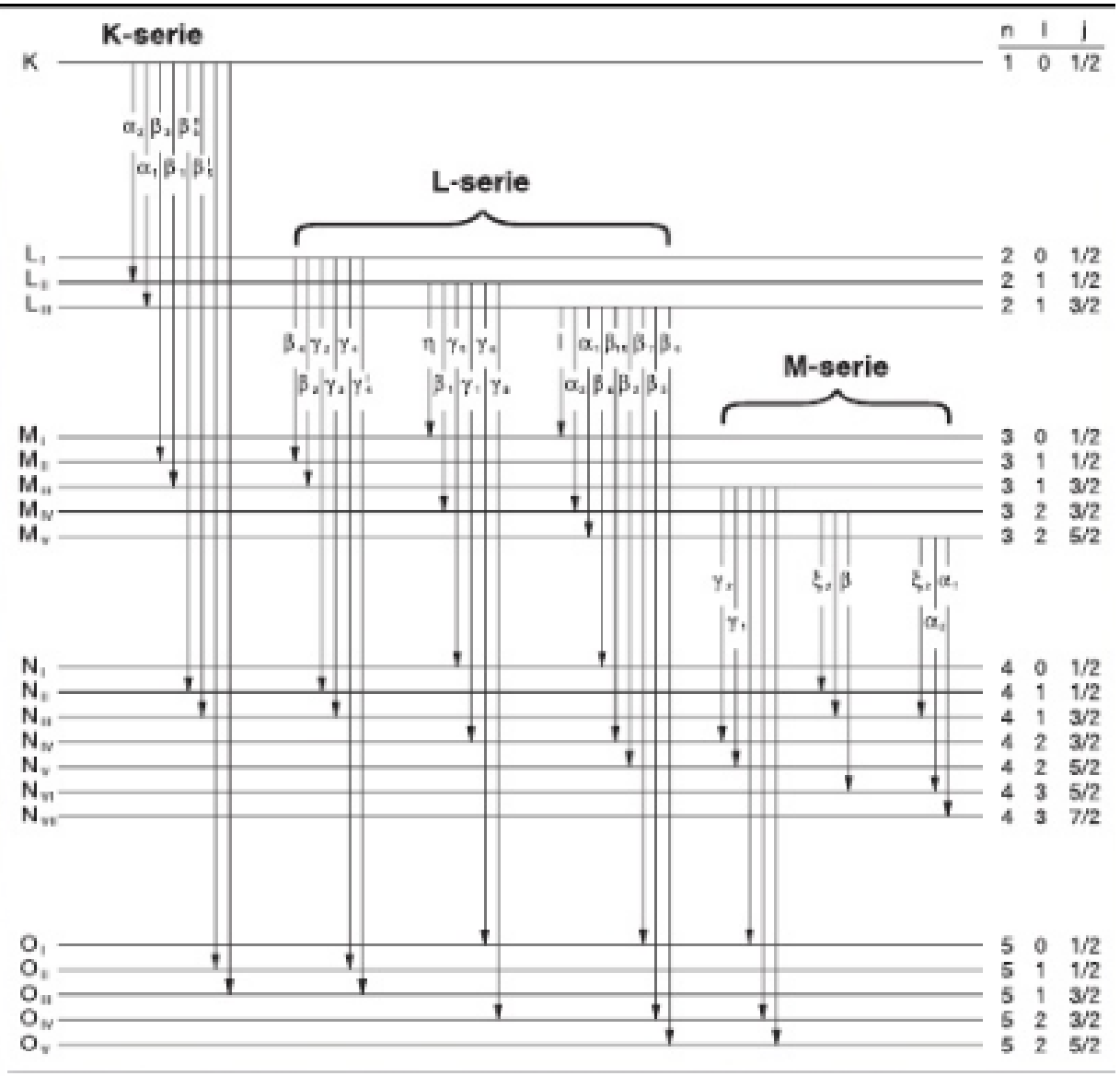
The incident ion (typically protons) eject inner shell electrons from
The target atoms which results in the emission of characteristic x-rays



