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Ion Beam Analysis Techniques for non-Destructive Profiling Studies

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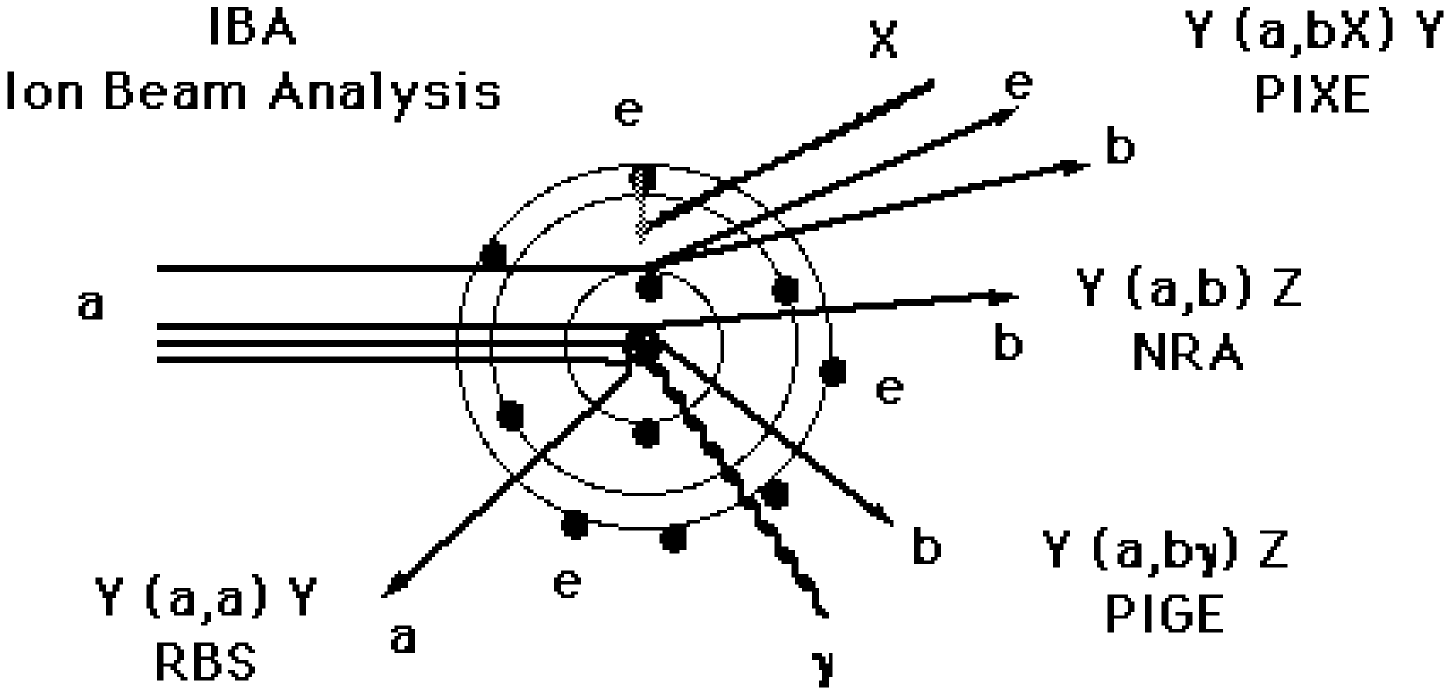
What is IBA?

Ion Beam Analysis (IBA) is based on the interaction, at both the atomic and the nuclear level, between accelerated charged particles and the bombarded material. When a charged particle moving at high speed strikes a material, it interacts with the electrons and nuclei of the material atoms, slows down and possibly deviates from its initial trajectory. This can lead to the emission of particles or radiation whose energy is characteristic of the elements which constitute the sample material.



IBA METHODS:

Method	Acronym	Interaction
Particle-Induced X-ray Emission	PIXE	Characteristic X-ray emission following ionization by the primary beam
Rutherford Backscattering Spectrometry	RBS	Elastic scattering at backward angles
Elastic or Nuclear (non-Rutherford) Backscattering Spectrometry	EBS	Elastic scattering at backward angles
Elastic Recoil Detection Analysis	ERDA	Elastic recoil at forward angles, not necessarily Rutherford
Nuclear Reaction Analysis	NRA	Nuclear reaction between incident beam and nuclei in the target, producing a light charged particle
Particle Induced Gamma – ray Emission	PIGE	Prompt γ-ray emission during ion beam irradiation

Summary of interactions of accelerated ion with atomic nucleus:

- **Elastic scattering (Coulomb and nuclear)**
- **Inelastic scattering (residual nucleus is excited)**
- **Nuclear reactions with emission of particles and γ-rays**

Positive Common Characteristics of IBA techniques:

- ***They are generally not destructive (least) and are thus suitable for use with delicate materials.***
- ***They are to a certain extent multielementary and produce high-accuracy quantitative results.***
- ***They require little or no preparation of the sample with the result that a specimen (like an artifact) could be directly analyzed.***
- ***Only very small quantities (mg) of sample are needed.***
- ***They permit the analysis of a very small portion of the sample by reducing the diameter of the ion beam to less than 0.5 mm.***

Negative Common Characteristics:

- *Some damage cannot be avoided (thermal, carbon buildup etc.)!*
- *A VdG type of accelerator is required.*
- *In most of the cases the experiments are carried out in vacuum chambers.*
- *Several experimental issues need to be addressed, thus a minimum knowledge of nuclear physics (experimental and theoretical) is mandatory.*
- *No direct information about the chemical environment can be produced.*
- *Issues like dating and authenticity testing can be addressed only indirectly.*
- *Unlike NAA, the IBA analysis concerns only a few microns below the surface of the samples.*
- *In most of the cases, a combination of techniques is required to solve a problem, and this implies time consuming experiments!*

THUS, DO WE REALLY NEED IBA?

YES, because it can solve problems that cannot be addressed by all the other existing techniques!

IBA PROFILING TECHNIQUES:

- *Rutherford Backscattering Spectroscopy / Nuclear Backscattering Spectroscopy (RBS / NBS) / Channeling*
- *Elastic Recoil Detection Analysis (ERDA)*
- *Nuclear Reaction Analysis (particle-particle and particle-gamma reactions)*

NON-PROFILING:

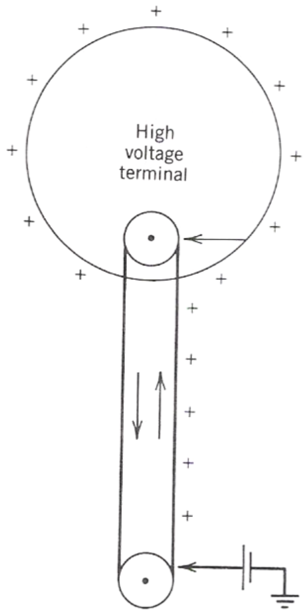
- *Charged Particle Activation Analysis (CPAA), Particle Induced X-Ray Emission (PIXE)*
- *Neutron Activation Analysis (NAA), Secondary Ion Mass Spectroscopy (SIMS)*

SPECIFIC REQUIREMENTS FOR ALL IBA TECHNIQUES:

- *Electrostatic accelerator (mainly VdG, single-ended or tandem)*
- *Scattering chamber (vacuum or in-air)*
- *Electronics*
- *Software for acquisition and spectral analysis*

The Cockcroft-Walton accelerator which was used for the first nuclear reaction experiment in 1932. Courtesy of the University of Cambridge, Cavendish Laboratory.

$p + {}^7Li \longrightarrow {}^4He + {}^4He$



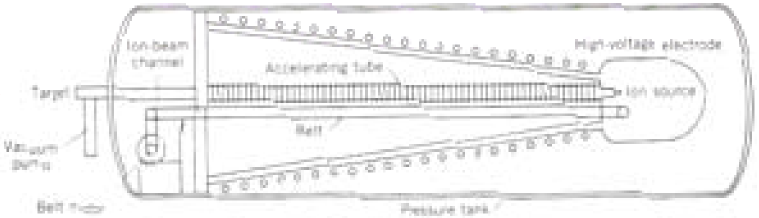


Diagram of Van de Graaff accelerator. The ion source is inside the high-voltage terminal, and both are contained in a pressure tank to inhibit sparking.

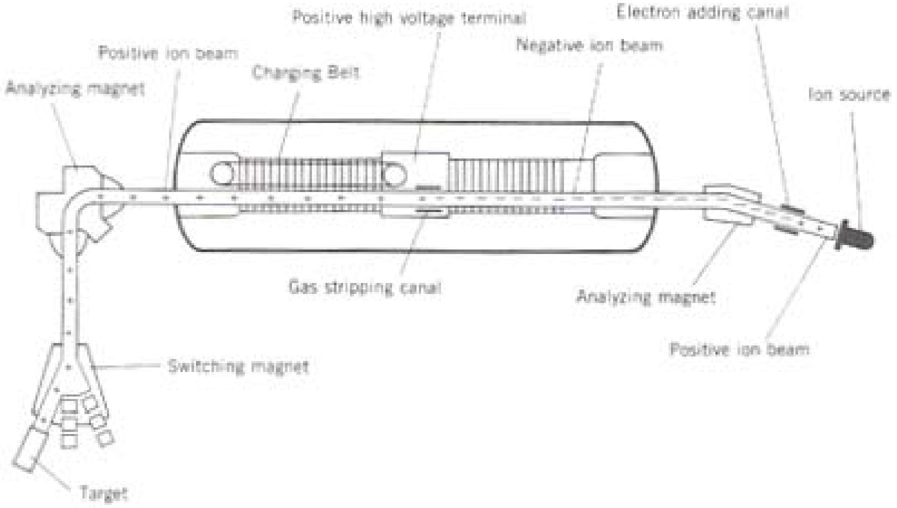


Diagram of tandem Van de Graaff accelerator. From R. J. Van de Graaff, *Nucl. Instrum. Methods* **8**, 195 (1960).

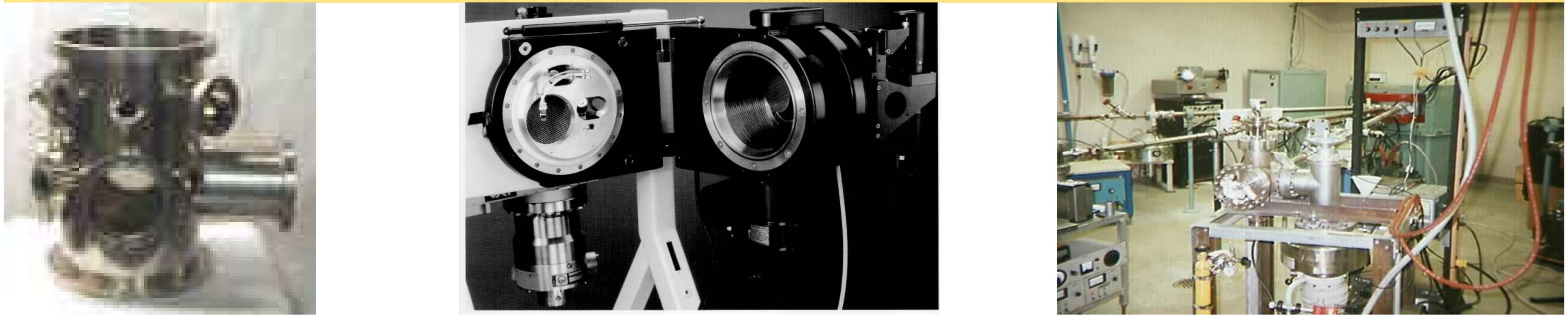
Single – ended VdG accelerator

Tandem type VdG accelerator

ION SOURCES (ESPECIALLY DESIGNED TO PRODUCE NEGATIVE IONS):

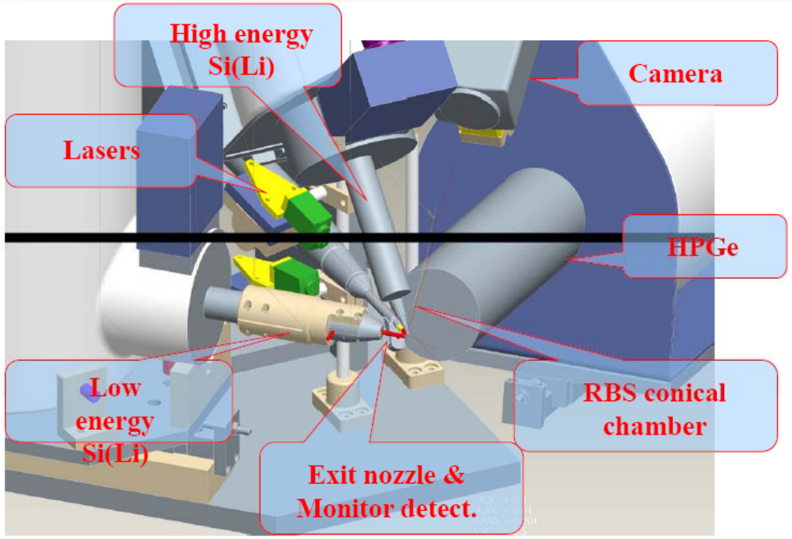
Duoplasmatron (for gaseous materials)

Cs - sputter (for solid materials)



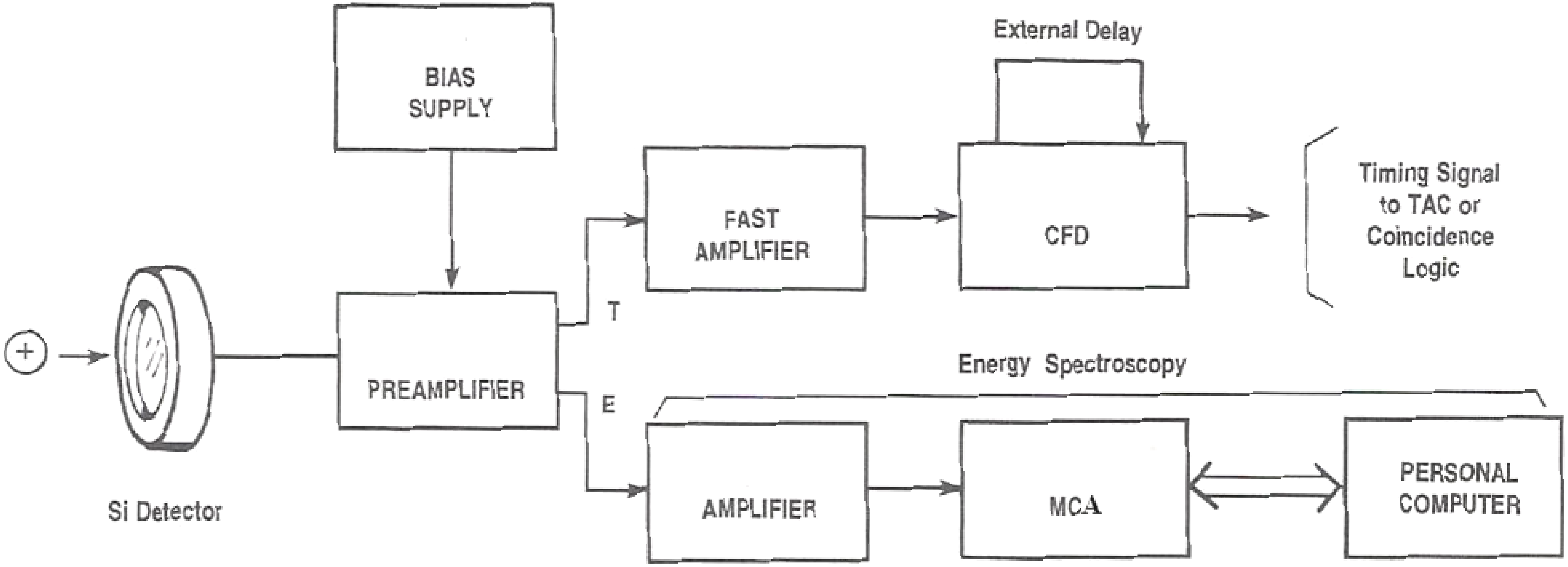
(a) (b) (c)

Several types of vacuum chambers: (a) with open – ends, (b) end – station / compact geometry, (c) end – station with full vacuum system attached to the accelerator line (rotary + turbo pumps)