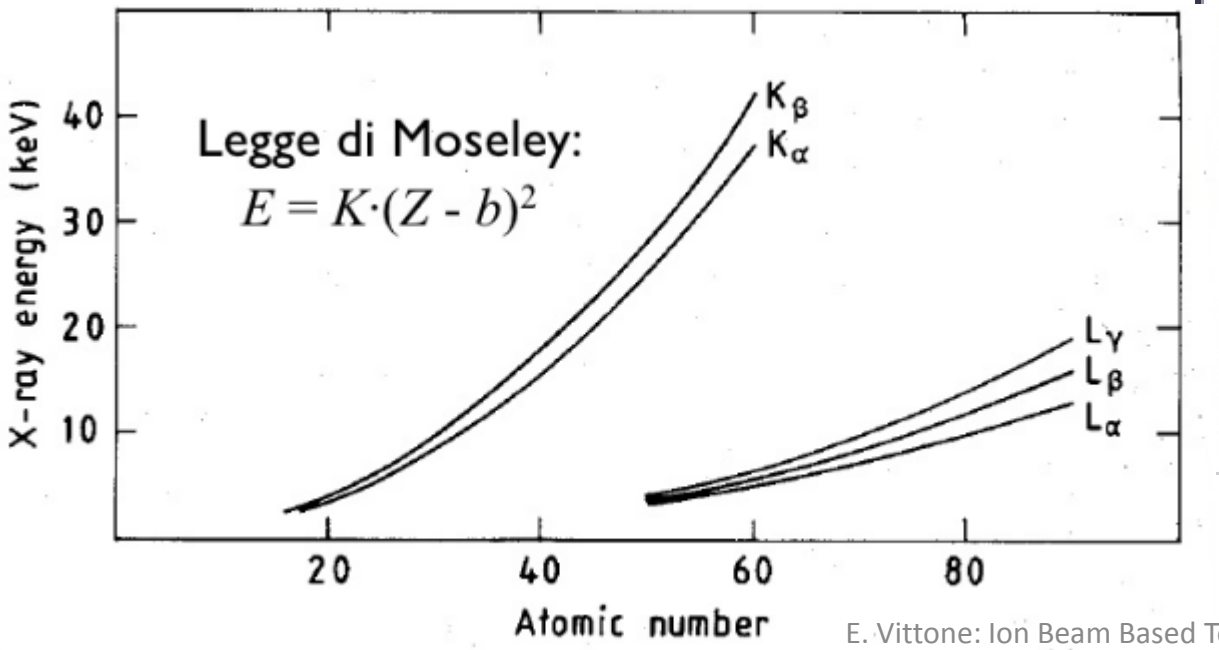


IBA-PIXE



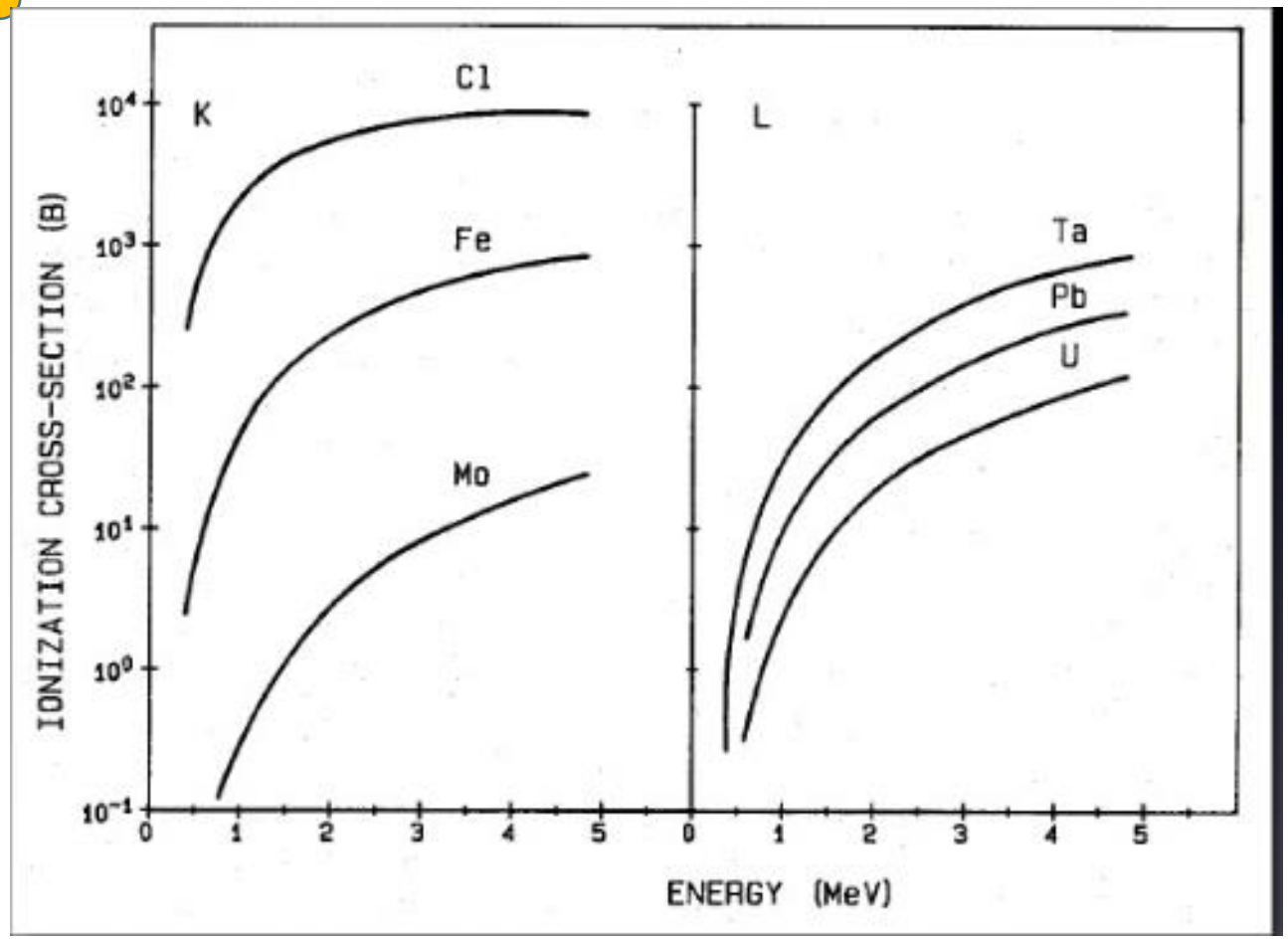


X-ray characteristic energies

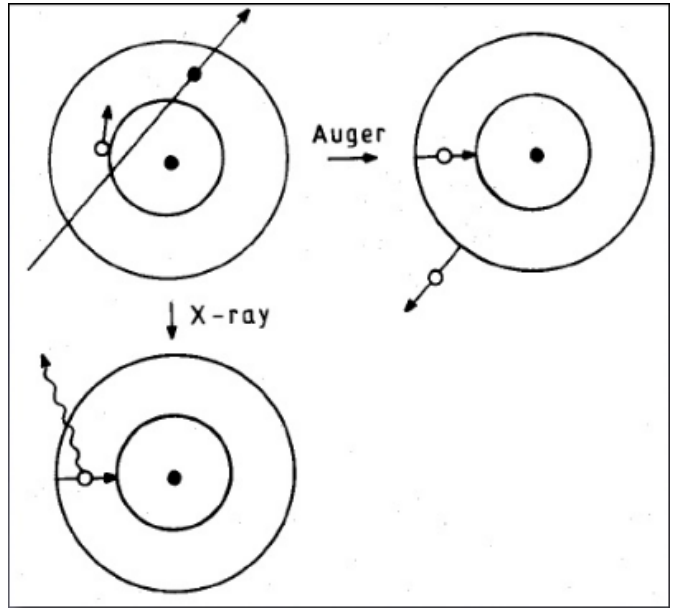


IBA-PIXE

Ionization cross-section



Relaxation atomic processes



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X-ray production cross sections

The efficiency of X-ray production is normally measured by the x-ray production cross-section. This is the fictitious effective area that a single atom exposes to the beam assuming that each time a particle enters that area an x-ray is produced. Units are barns (1 barn = 10^{-24} cm^2).

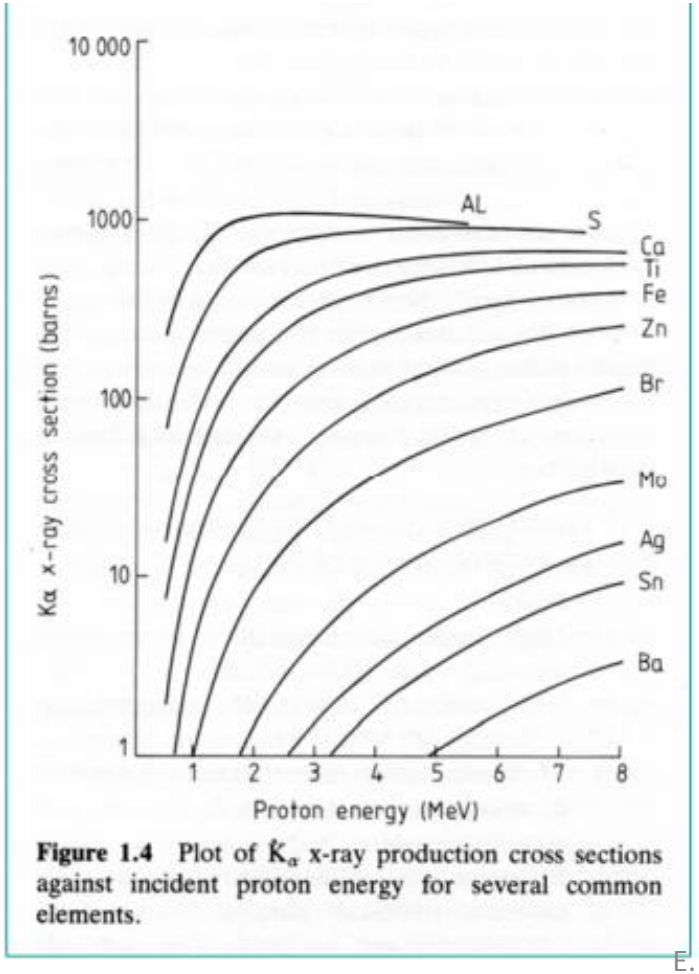


Figure 1.4 Plot of K_α x-ray production cross sections against incident proton energy for several common elements.