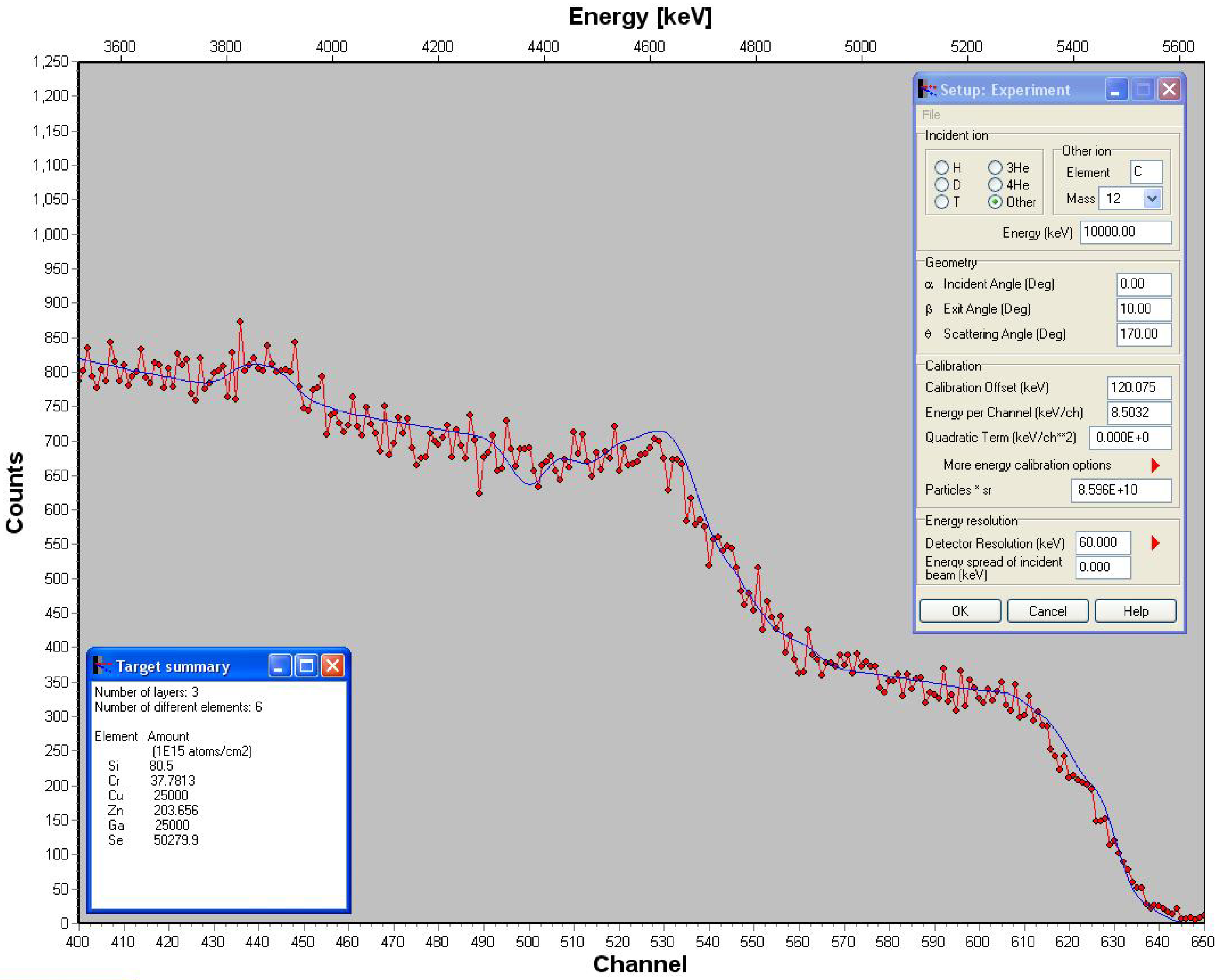
Typical external beam facility for milli – or micro - beam

Typical circuit diagram:



Pulse-Height (Energy) Spectrometry with a Si Charged-Particle Detector, Including Derivation of an Optional Timing Signal.

Typical example of software analysis: SIMNRA



Incident ion

○ H ○ D ○ T ○ 3He ○ 4He ● Other

Other ion

Element: C

Mass: 12

Energy (keV): 10000.00

Geometry

α Incident Angle (Deg): 0.00

β Exit Angle (Deg): 10.00

θ Scattering Angle (Deg): 170.00

Calibration

Calibration Offset (keV): 120.075

Energy per Channel (keV/ch): 8.5032

Quadratic Term (keV/ch**2): 0.000E+0

Particles * sr: 8.596E+10

Energy resolution

Detector Resolution (keV): 60.000

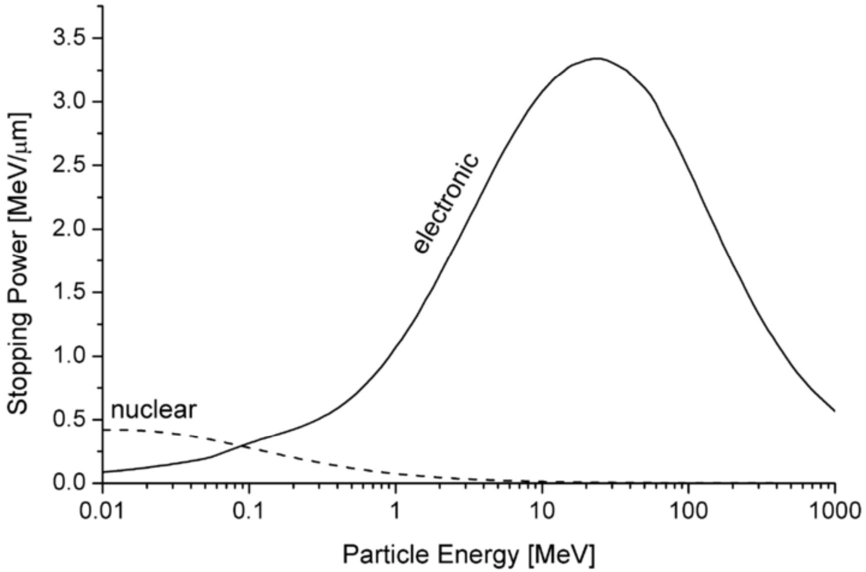
Energy spread of incident beam (keV): 0.000

Number of layers: 3

Number of different elements: 6

Element	Amount (1E15 atoms/cm2)
Si	80.5
Cr	37.7813
Cu	25000
Zn	203.656
Ga	25000
Se	50279.9

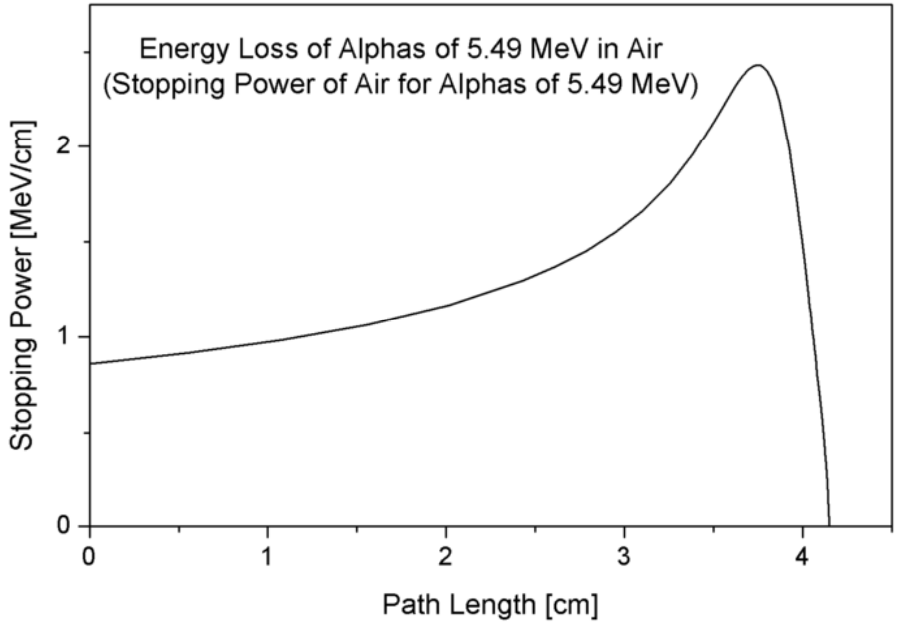
A short introduction in physics: The interaction of charged particles with matter



$$S(E) = -\frac{dE}{dx}$$

Stopping power = Average energy loss per unit length inside the material

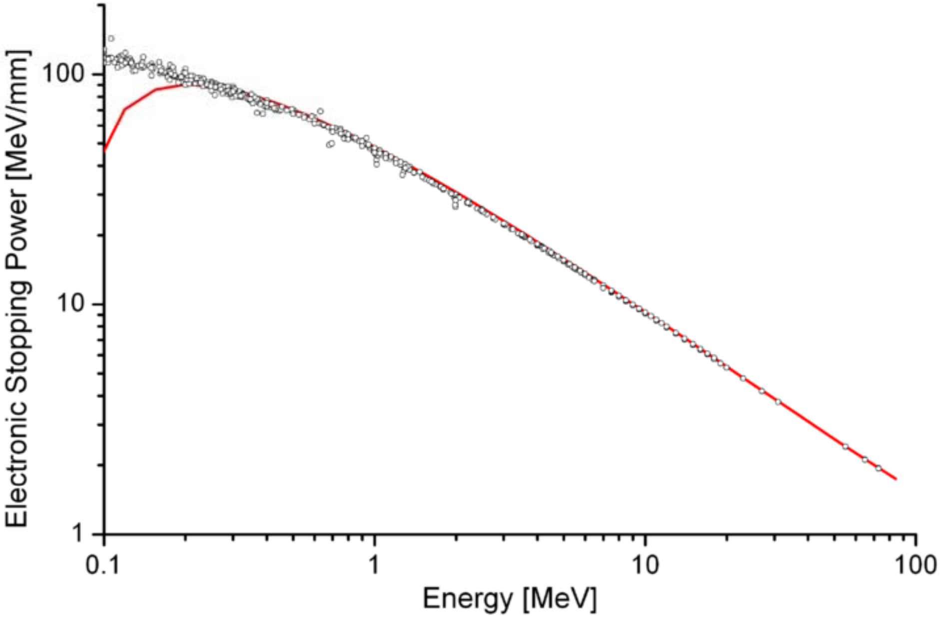
Bragg peak (near the end of range region)

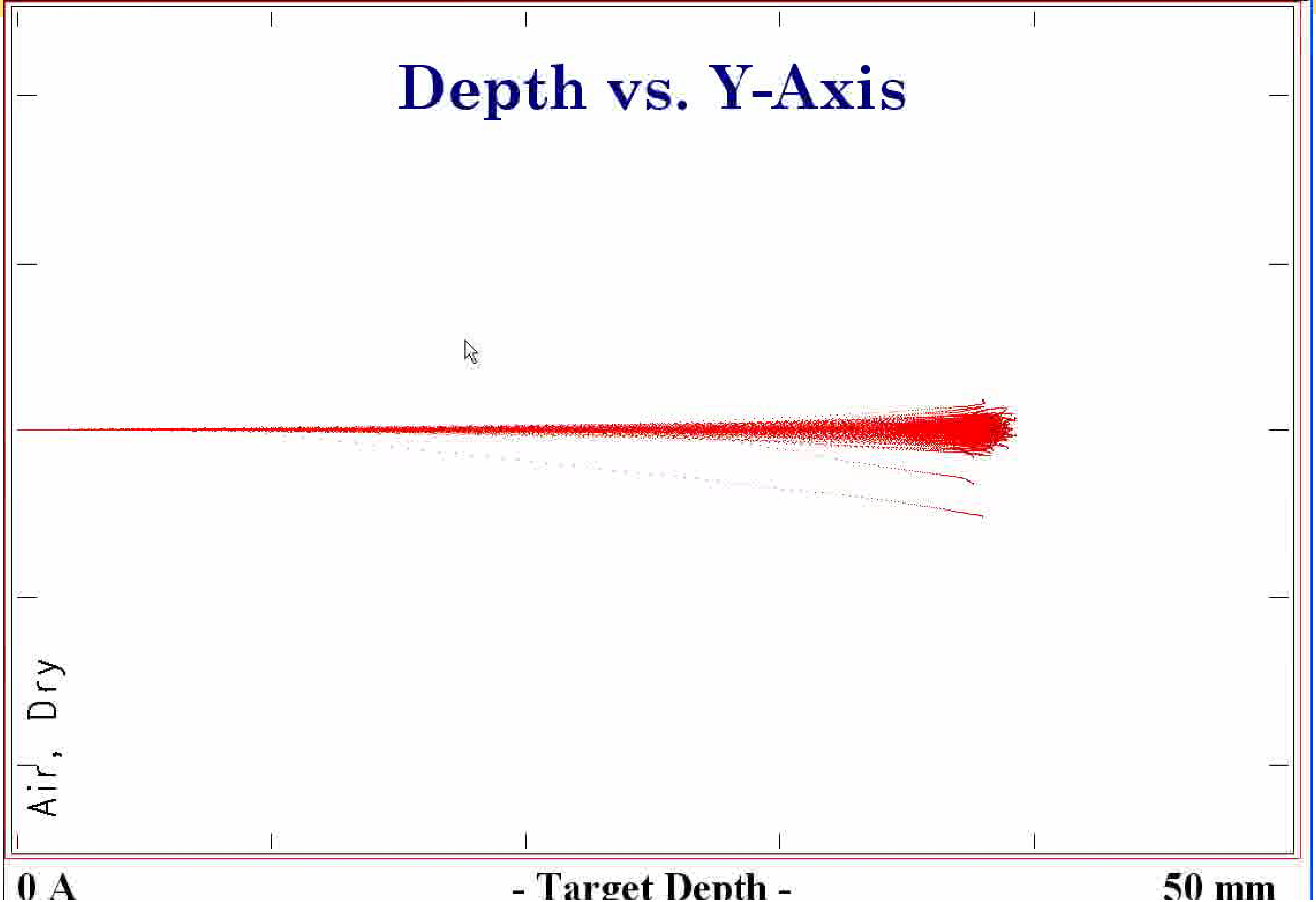


The relativistic version of the Bethe-Block formula (1932):

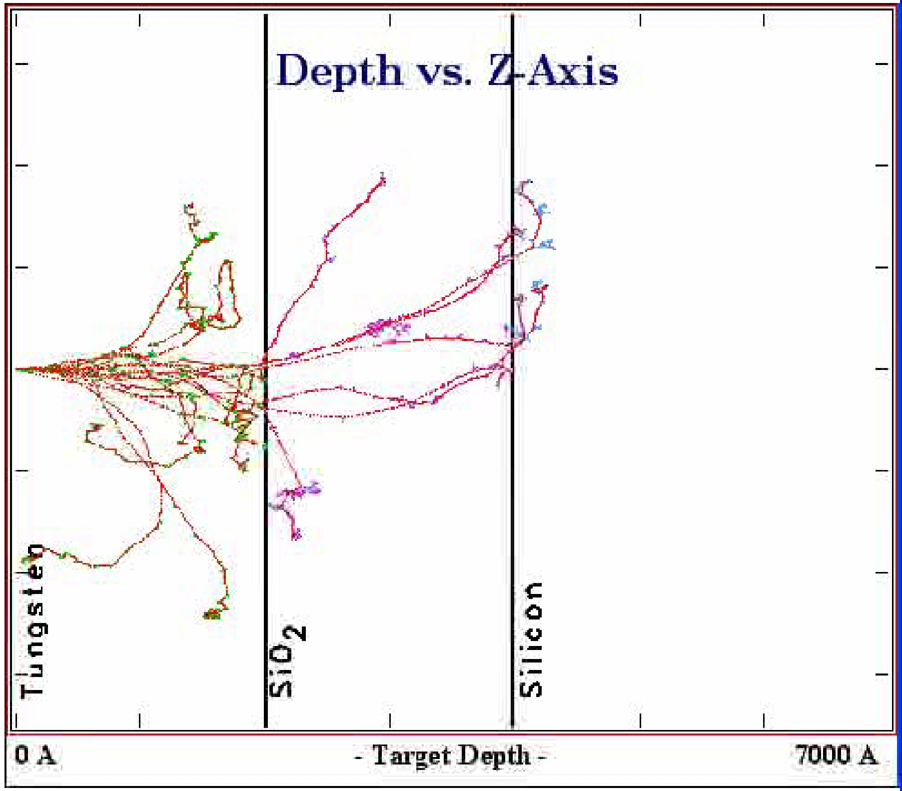
$$-\frac{dE}{dx} = \frac{4\pi}{m_e c^2} \cdot \frac{nz^2}{\beta^2} \cdot \left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \cdot \left[\ln\left(\frac{2m_e c^2 \beta^2}{I \cdot (1-\beta^2)}\right) - \beta^2\right]$$