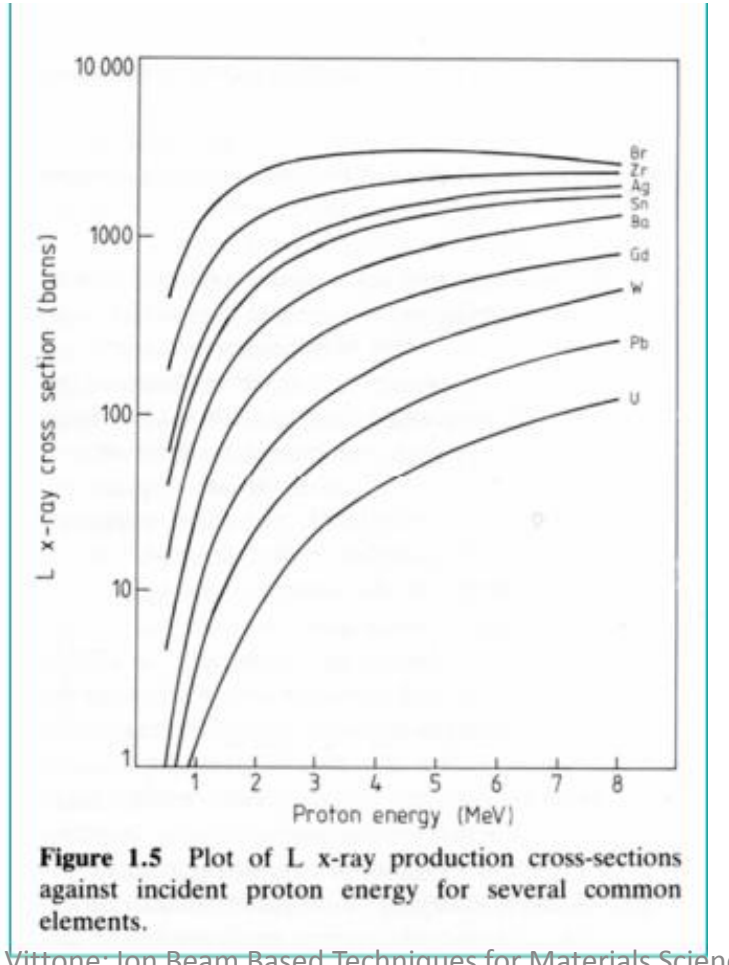


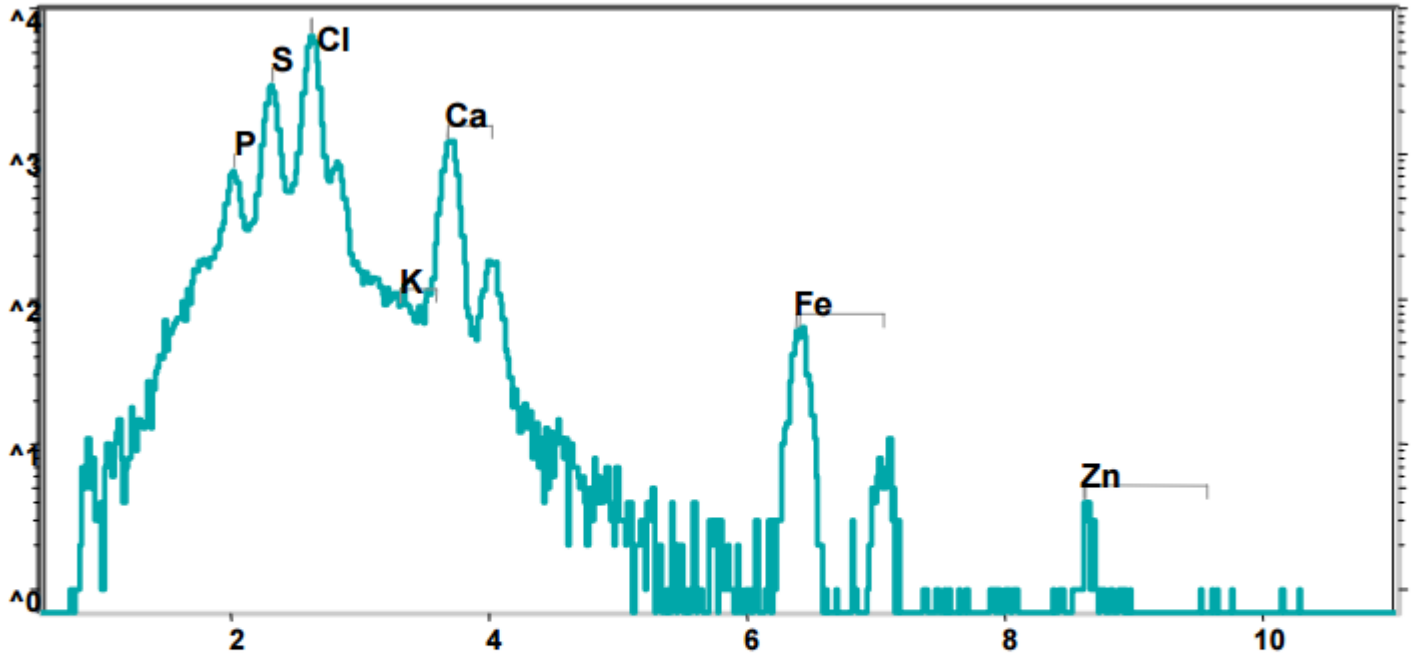
Figure 1.5 Plot of L x-ray production cross-sections against incident proton energy for several common elements.

Note that typical RBS cross sections are measured in barns and nuclear reaction cross sections are measured in millibarns.

PIXE is a very high yield technique

IBA-PIXE

"Normal" PIXE spectrum



PIXE spectrum of a thin protein sample acquired using 2.5 MeV protons. This shows clear well-resolved peaks, a low energy bremsstrahlung peak with a cut-off energy of around 5.5 keV (the theoretical value for 2.5MeV protons) and a negligible background above this.

PIXE is capable of achieving detection limits around **1 part per million** (w/w)

Using a microbeam (sampling volume 1 μm^3) this corresponds to an absolute detection limit of around **10^{-18}g (1 attogram, or around 10^6 atoms)**

IBA-PIXE

Thin samples

Total Yield of x-ray generated in a PIXE experiment

We will assume:

1. the sample is a very thin layer with N_T target atoms per cm^2.
2. the beam has a flux of N_B protons per second (i.e. current, $I = N_B e$ ampere)
3. we are irradiating uniformly an area of A cm^2 for a time t seconds (we will see that the irradiated area cancels out).

The total effective x-ray production cross section in the irradiated area is then

$AN_T\sigma_X(E)\times10^{-24}$ cm^2 where σ_X is the value of the x-ray cross section in barns

The number of beam particles per cm^2 is $N_B t/A$, so the total number of photons created is

$$N_X = N_T N_B t \sigma_X(E)\times10^{-24}$$

or

$$N_X = N_T I t \sigma_X(E)\times10^{-24}/e$$

or

$$N_X = N_T Q \sigma_X(E)\times10^{-24}/e$$

Where Q is the total beam charge in C and e is the electronic charge, 1.6×10^{-19} C

IBA-PIXE

Thin samples

Assuming that the X-rays are emitted isotropically and that the detector has a solid angle of Ω sr and an intrinsic efficiency of $\varepsilon(E_x)$, the total number of detected X-rays is

$$N_X = N_T Q \sigma_X(E) \Omega \varepsilon(E_X) \times 10^{-19} / 4\pi e$$

This can be written in terms of the areal density of the target atoms, m μg cm^{-2} as follows:

$$N_X = mQY(E)\Omega\varepsilon(E_x)$$

where

$$Y(E) = \frac{\sigma_X(E) \times 10^{-24}}{4\pi e A m_P} \approx 3 \times 10^5 \frac{\sigma_X(E)}{A} \text{ counts}/\mu\text{C}/\mu\text{gcm}^{-2}/\text{sr}$$

where Am_P is the mass of the target atom.