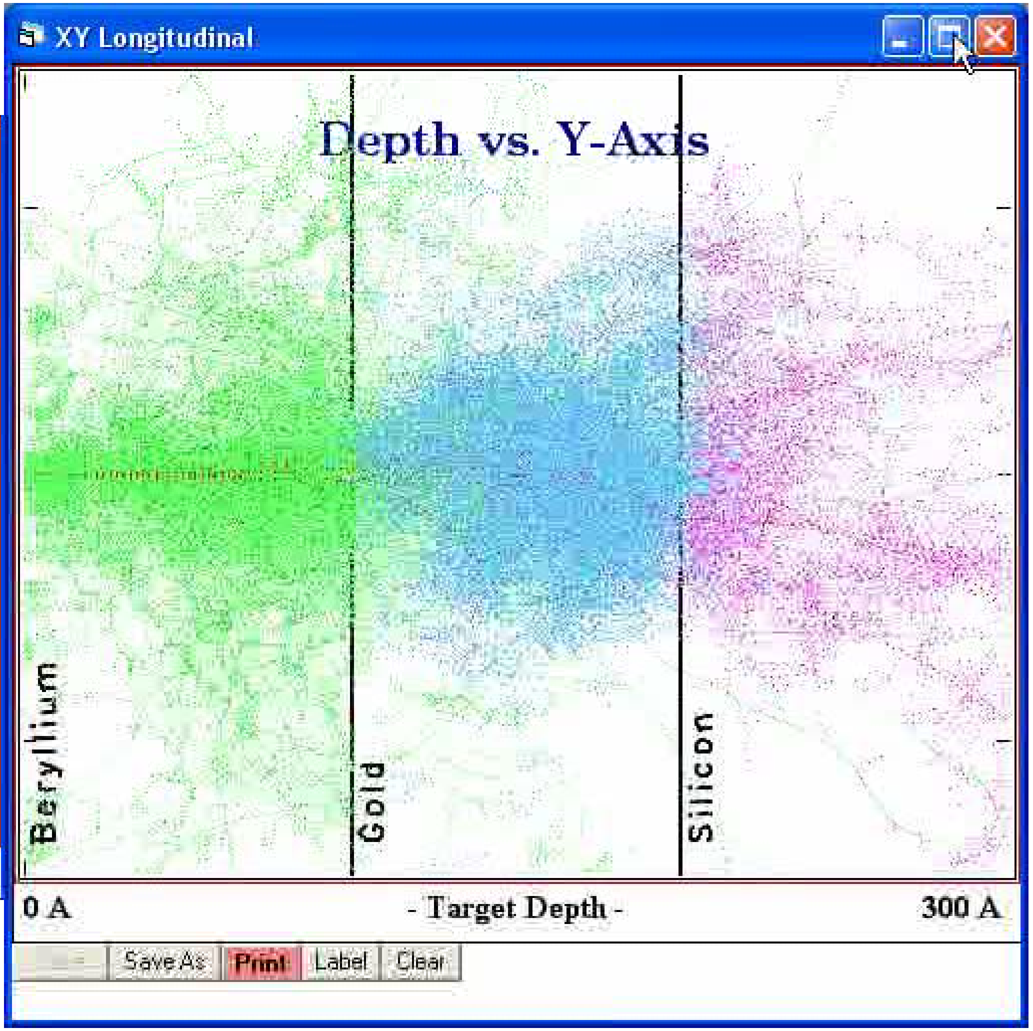
β	$= v / c$
v	velocity of the particle
E	energy of the particle
x	distance travelled by the particle
c	speed of light
ze	particle charge
e	charge of the electron
m_e	rest mass of the electron
n	electron density of the target
I	mean excitation potential of the target




Depth vs. Y-Axis
Air, Dry
0 A
- Target Depth -
50 mm

2. What happens when a keV-ion interacts with matter?

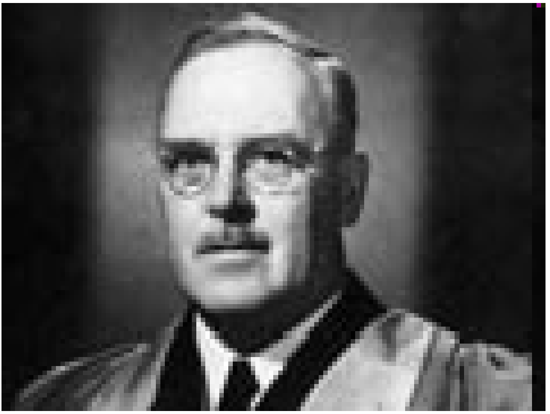




Ernest Rutherford
(1871 – 1937)

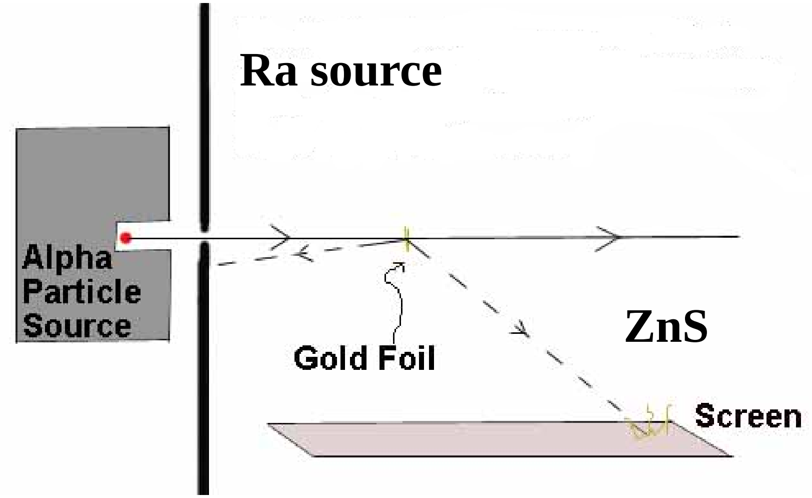
- A great talent from New Zealand. Maybe the greatest experimental physicist of his era after Faraday.
- 1899 – Discovery and study of α and β radiation. Distinction on the basis of penetrability and measurement of charge. Professor in McGill, Canada till 1907. He named ‘γ-rays’. He discovered the law of radioactivity and the existence of nuclear reactions. He measured the age of Earth along with Soddy and Hahn.
- Professor in Manchester till 1919. Famous ‘gold foil’ experiment with Geiger and Marsden. First nuclear model suggestion. First study of a nuclear reaction: $^{14}N + \alpha \dashrightarrow {}^{17}O + p$
- Professor at Cavendish, Cambridge in the place of J.J. Thomson till his death. Collaboration with N. Bohr in the new ‘atomic model’. Theoretical prediction for the existence of neutron. Brilliant team of students and collaborators: Cockroft, Walton, Chadwick, Wilson, Appleton.
- Nobel prize in Chemistry (!), 1908. In his speech he said: ‘It was the quickest transition in my life’!

Hans Geiger
(1882 – 1945)

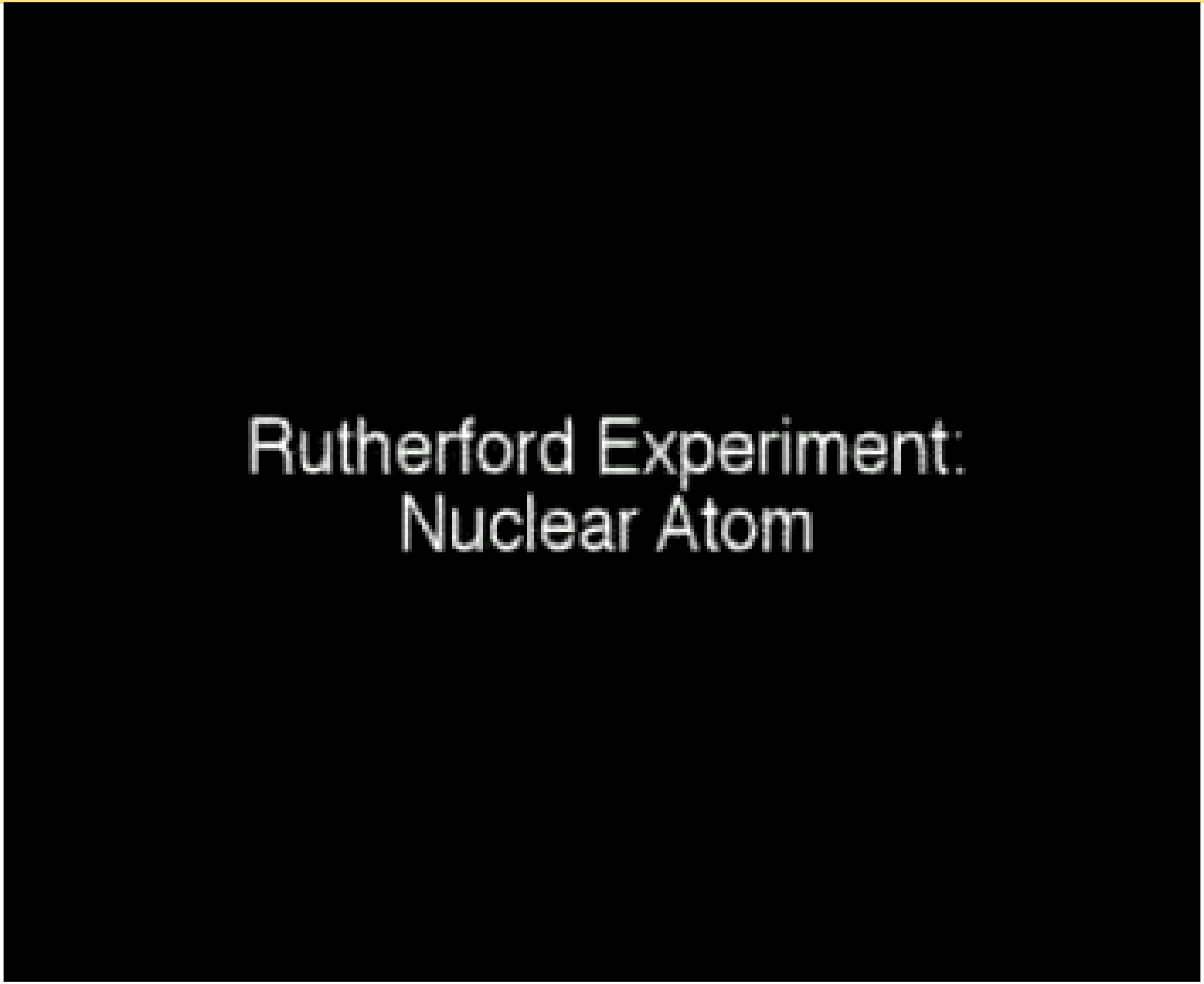


Ernest Marsden,
(1889 – 1970)

1909-2009: 100 YEARS OF NUCLEAR PHYSICS



E. RUTHERFORD: ***‘It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you. On consideration, I realized that this scattering backward must be the result of a single collision, and when I made calculations I saw that it was impossible to get anything of that order of magnitude unless you took a system in which the greater part of the mass of the atom was concentrated in a minute nucleus. It was then that I had the idea of an atom with a minute massive centre, carrying a charge.’***



Rutherford Experiment:
Nuclear Atom

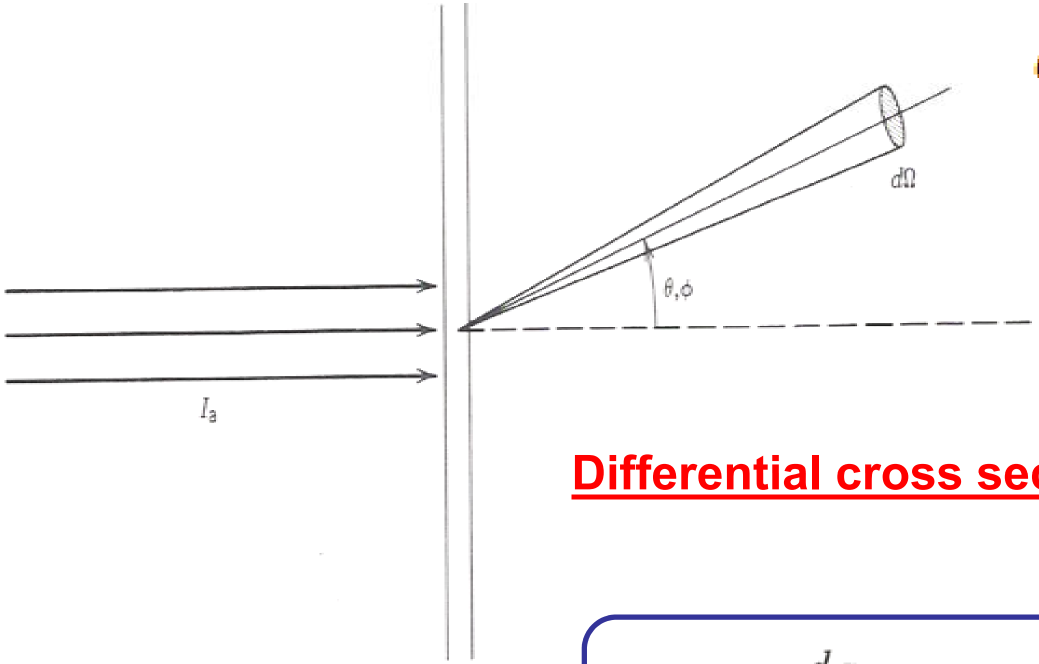
A short introduction in physics: The definition of the cross section

$$\boxed{\sigma = \frac{R_b}{I_a N_t}}$$

I_a = Current of incident particles per unit time (s^{-1})

R_b = Rate of outgoing particles (s^{-1})

N_t = Areal density of target atoms ($\#/cm^2$)



$$d\sigma = \frac{dR_b}{I_a N_t} \longrightarrow$$

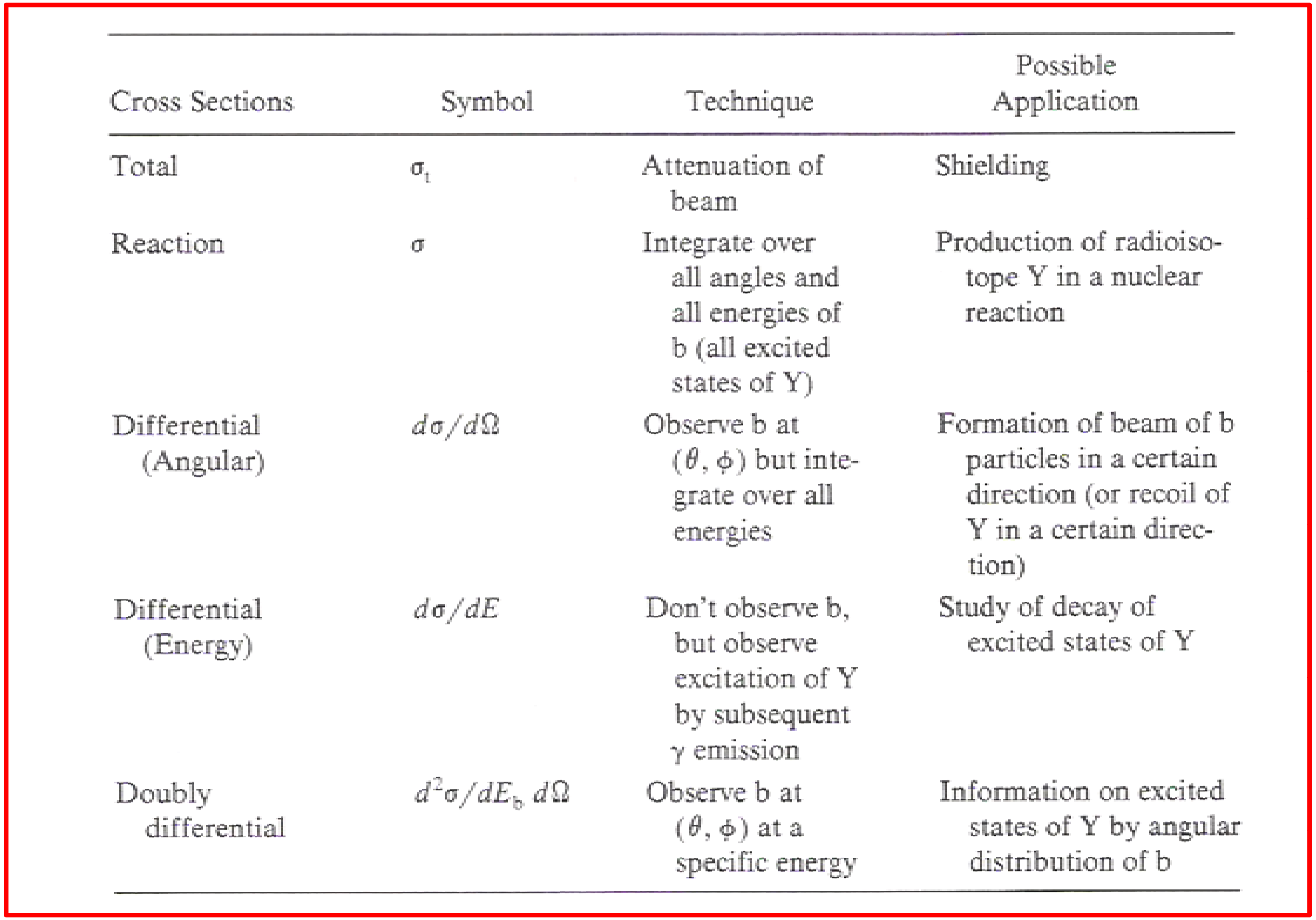
$$dR_b = \frac{r(\theta,\varphi)\,d\Omega}{I_a N_t 4\pi} \longrightarrow$$

Differential cross section:

$$\boxed{\frac{d\sigma}{d\Omega} = \frac{r(\theta,\varphi)}{I_a N_t 4\pi}}$$

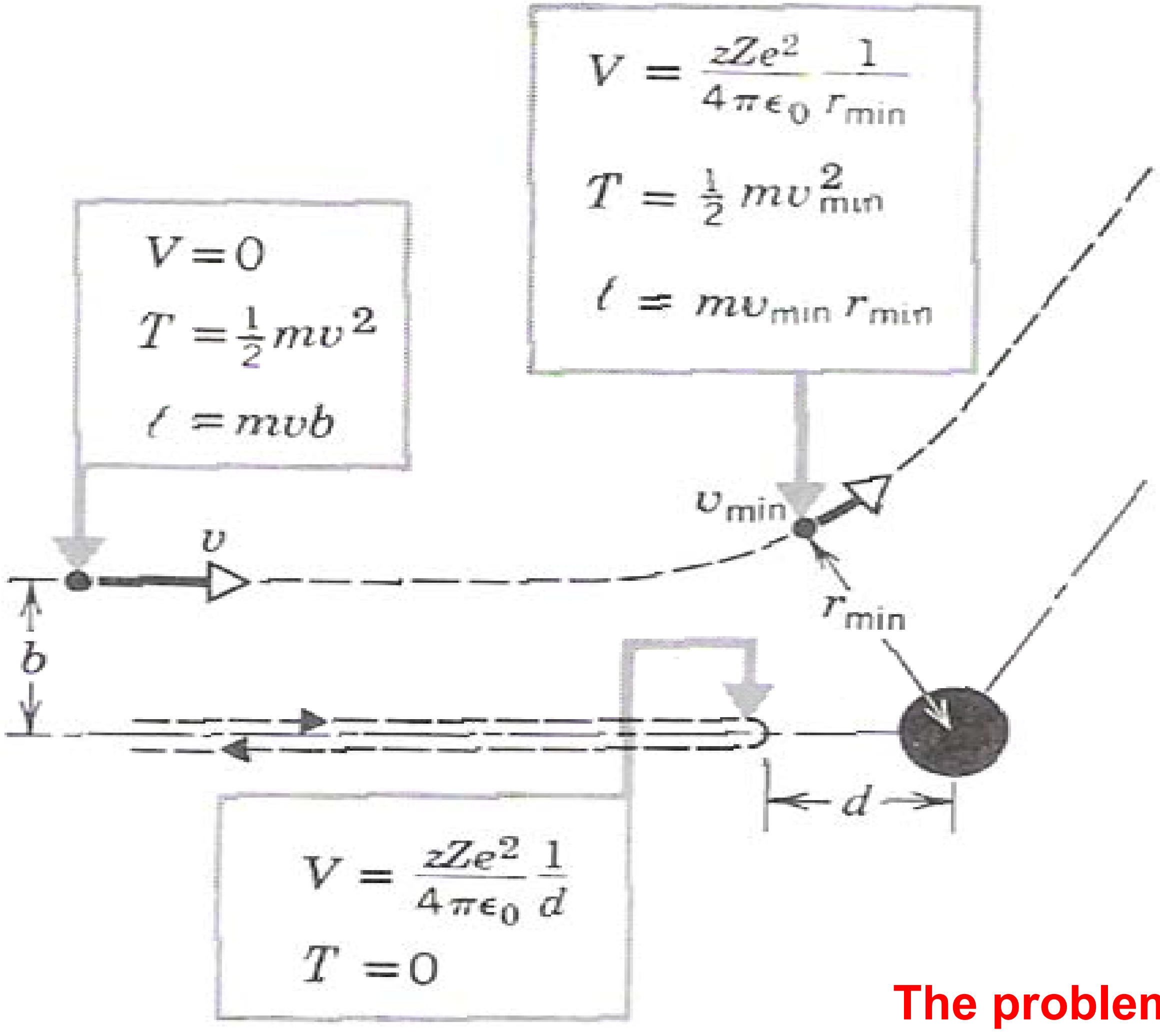
$$\boxed{\sigma = \int \frac{d\sigma}{d\Omega}\, d\Omega = \int_0^{\pi} \sin\theta\, d\theta \int_0^{2\pi} d\phi\, \frac{d\sigma}{d\Omega}}$$

$$a + X \longrightarrow b + Y$$



Cross Sections	Symbol	Technique	Possible Application
Total	σ_t	Attenuation of beam	Shielding
Reaction	σ	Integrate over all angles and all energies of b (all excited states of Y)	Production of radioisotope Y in a nuclear reaction
Differential (Angular)	$d\sigma/d\Omega$	Observe b at (θ, ϕ) but integrate over all energies	Formation of beam of b particles in a certain direction (or recoil of Y in a certain direction)
Differential (Energy)	$d\sigma/dE$	Don't observe b, but observe excitation of Y by subsequent γ emission	Study of decay of excited states of Y
Doubly differential	$d^2\sigma/dE_b\, d\Omega$	Observe b at (θ, ϕ) at a specific energy	Information on excited states of Y by angular distribution of b

A short introduction in physics: The Rutherford scattering



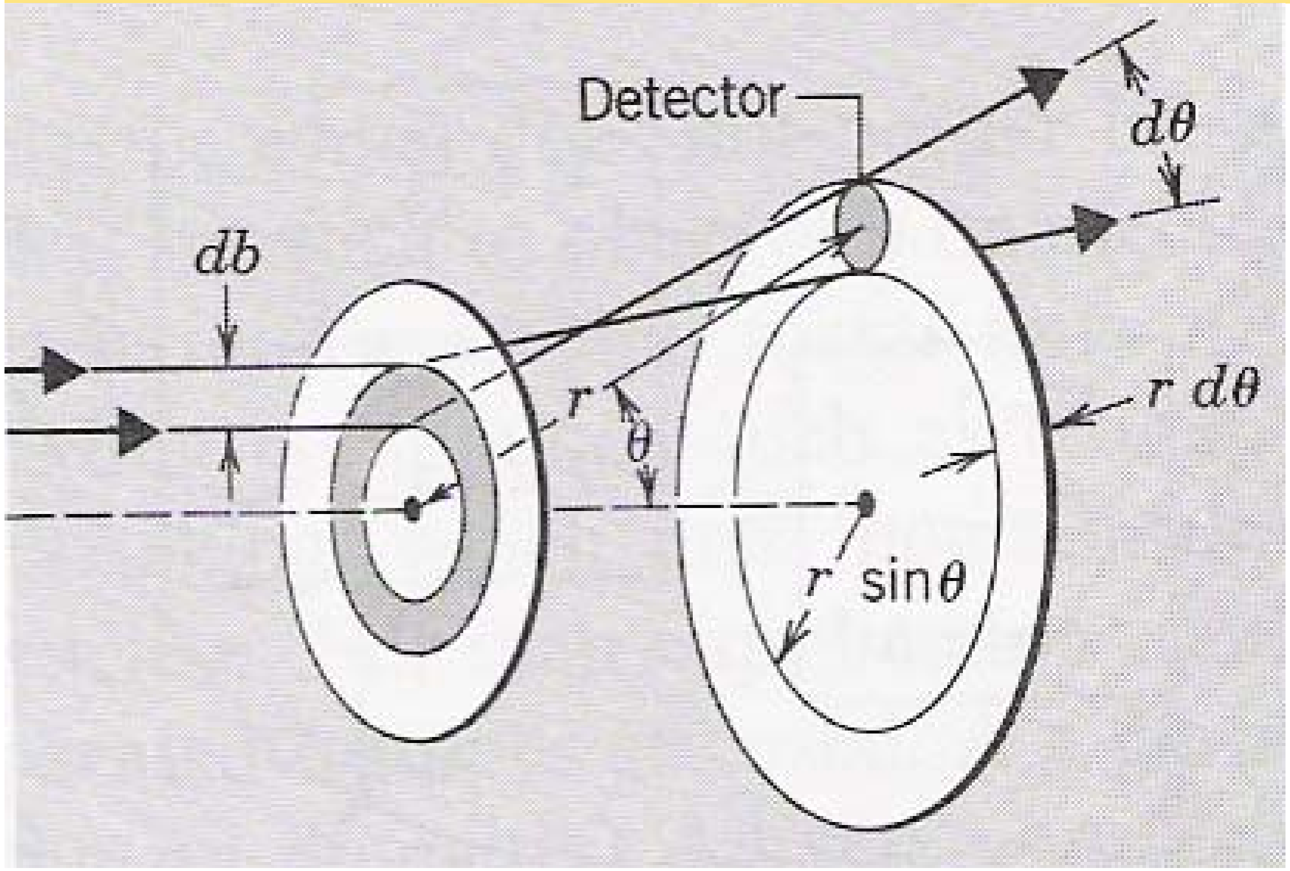
$$\frac{1}{2}mv_0^2 = \frac{1}{4\pi\epsilon_0}\frac{zZe^2}{d}$$

d = distance of closest approach
b = impact parameter

$$\frac{1}{2}mv_0^2 = \frac{1}{2}mv^2 + \frac{1}{4\pi\epsilon_0}\frac{zZe^2}{r}$$

(random position)

The problem presents cylindrical symmetry (or φ – invariance)



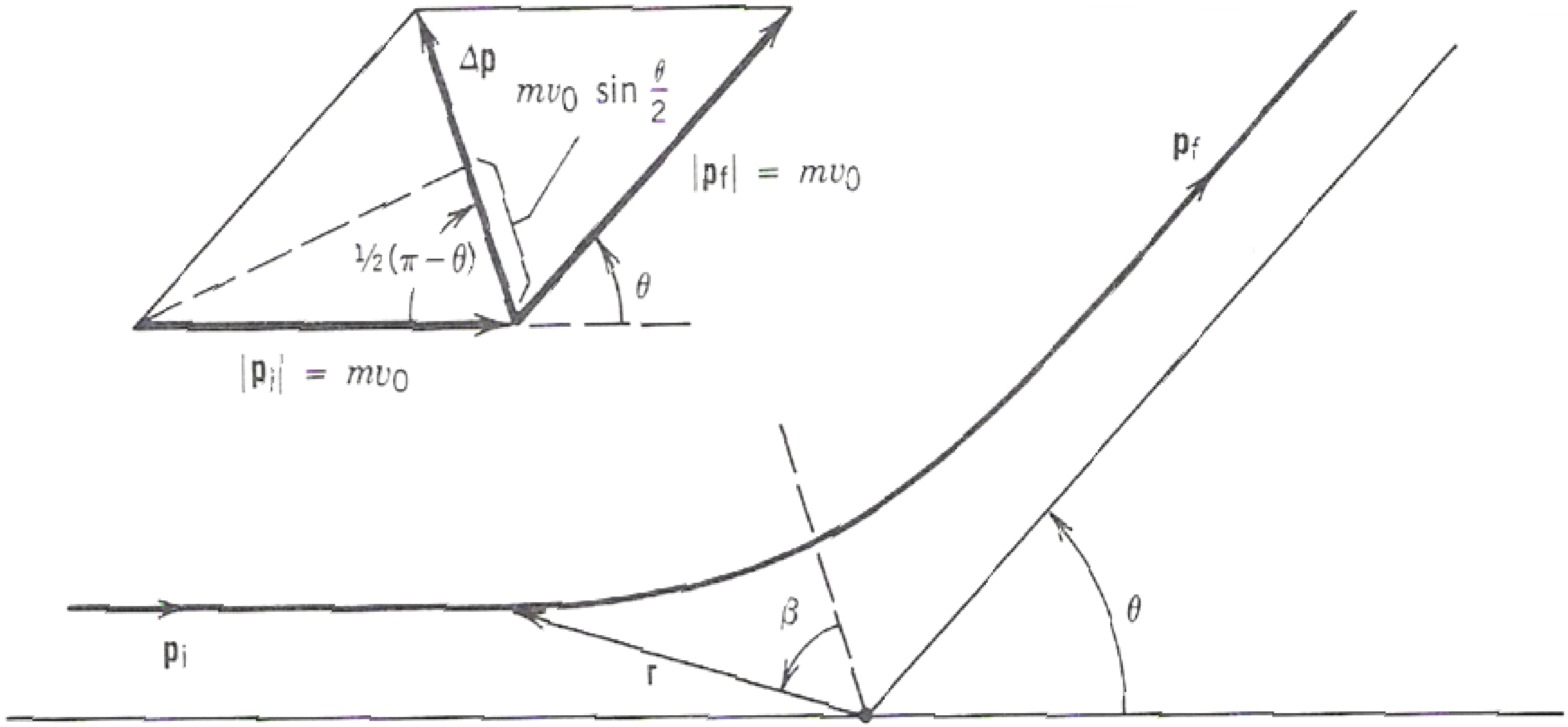
($nx = N_t$)

$$f = nx\pi b^2$$

(f = fraction of the incident particles with impact parameters less than b)

$$df = nx(2\pi b\,db)$$

(df = fraction of the incident particles that pass through the annular ring)



$$\Delta p = 2mv_0 \sin\frac{\theta}{2} \quad + \quad \Delta p = \int dp = \int F\,dt = \frac{zZe^2}{4\pi\epsilon_0}\int \frac{dt}{r^2}\cos\beta$$

$$v = \frac{dr}{dt}\hat{r} + r\frac{d\beta}{dt}\hat{\beta} \Longrightarrow \ell = |mr \times v| = mr^2\frac{d\beta}{dt}$$

$$mv_0 b = mr^2\frac{d\beta}{dt}$$

$$\frac{dt}{r^2} = \frac{d\beta}{v_0 b}$$

$$\boxed{\begin{aligned}\Delta p &= \frac{zZe^2}{4\pi\epsilon_0 v_0 b}\int_{-(\pi/2-\theta/2)}^{+(\pi/2-\theta/2)}\cos\beta\, d\beta \\ &= \frac{zZe^2}{2\pi\epsilon_0 v_0 b}\cos\frac{\theta}{2}\end{aligned}}$$

And taking into account that:

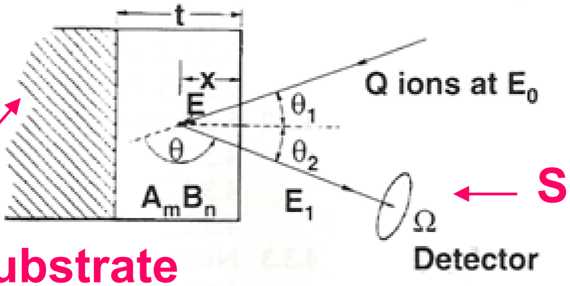
$$\Delta p = 2mv_0 \sin\frac{\theta}{2} \Longrightarrow \boxed{b = \frac{d}{2}\cot\frac{\theta}{2}}$$

$$\left.\begin{aligned} |df| &= \pi n x \frac{d^2}{4} \cot\frac{\theta}{2} \csc^2\frac{\theta}{2}\, d\theta \\[2em] r(\theta,\phi) &= \frac{I_a |df|}{d\Omega/4\pi} \end{aligned}\right\} \Longrightarrow$$

$$\Longrightarrow \boxed{\frac{d\sigma}{d\Omega} = \left(\frac{zZe^2}{4\pi\epsilon_0}\right)^2 \left(\frac{1}{4T_a}\right)^2 \frac{1}{\sin^4\dfrac{\theta}{2}}}$$

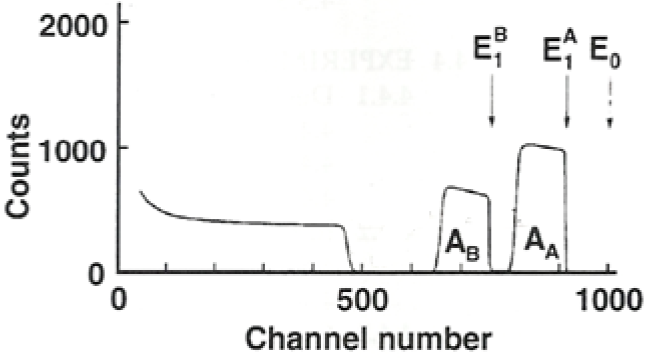
(Differential cross section / Rutherford formula in the c.m. system)

Rutherford Backscattering Spectrometry (RBS)



SSB

Light substrate



$$K_i \equiv E_1^i / E_0$$

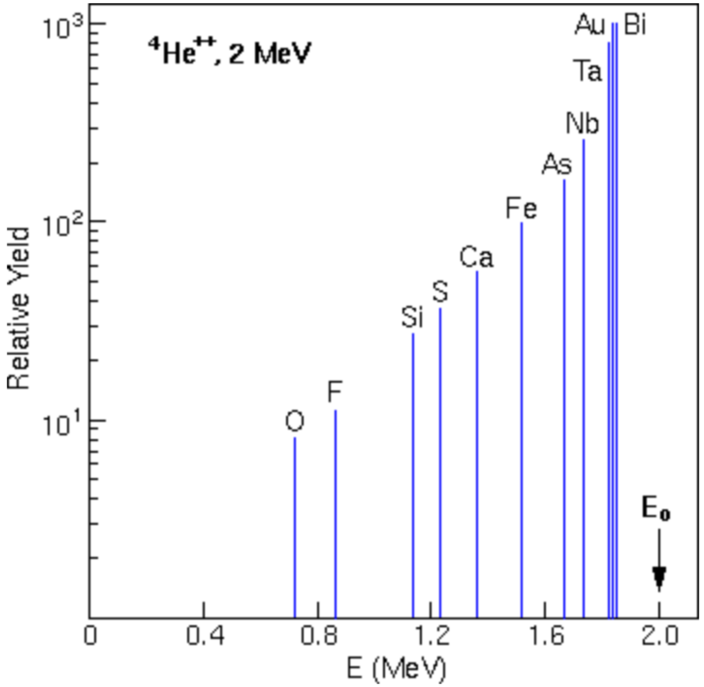
$$K = \left[\frac{\left(M_2^2 - M_1^2 \sin^2\theta\right)^{1/2} + M_1 \cos\theta}{M_1 + M_2}\right]^2$$

$$\sigma_R(E,\theta) = \left(\frac{Z_1 Z_2 e^2}{4E}\right)^2 \times \frac{4\left[\left(M_2^2 - M_1^2 \sin^2\theta\right)^{1/2} + M_2 \cos\theta\right]^2}{M_2 \sin^4\theta \left(M_2^2 - M_1^2 \sin^2\theta\right)^{1/2}}$$