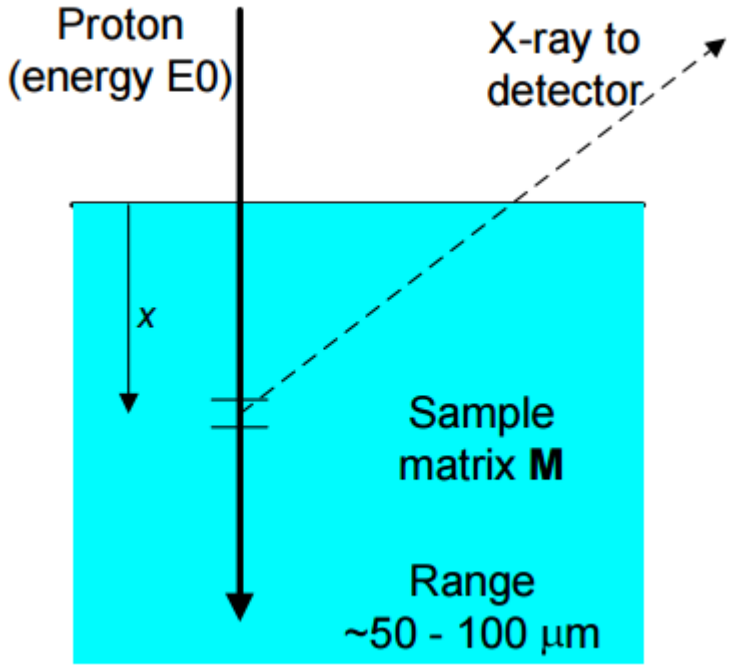
Y is the thin target PIXE yield. This is a function of the Z and A of the target atom, the type and energy of the incident ion and the measured X-ray transition.

Typical values (e.g. for Ca Ka X-rays induced by 3MeV protons) are ~10^6 cts/μC/μgcm^{-2}/sr

IBA-PIXE

Thick samples

Absorption of the emitted x-ray



At depth x:

- Proton energy, E(x) depends on E0, *x* and stopping power, S, of **M**
- X-ray production cross section, σ, depends on E(x) and Z
- Absorption of emitted x-ray depends on the X-ray mass absorption coefficient, μ, of **M**, the energy of the xray and the angle of the detector

$$dN_Z = KQc_Z\sigma_x(Z,E)\Omega\varepsilon(E_Z)\exp\left(-\mu(\mathbf{M},E_Z)\frac{x}{\cos\theta}\right)dx$$

where c_Z is now the mass fraction of Z in the matrix

Software Packages
AXIL, GEOPIXE II, PIXYKLM, GUPIX/Dan32

IBA-PIXE

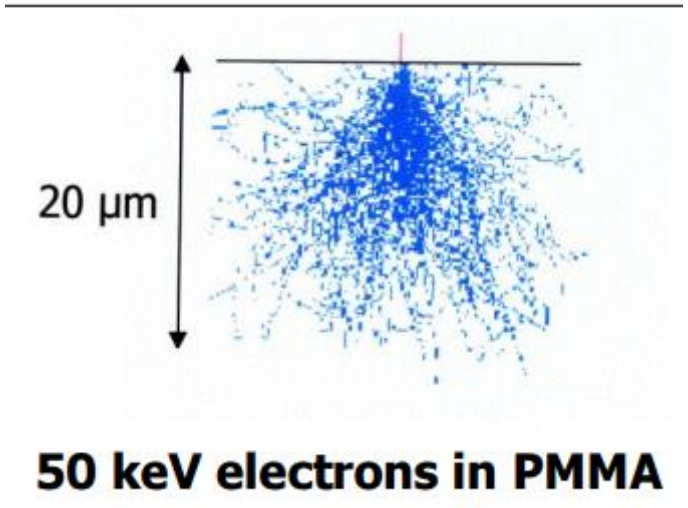
PIXE Advantages

- **Rapid, sensitive and non - destructive analyses**
- **Quantitative analysis; LOW DETECTION LIMIT**
- **Minimum detectable x-ray energy: 1 keV →All the elements with Z>11 can be simultaneously detected**
- **PIXE is the analogon to Energy Dispersive X-ray analysis (EDX) with electron microprobe.**
- **Trace element analysis using PIXE has a detection limit orders of magnitude lower than can be attainable by x-ray spectrometry techniques using electron excitation.**
- **Under favorable conditions, a detection limit ~1 ppm for thin foils and ~10 ppm for thick samples can be achieved.**

http://indico.ictp.it/event/a05196/session/16/contribution/8/material/0/0.pdf

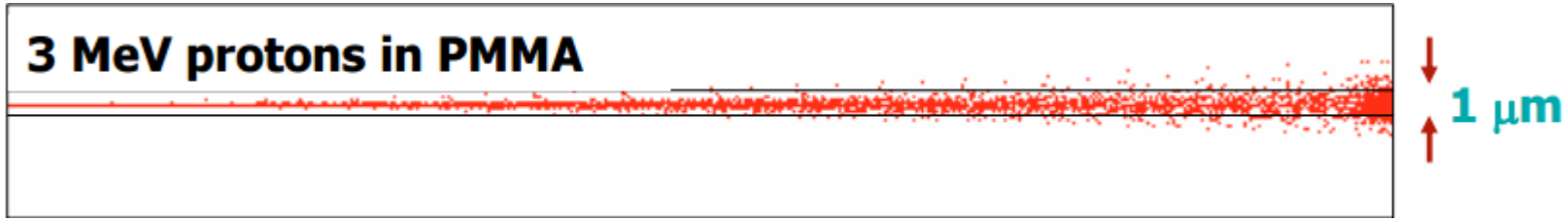
IBA-PIXE

Sources of background:



Primary proton bremsstrahlung

High mass of protons means that they have very small deflection at each electron collision. This means that primary bremsstrahlung is essentially absent.