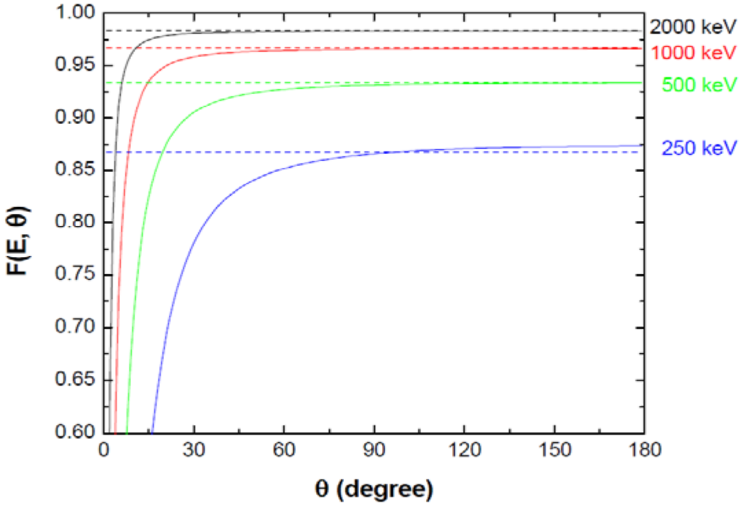
Experimental Yield

Atoms/cm²

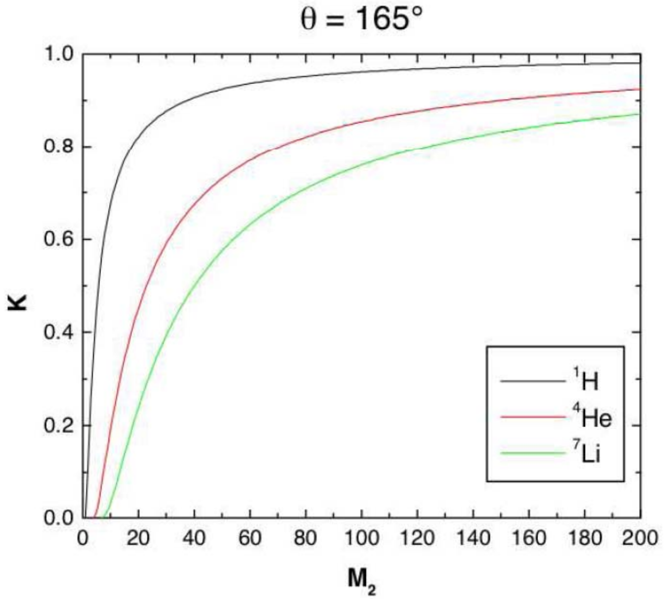
$$(Nt)_i = \frac{A_i \cos\theta_1}{Q\Omega\sigma_i\,(E,\theta)}$$



The relative yield differs between high – and low-Z nuclei by almost two orders of magnitude, thus RBS is ideal for heavy elements on light substrates.



Actual cross-sections deviate from Rutherford at low energies for all projectile-target pairs. This is caused by partial screening of the nuclear charges by the electron shells surrounding both nuclei. This screening is taken into account by a correction factor F: $\sigma = F \sigma_R$



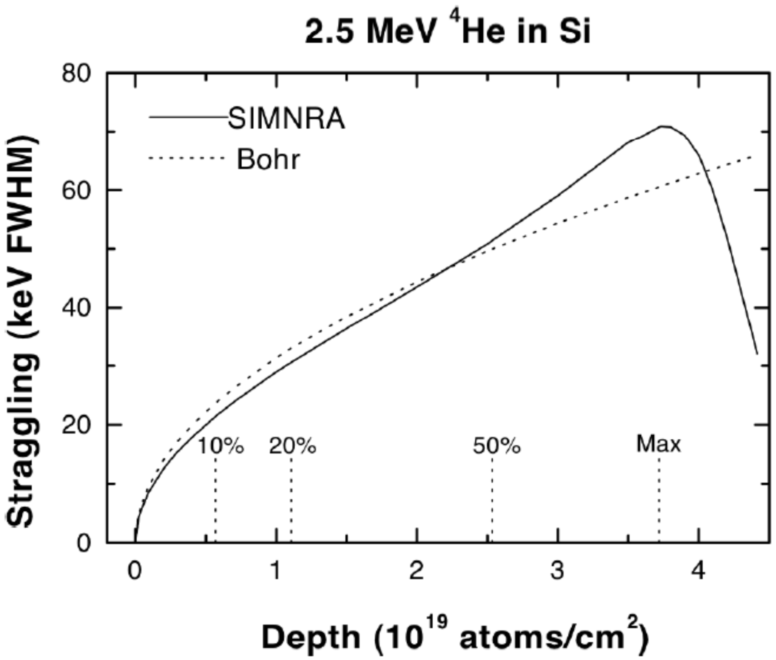
The kinematic factor varies dramatically with the ion beam mass and approaches unity for protons impinging on heavy elements. It depends only on the mass ratio M_1/M_2 and on the scattering angle θ.

$$\Delta E_1 = E_0(4-\delta^2)\left(\frac{M_1}{M_2^2}\right)\Delta M_2$$

$$\delta = \pi - \theta$$

To obtain good mass resolution, the coefficient of ΔM_2 has to be as large as possible. To accomplish this one can:

- ✓ ***Increase E_0***
- ✓ ***Increase M_1***
- ✓ ***Set θ very close to 180^o***

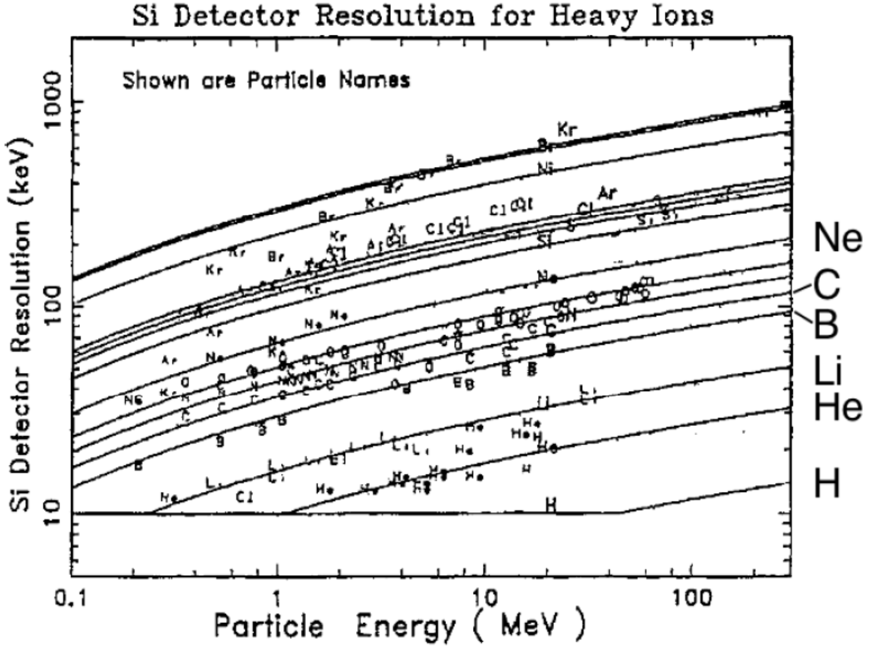


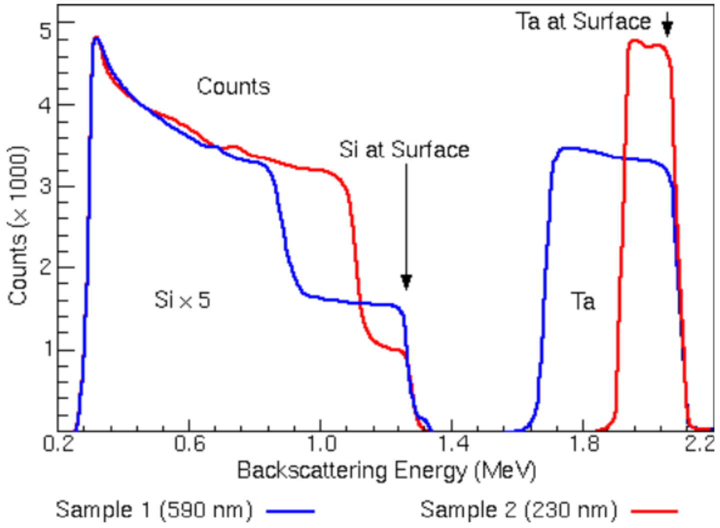
Two basic phenomena affecting RBS measurements:

Energy straggling of the incident ions

and

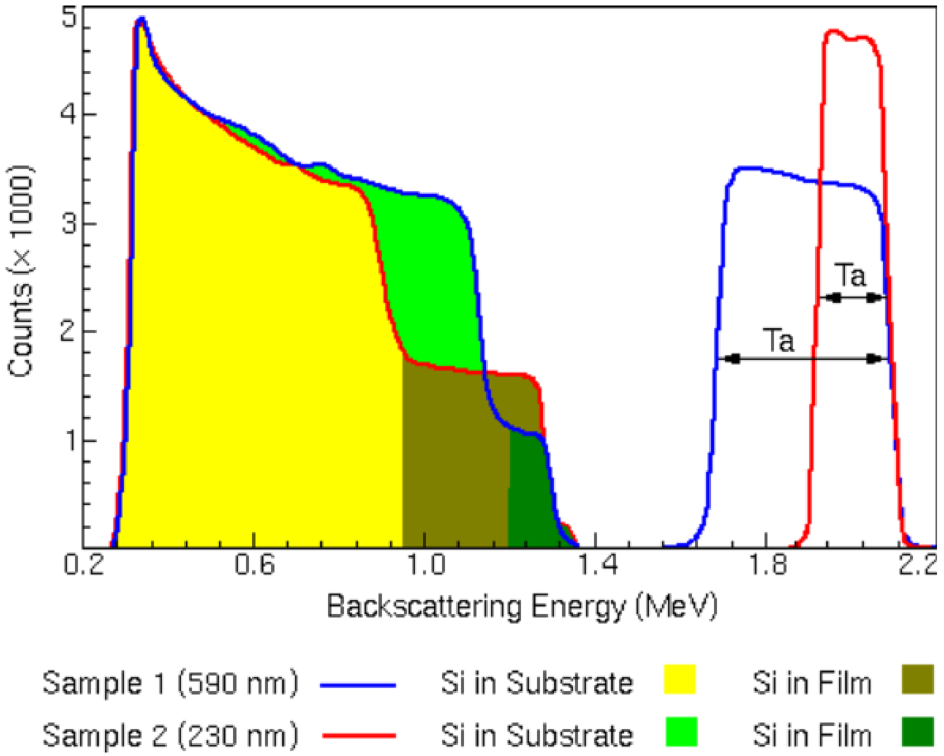
Limited resolution of the SSB detectors

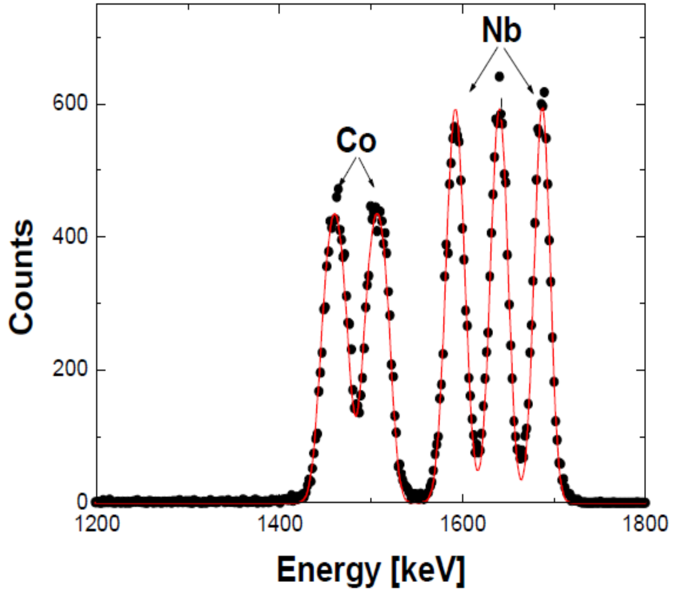




Step by step analysis of two thin Ta_xSi_y silicides on a Si substrate, using 2.2 MeV α-particles

RBS spectra are analyzed from high to low energies (right to left)

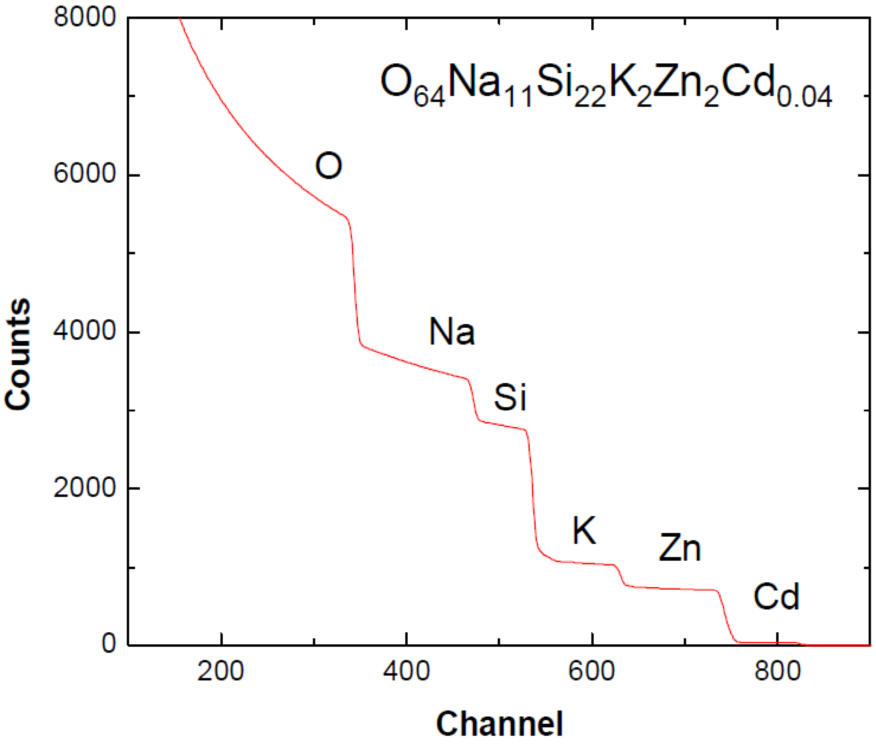


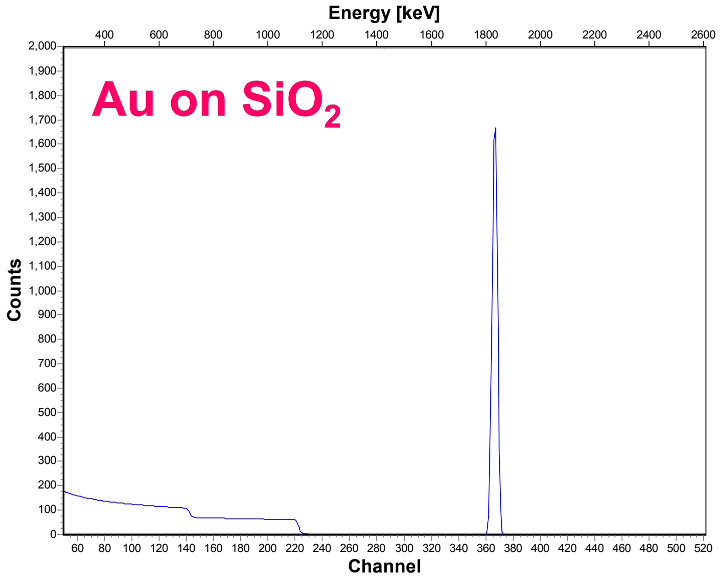


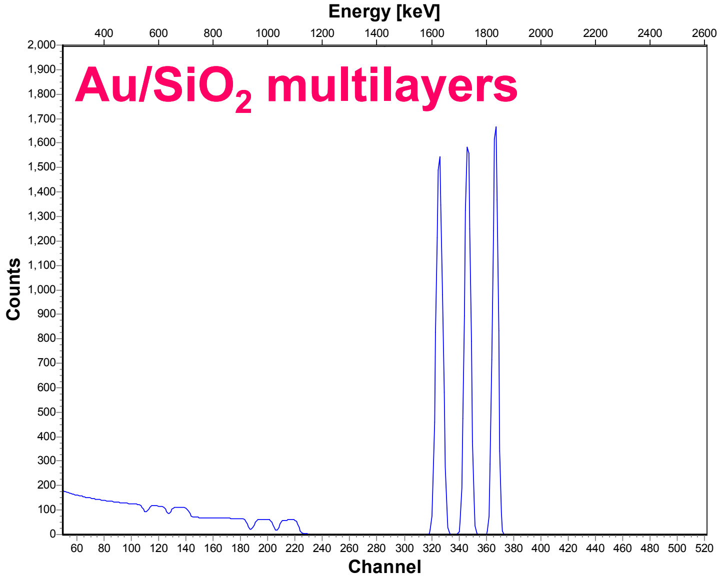
Multilayered structure

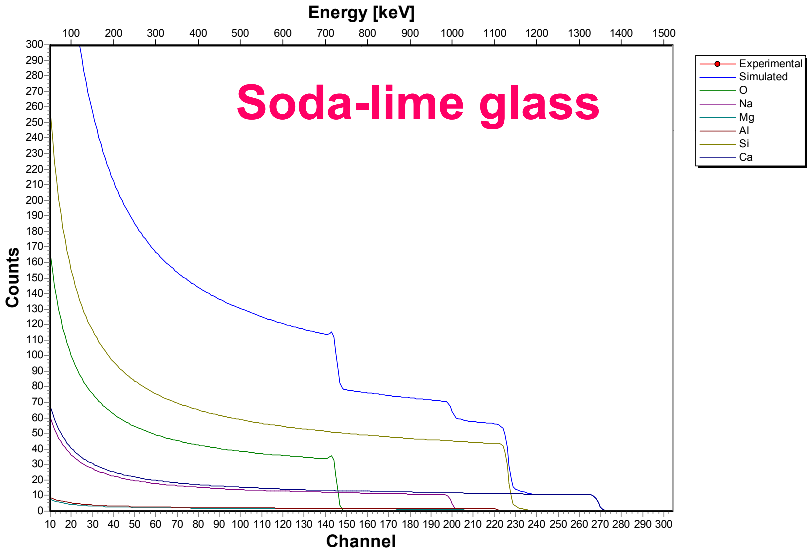
Nb: 1.0×10^{17} at/cm^2
Co: 2.2×10^{17} at/cm^2