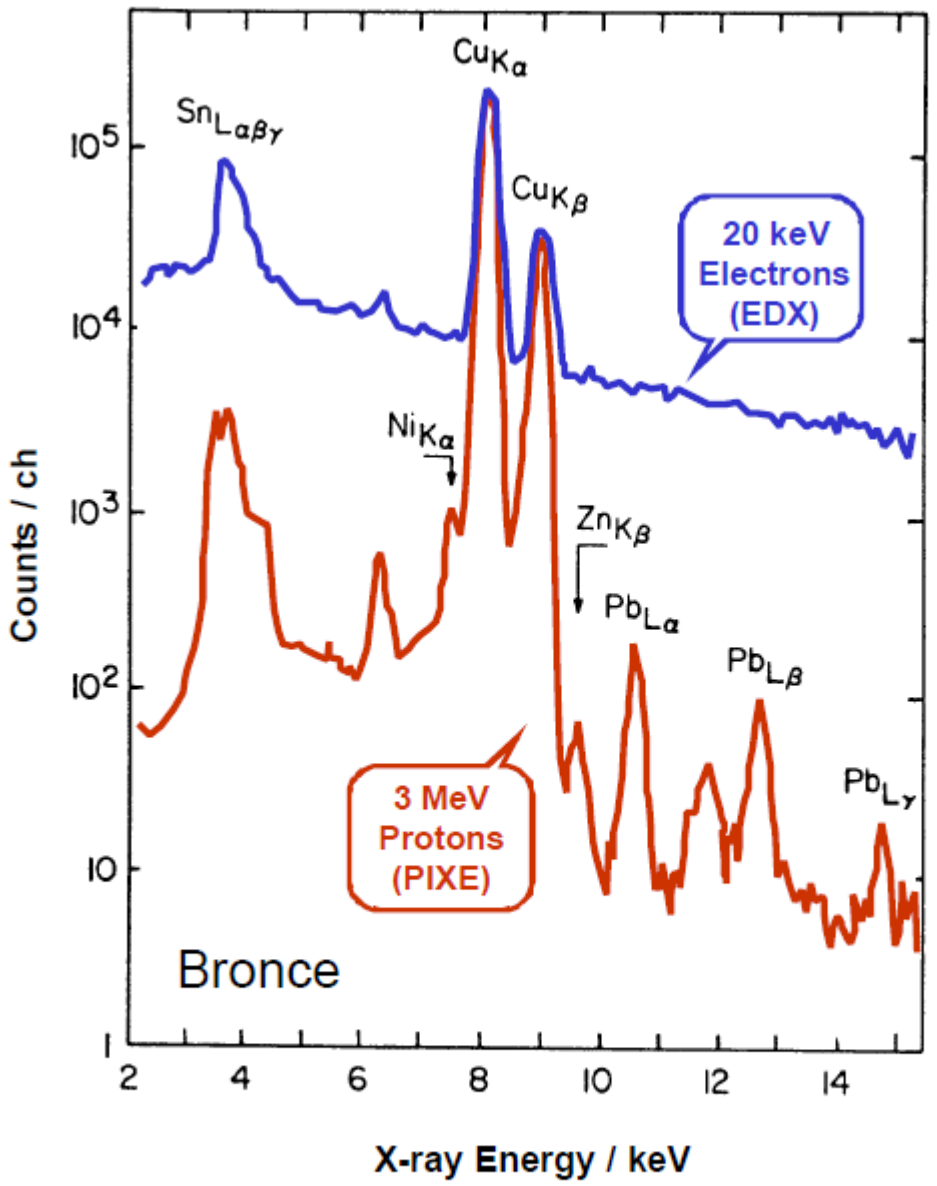


Secondary electron bremsstrahlung (SEB)

- **The electron removed by ionisation may either collide with nearby electrons and eventually stop, or execute an orbit returning to its parent atom (synchrotron radiation). In each case bremsstrahlung is emitted.**
- **The maximum energy that can be transferred to an electron in a proton-electron collision is or about 6.5 keV for 3MeV protons. This means that SEB only affects the lower energy part of the spectrum.**
- **SEB is a secondary process! The number of secondary electrons created is orders of magnitude lower than the number of primary particles**