Ceramic glass – thick target



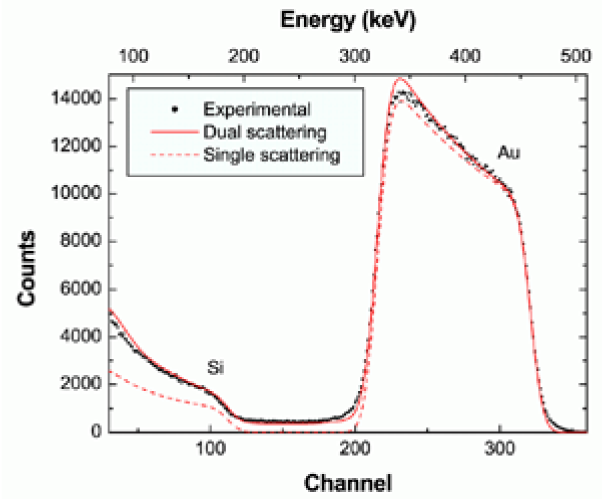

Au on SiO_2


Au/SiO_2 multilayers

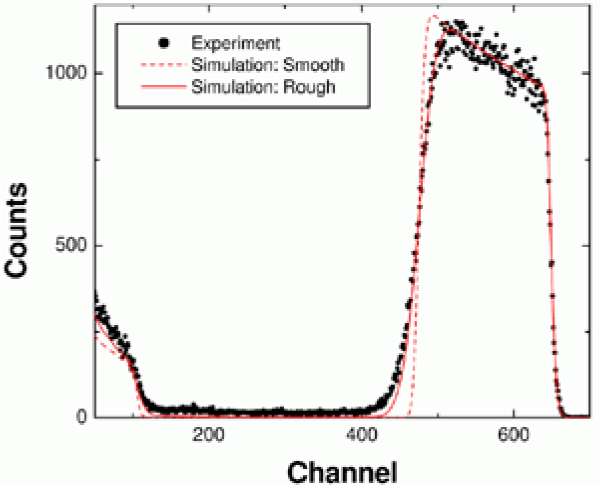

Soda-lime glass

2 MeV ^{4}He, θ=165°

RBS examples demonstrating the power of the technique



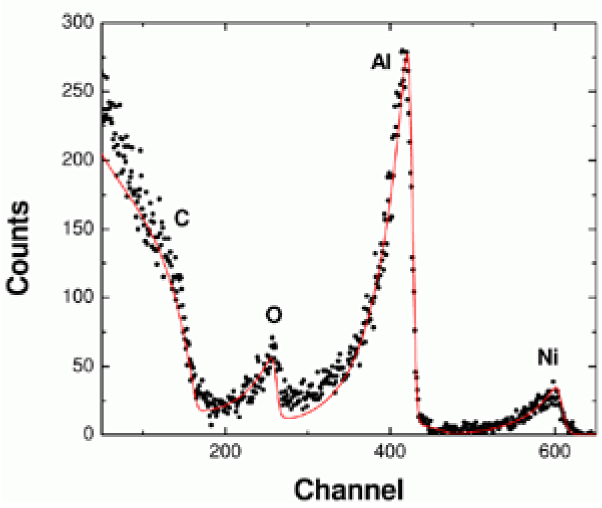
500 keV ^{4}He



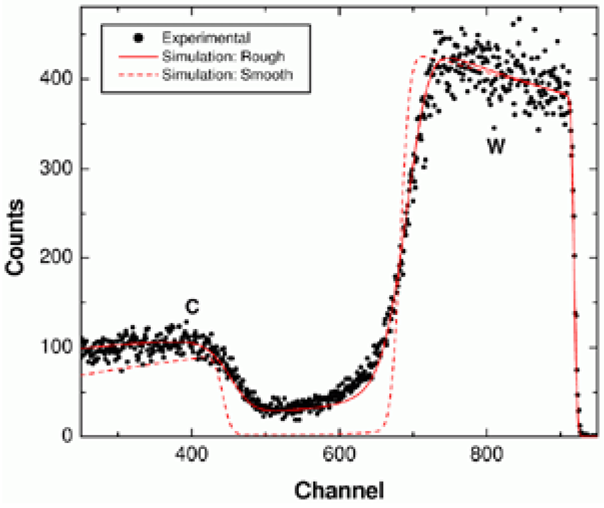
1.5 MeV ^{4}He

θ=165°

2 MeV ^{4}He



2.5 MeV ^{1}H



Main RBS difficulties:

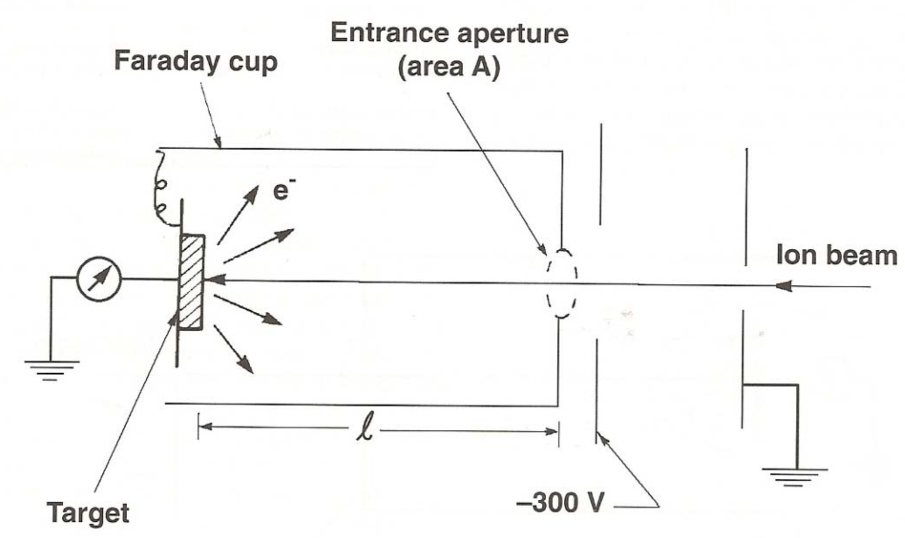
- ✓**Plural scattering**
- ✓**Rough surfaces**
- ✓ **Crystalline targets**
- ✓**Light elements on heavy substrates**

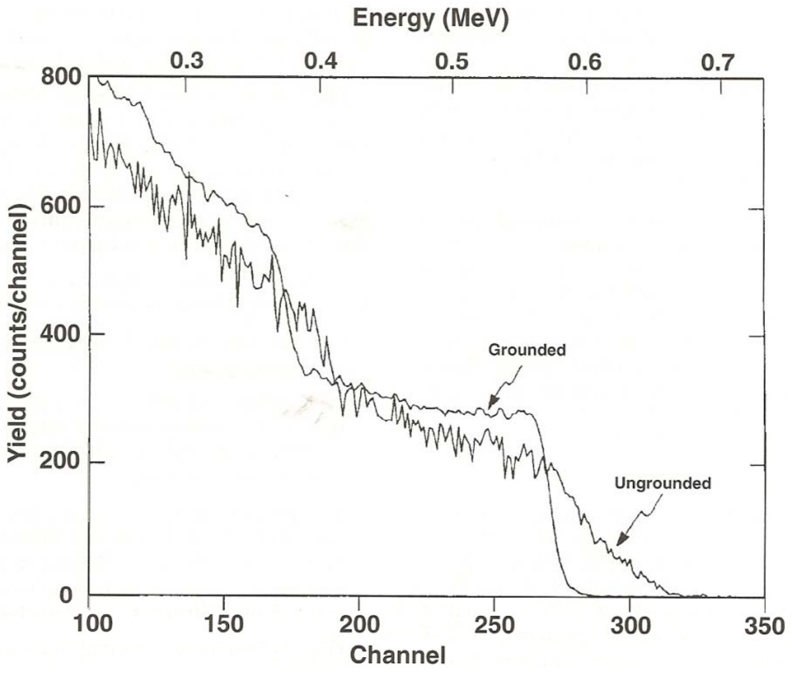
Other important RBS difficulties:

✓ Measurement of the charge

✓ Charging of surface in the case of insulators

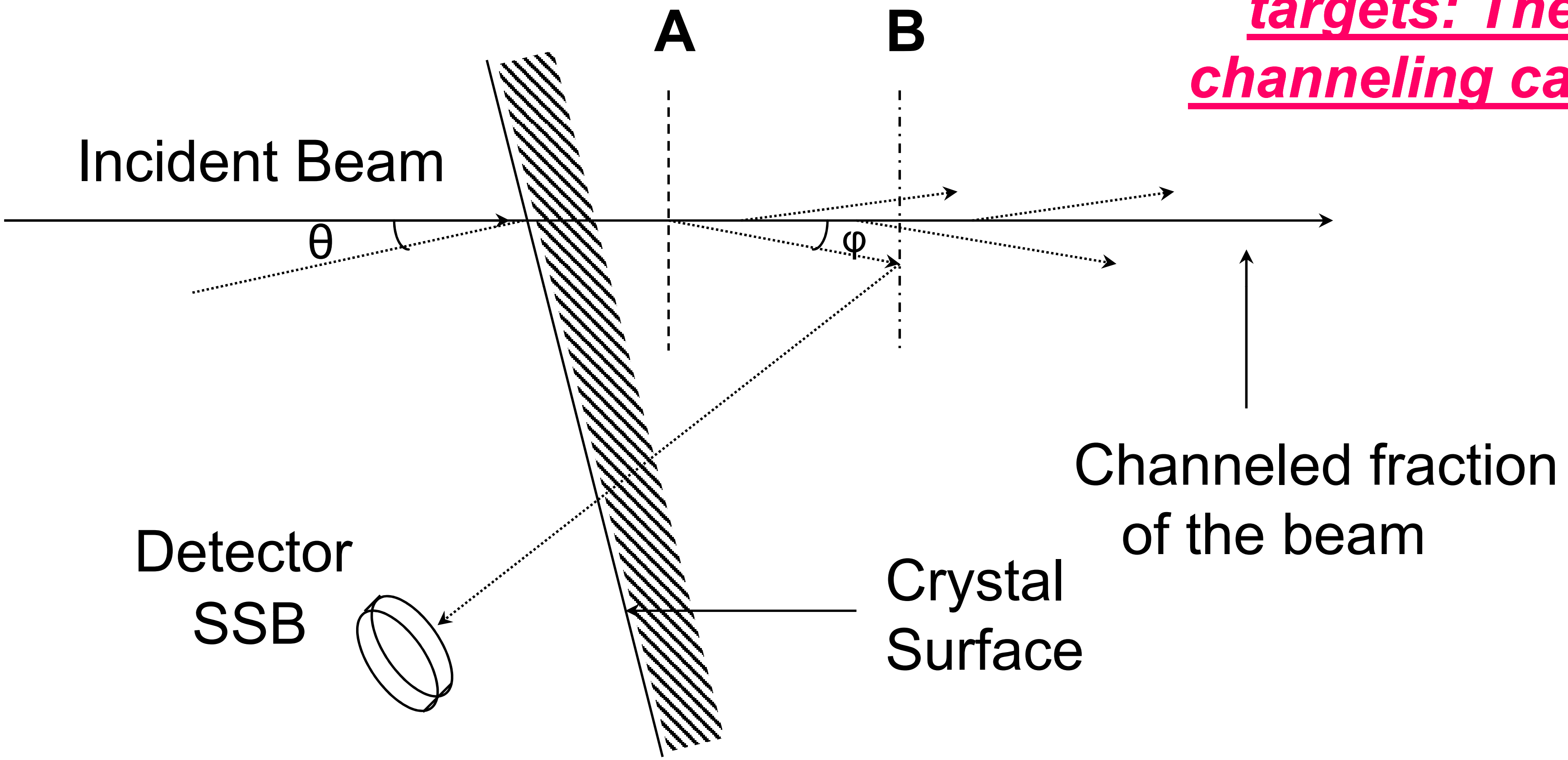
✓ Other problems (sputtering, heating, solid angle calibration, accelerator calibration, non-uniformity of targets, Δm, signal mixing etc.)



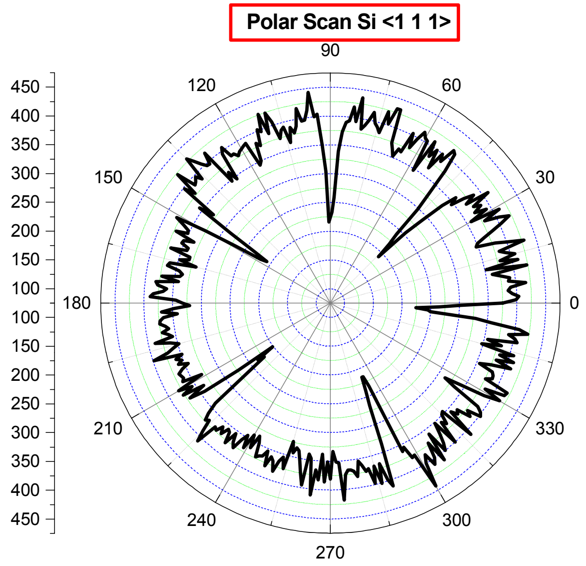


The problem of crystalline targets: The channeling case

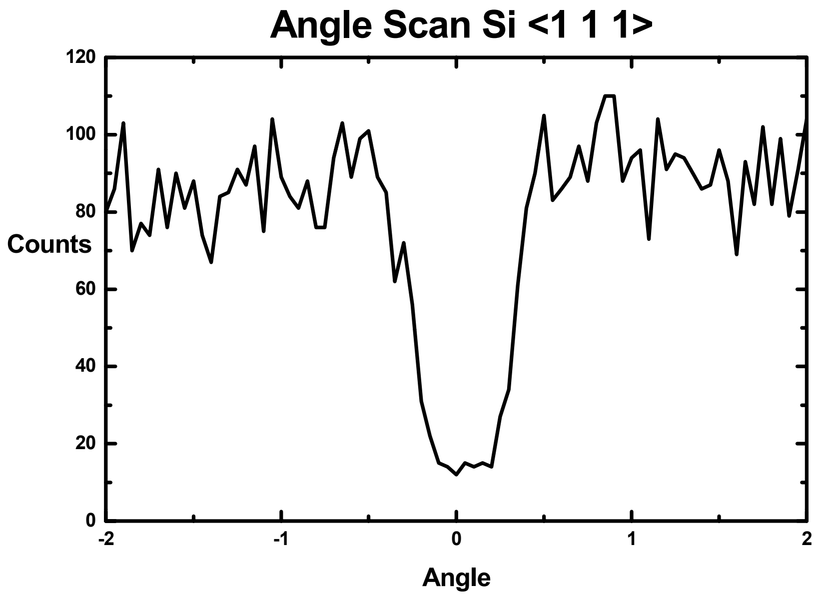
A = point of dechanneling
B = point of backscattering



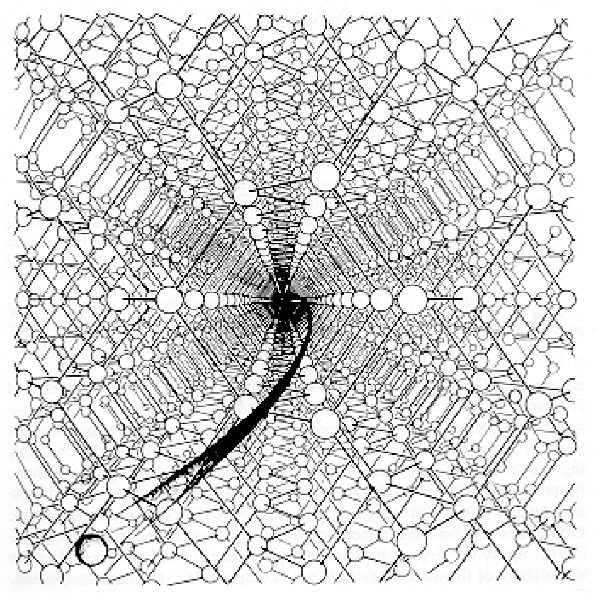
θ = alignment angle with crystal axis
φ = small dechanneling angle