IBA-PIXE

Very low background (no primary bremsstrahlung), so ppm detection limits

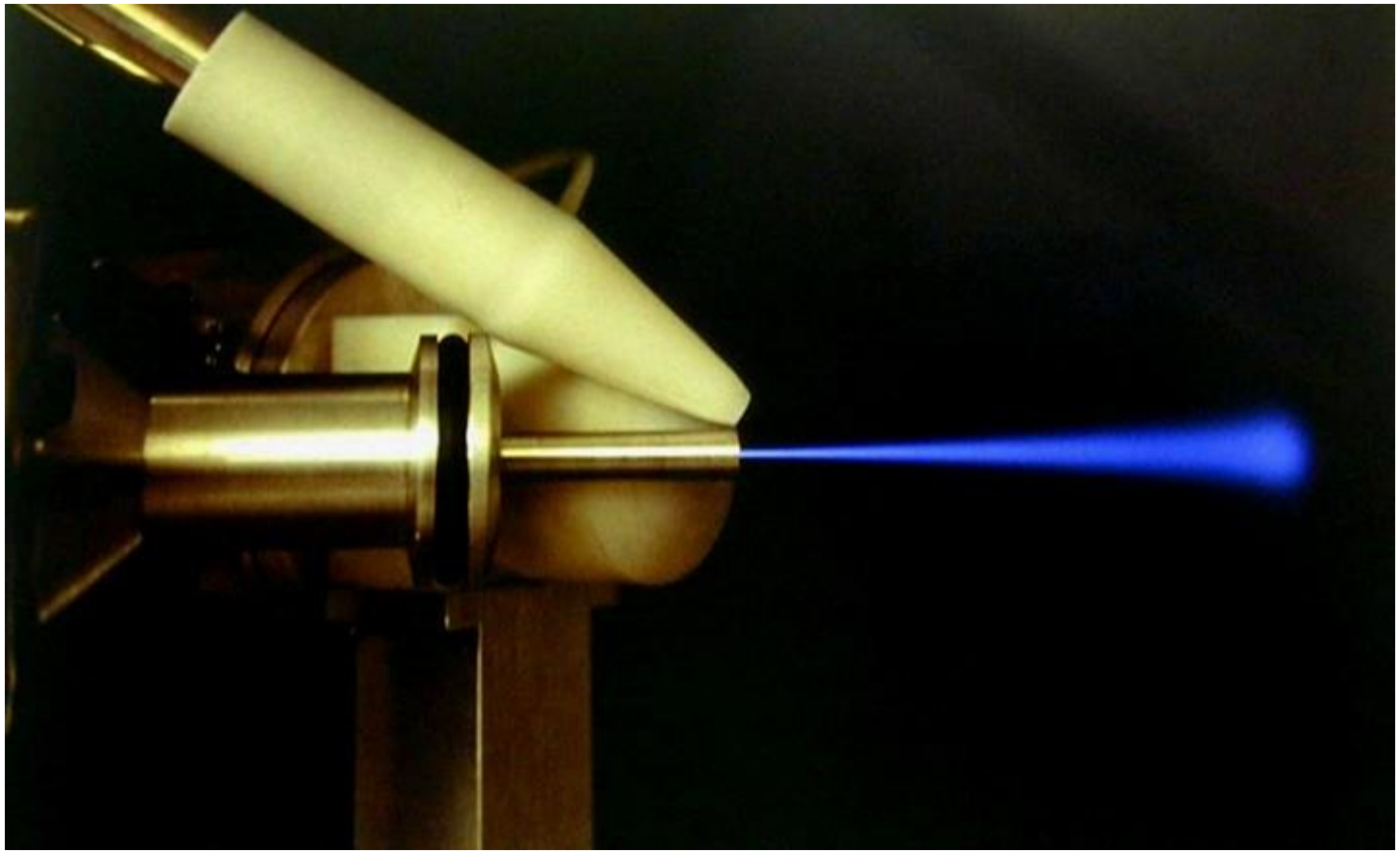


. 12 Comparison of PIXE and EDX. PIXE is generally approx. 100 times more sensitive.

IBA-PIXE

External Beam

Uniersity of Florence - LABEC



Application in cultural heritage
Non vacuum-compatible objects
(e.g. biological samples)