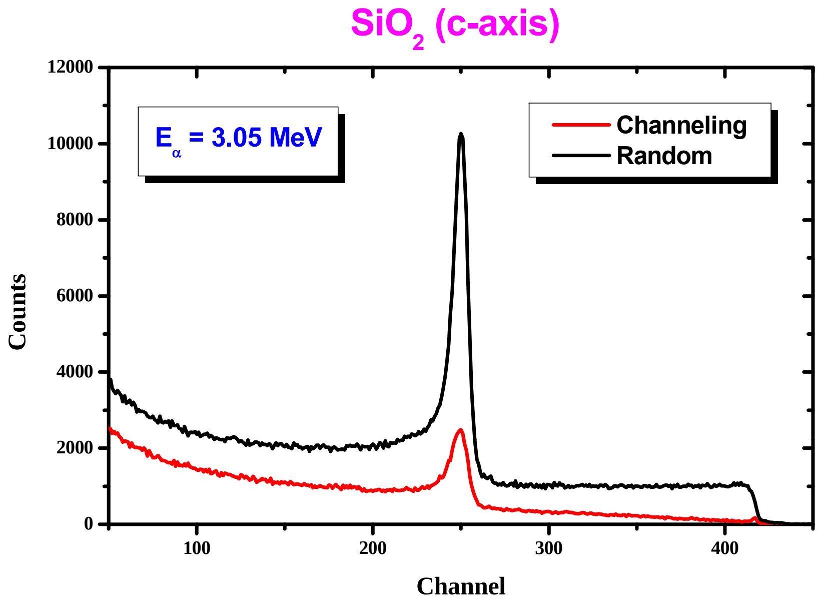


Polar Scan Si <1 1 1>



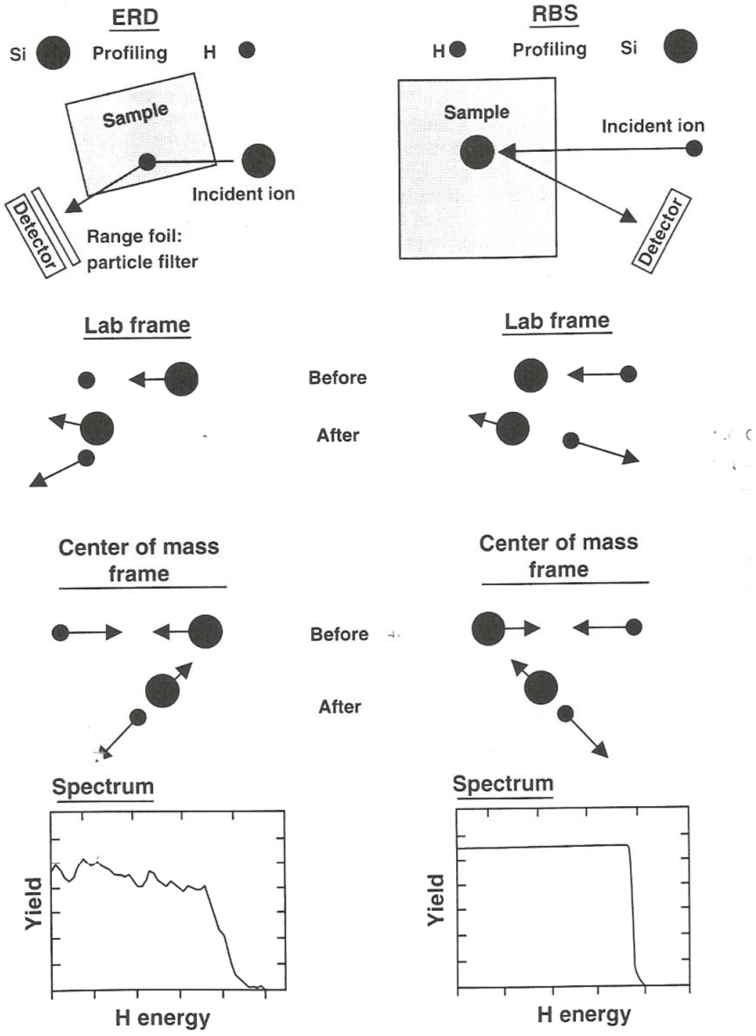
Angle Scan Si <1 1 1>

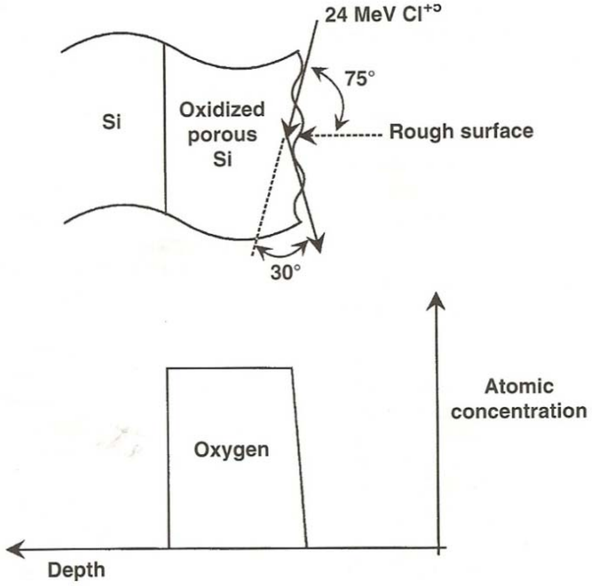


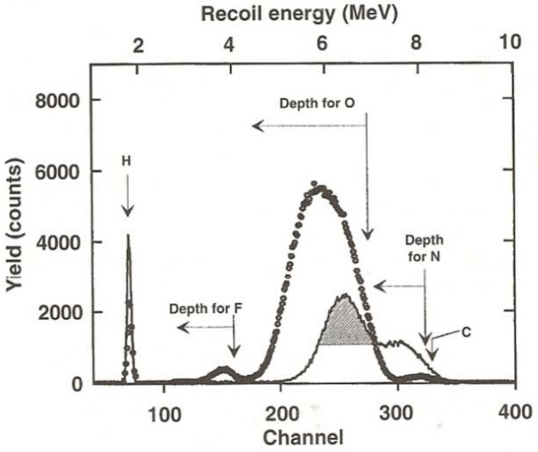


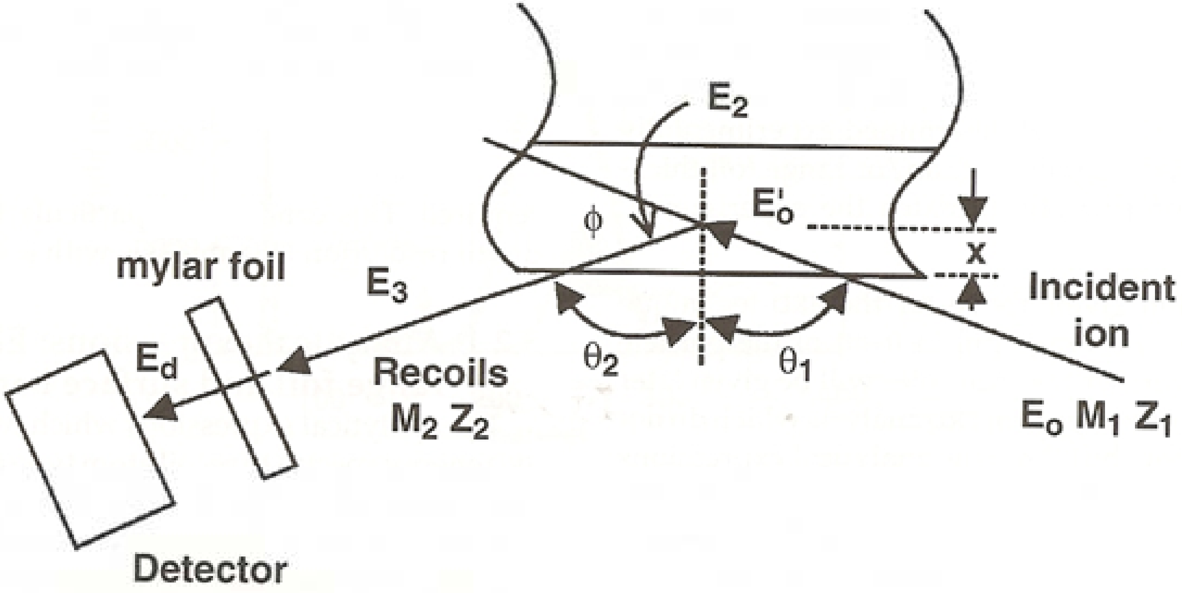
SiO$_2$ (c-axis)

The problem of light element detection: ERDA (Elastic Recoil Detection Analysis)

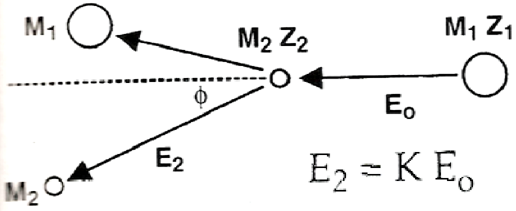








Kinematics lab frame



$$E_2 = K\,E_o$$

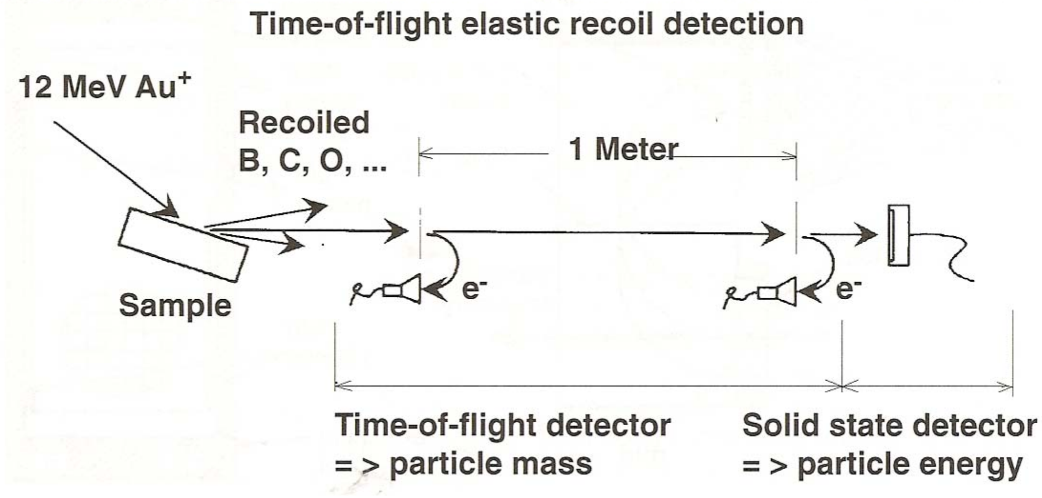
$$K = \frac{4\,M_1\,M_2\cos^2\phi}{(M_1+M_2)^2}$$

$$\sigma_r(E'_o,\phi) = \frac{[Z_1\,Z_2\,e^2\,(M_1+M_2)]^2}{[2\,M_2\,E'_o]^2\cos^3\phi}$$

$$Y_r(E_d) = \frac{Q\,N_r(x)\,\sigma_r(E'_o,\phi)\,\Omega\,\delta E_d}{\cos\Theta_1\,dE_d/dx}$$

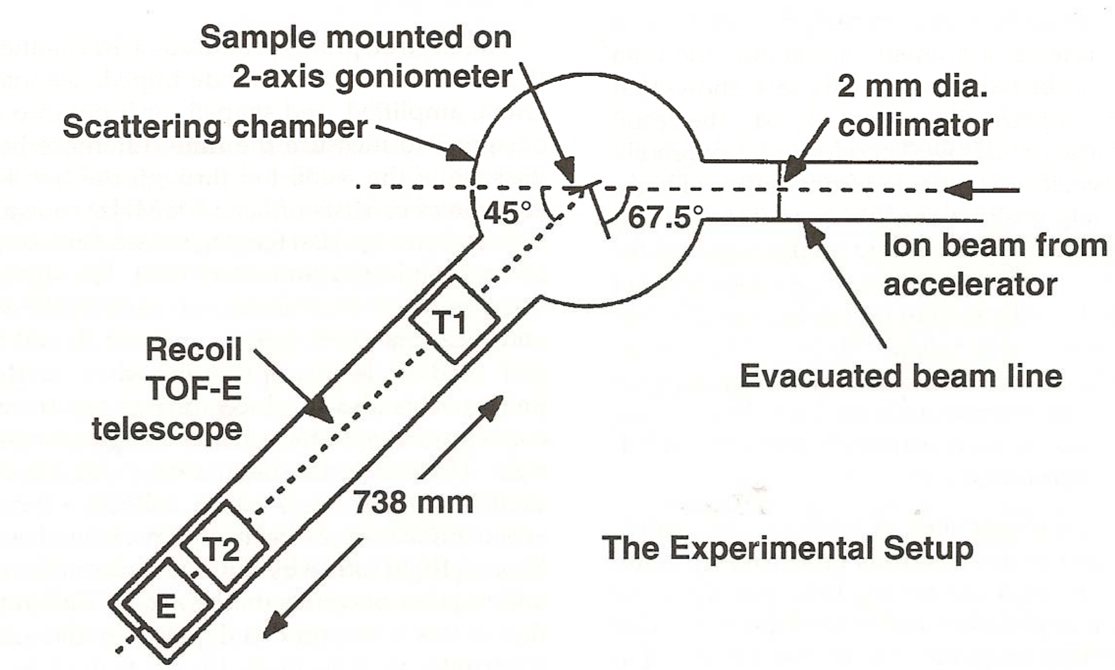
ERDA is complementary to RBS

New trends in ERDA measurements: TOF-ERDA



Main problems:

1. Need for high energy heavy ions (big accelerators)
2. Limited analyzing depth (~1 μm)



Other solutions in the problem of light element detection: EBS, resonances in elastic scattering

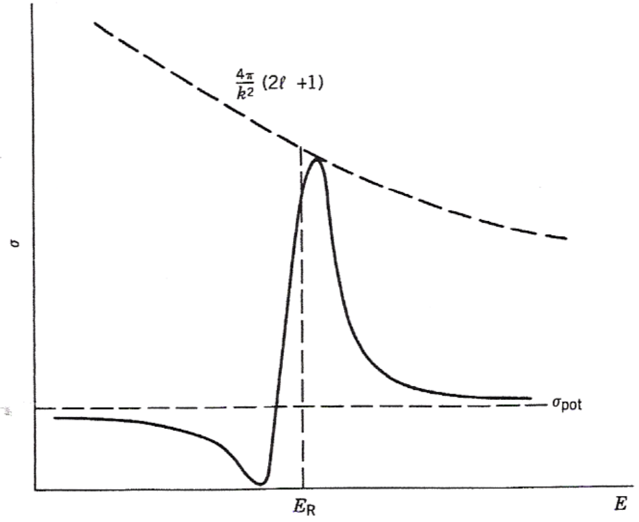
a+X → C* → a+X

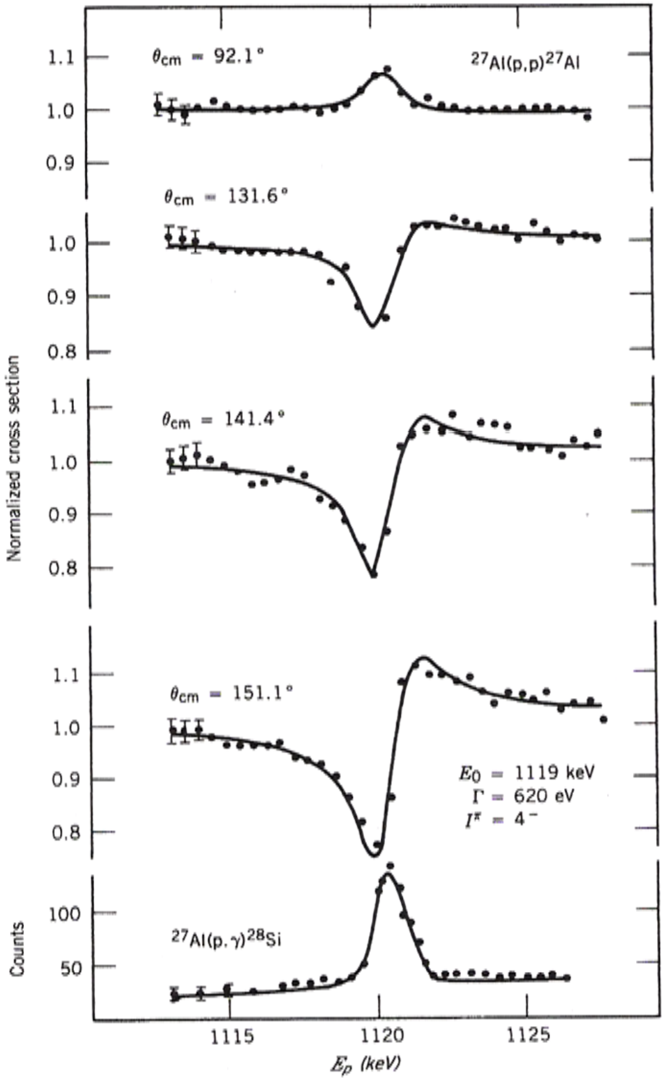
e.g. $E_p + Q = E_R$

+ Potential Scattering (Rutherford) = Always an Increase?