http://www.le.infn.it/ifae/PDF/N.Grassi-UltimaVersione.pdf

http://slideplayer.com/slide/10496042/

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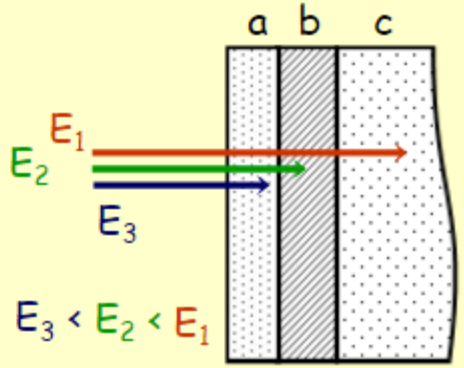
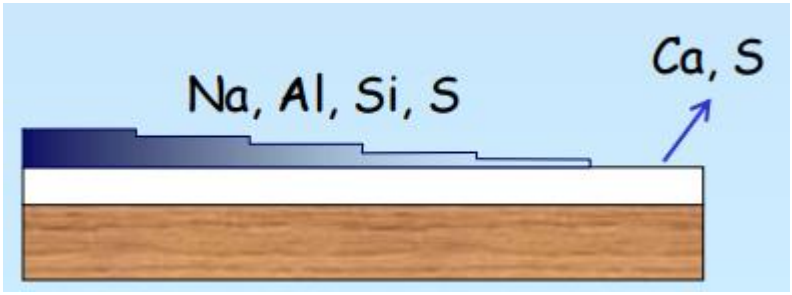
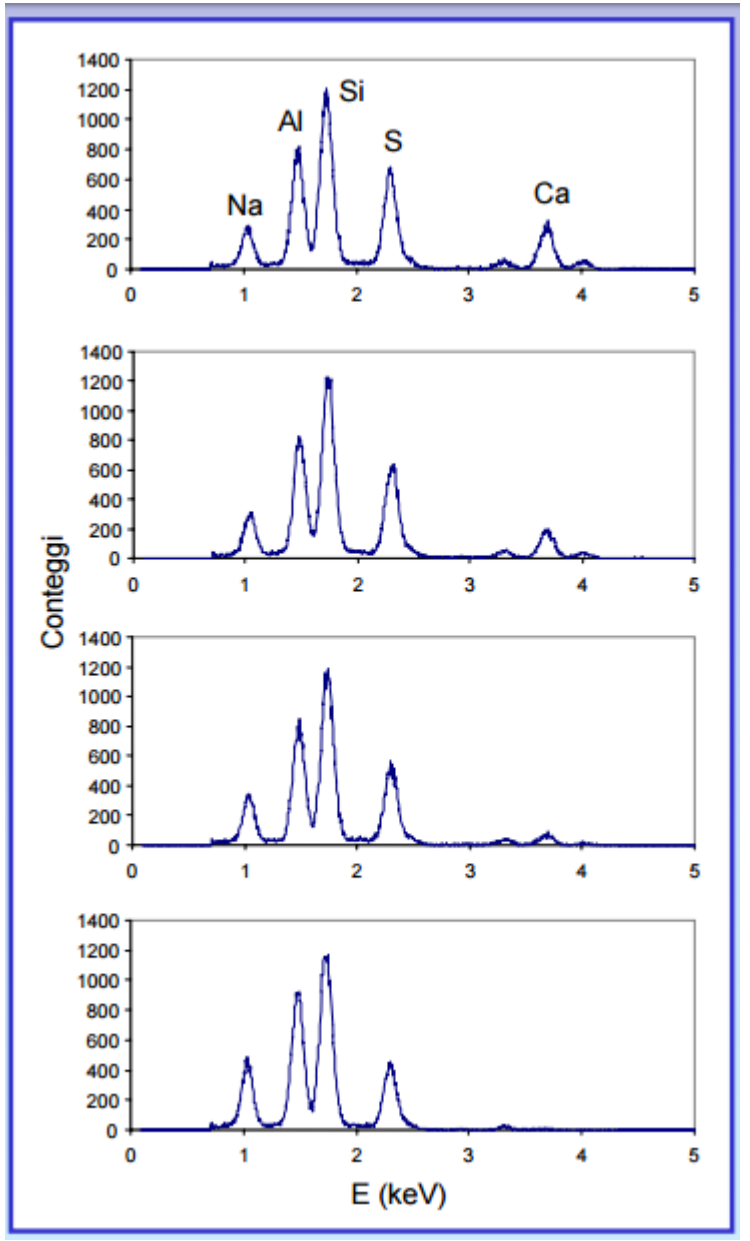
Differential PIXE

Measurements on the same spot with different beam energies



Wooden tablet with a plaster base and Painted with layers of different thickness of lapis lazuli





IBA-PIXE

Elements	Al - U
Standard Conditions	3 MeV proton beam Si(Li), Ge detector 10 minutes per sample
Precision	Stoichiometry: 5% relative Generally used for trace element analysis Absolute concentrations mainly by calibration standards
Sensitivity	1 to 100 ppm, depending on Z and matrix
Depth Resolution	No depth information
Remarks	Probed depth is tens of μm Often used with raster imaging (proton microprobe)

Summary of PIXE

- High yield (rapid!) trace element analysis
- Detects all elements simultaneously
  - Element range set by detector response: typically Na – U
- Very low background (no primary bremsstrahlung), so ppm detection limits
- Yield can be calculated from fundamental physics, so you can get good accuracy with a minimal dependence on standard reference materials.

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Technique	Measured signal	Spatial Resolution (μm)	Depth resolution (μm)	Detectable elements (Z)	Detection sensitivity (wppm)	Quantitativity (%)
PIXE	X-rays	0.3	5	>11	0.1	5
RBS	Backscattered ions	0.5	0.02	>2	1	3
NRA	Charged particle reaction products	1	0.005	All low Z	0.01	3
ERDA	Forward scattered sample ions	>1	0.005	<15	500	3
SIMS	Sample ions	0.05	0.005	All	0.001-10	50
AES	Auger electrons	0.1	0.001	>2	10000	50
XPS	Photoelectrons	1000	0.002	>2	1000	50
EDS	X-rays	0.5	1	>6	100	1
XRF	X-rays	3	5	>11	1	5

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Biblio and Web - graphy

C. Jeynes, R.P. Webb, A. Lohstroh
Ion Beam Analysis: A century of exploiting the electronic and nuclear structure of the atom for materials characterization
https://www.surrey.ac.uk/ati/ibc/files/IBAchapter-Final.pdf

P. Mandò,
Applications of nuclear techniques to Art & Archaeology
http://slideplayer.com/slide/10496042/

J. Grime,
Broadbeam PIXE – Concepts and Applications
http://indico.ictp.it/event/a05196/session/16/contribution/8/material/0/0.pdf

M. Döbeli
Material Analysis
http://cas.web.cern.ch/cas/Pruhonice/PDF/Doebeli.pdf

M. Mayer
Rutherford Backscattering Spectrometry (RBS)
http://users.ictp.it/~pub_off/lectures/lns022/Mayer_1/Mayer_1.pdf

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Biblio and Web - graphy

IAEA TECDOC 1190
Instrumentation for PIXE and RBS
http://www-pub.iaea.org/books/iaeabooks/5966/Instrumentation-for-PIXE-and-RBS

M. Chiari
La tecnica RBS
www.slideshare.net/max0068/chiari-lezione-su-rutherford-backscattering-spectrometry-rsb-2012

M. Chiari
La tecnica PIXE
https://www.slideshare.net/max0068/chiari-lezione-su-particle-induced-xray-emission-pixe-2012

Y. Wang, M. Nastasi
Handbook of Modern Ion Beam Materials Analysis
Material Research Society, 2° edition, 2009, www.mrs.org