NO, (dual nature)

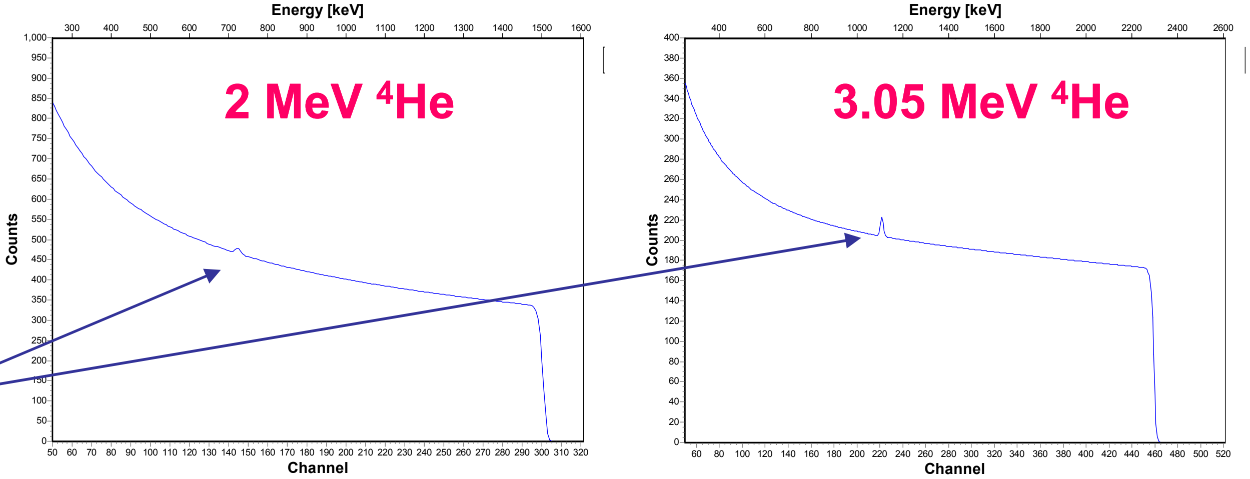
$$\sigma = \frac{\pi}{k^2} g \frac{(\Gamma_{aX})^2}{(E - E_R)^2 + \Gamma^2/4}$$



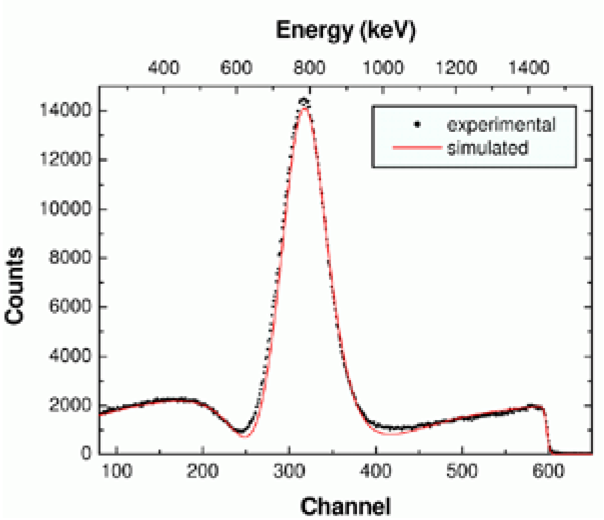


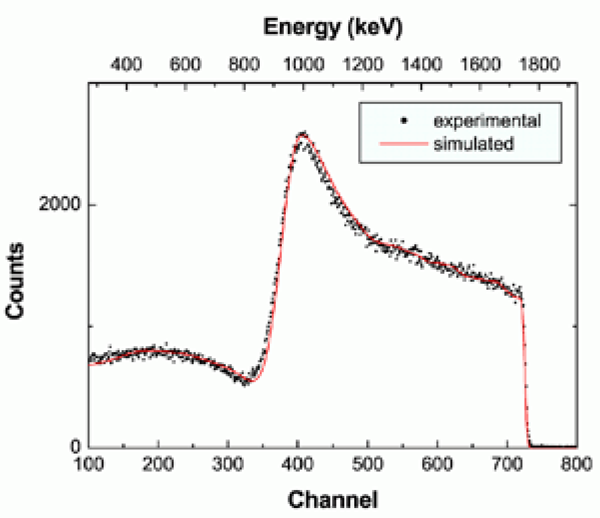
<u>EBS:</u> Formation of a compound nucleus → Interference between resonant and potential scattering

Ultra thin oxidized Fe on a pure Fe substrate



2 MeV protons on carbon and silicon at 165°

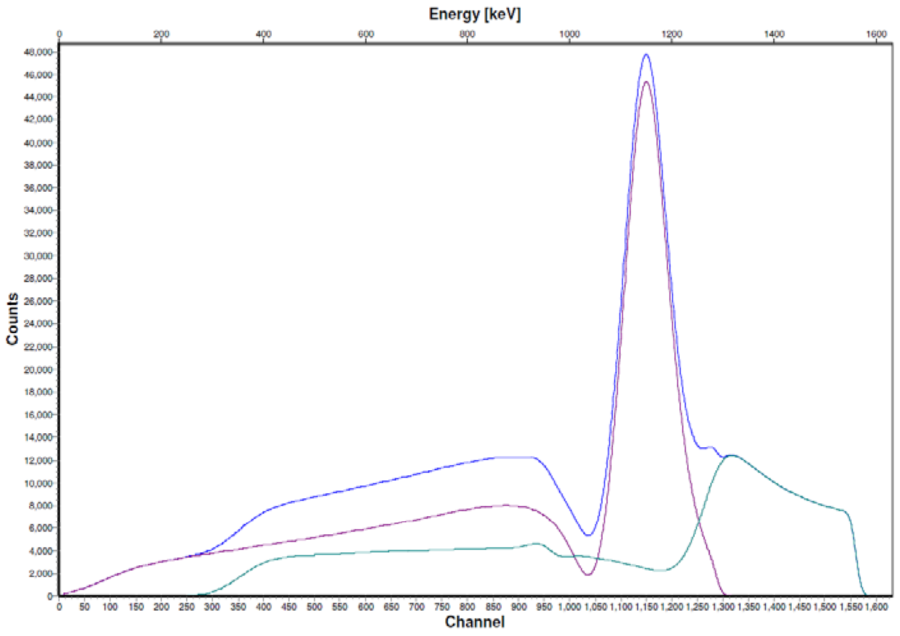




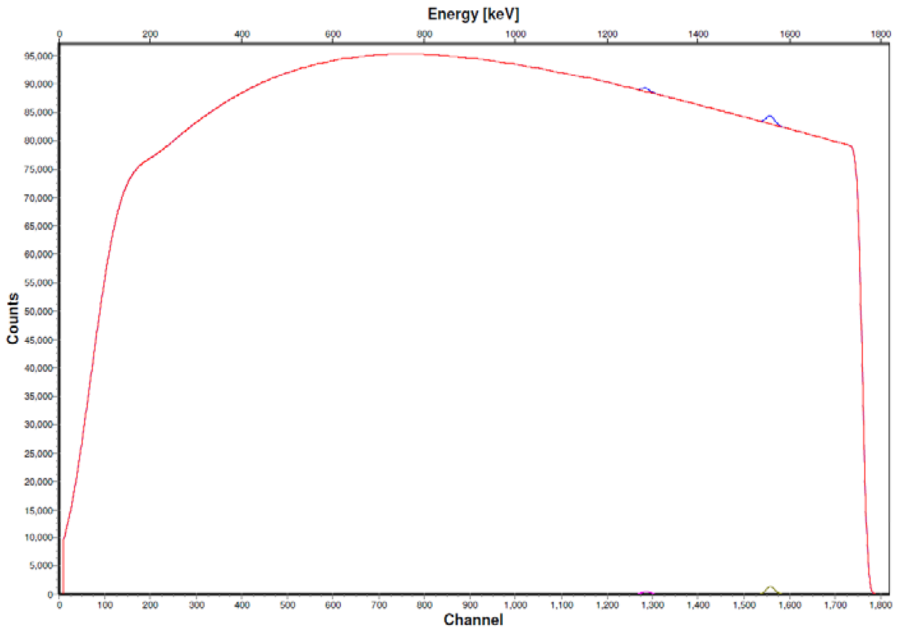
Main difficulties in employing EBS:

1. Need for accurate/evaluated differential cross sections from literature
2. Overlapping resonances of different light elements
3. The (heavy) matrix may sometimes be important, impeding the analysis

E_p = 1.8 MeV (Si, C, total)



E_p = 1.8 MeV (Thin SiC layer on Au)

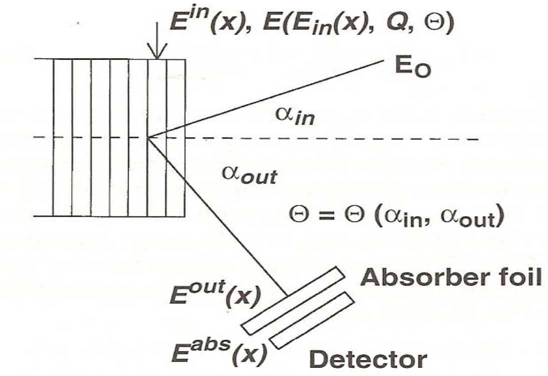


Nuclear Reaction Analysis (particle-particle)

NRA: Well – established nowadays as one of the principal IBA techniques for accurate quantitative depth profiling of light elements in complex matrices.

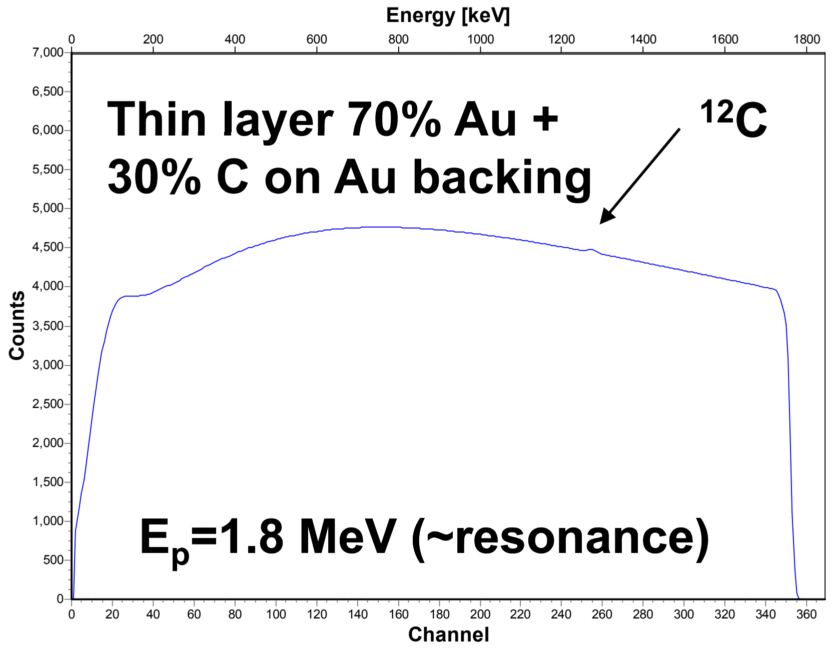
Based on the use of nuclear reactions. More frequently used:

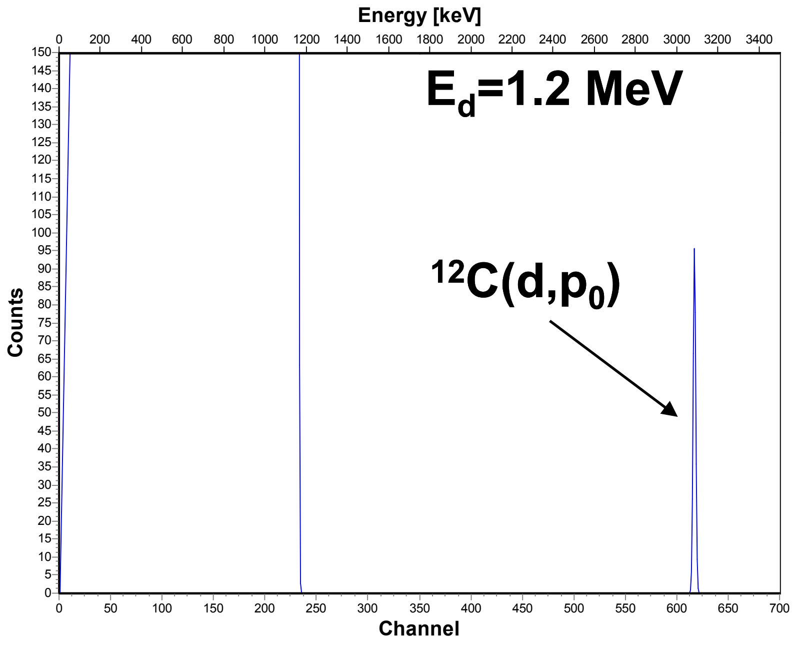
1. (p,α): **Low Q-value (^{6}Li, ^{9}Be, ^{10}B, ^{27}Al) and high Q-value (^{7}Li, ^{11}B, ^{18}O, ^{19}F, ^{23}Na, ^{31}P). No absorber foil can be applied. Highly selective.**
2. (α,p): **Very few elements have positive Q-values (^{10,11}B, ^{19}F, ^{23}Na, ^{27}Al, ^{31}P, ^{35}Cl) thus the background is severely reduced. Cross sections are high enough only at high beam energies.**
3. (d,p) and (d,α): **Almost all light isotopes have high positive Q-values. They permit simultaneous analysis of many light elements in complex matrices (e.g. C, O, N, B, S etc.) at the expense of peak overlaps or background interference in some cases. Require very low beam energies. Radiation safety precautions are mandatory because the (d,n) reaction channel is almost always open.**
4. *Less frequently used: (p,d), (p,^{3}He), ^{3}He-NRA*

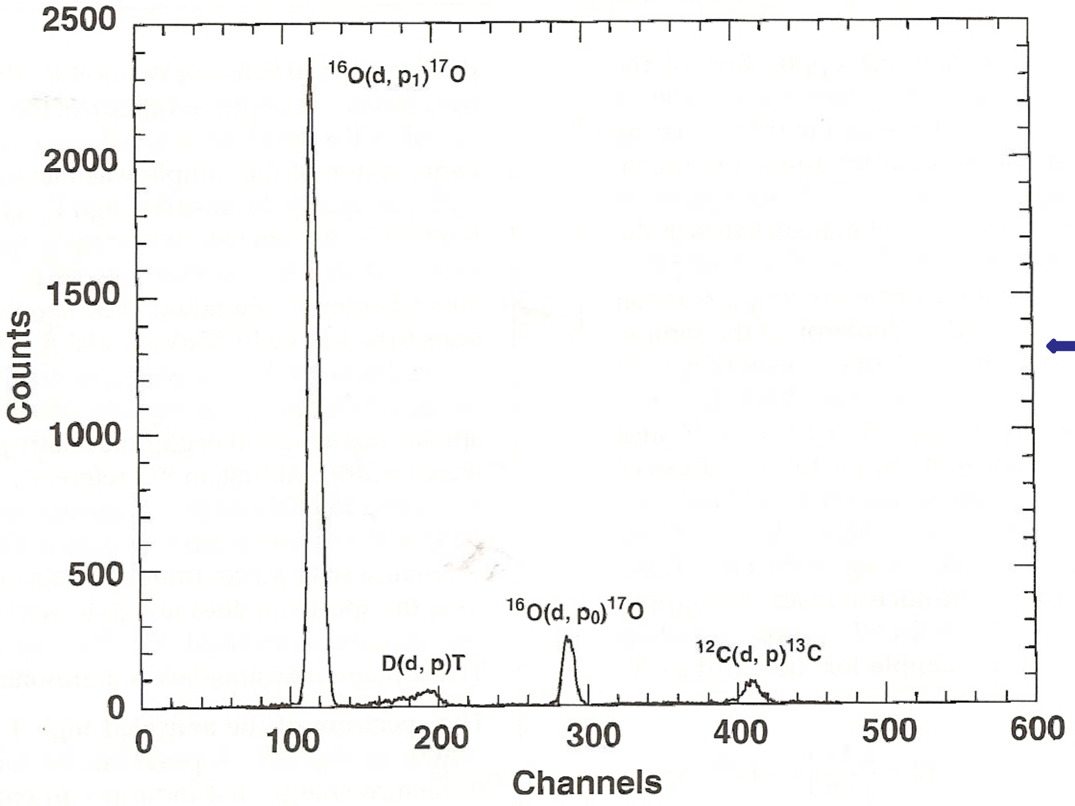


Similar experimental setup

e.g. The ‘carbon problem’: RBS is weak, EBS can be applied only in certain cases (no other interfering light elements present, no high-Z matrix, very case-specific measurements):







834 keV deuterons on a thick SiO_2/Si sample, using an absorber foil in front of the detector

Interesting points:

- ***Excitation of all possible kinematically permitted states***
- ***Excitation of several isotopes***
- ***Excitation of unwanted, background isotopes!***

Special NRA Characteristics:

POSITIVE

✓ ***High isotopic selectivity***

✓ ***The matrix is not so important***

✓ ***Clear isolated peaks with practically no background***

✓ ***If the deuteron beam is adopted, one can achieve simultaneous analysis of most of the main light elements (C, O, N, F, B, Li)***

NEGATIVE

➲ ***Not many cross sections available in literature / theoretical evaluation pending***

➲ ***Usually time-consuming studies***

➲ ***Not all the elements present low enough MDLs***

➲ ***Radiation safety is sometimes an issue***

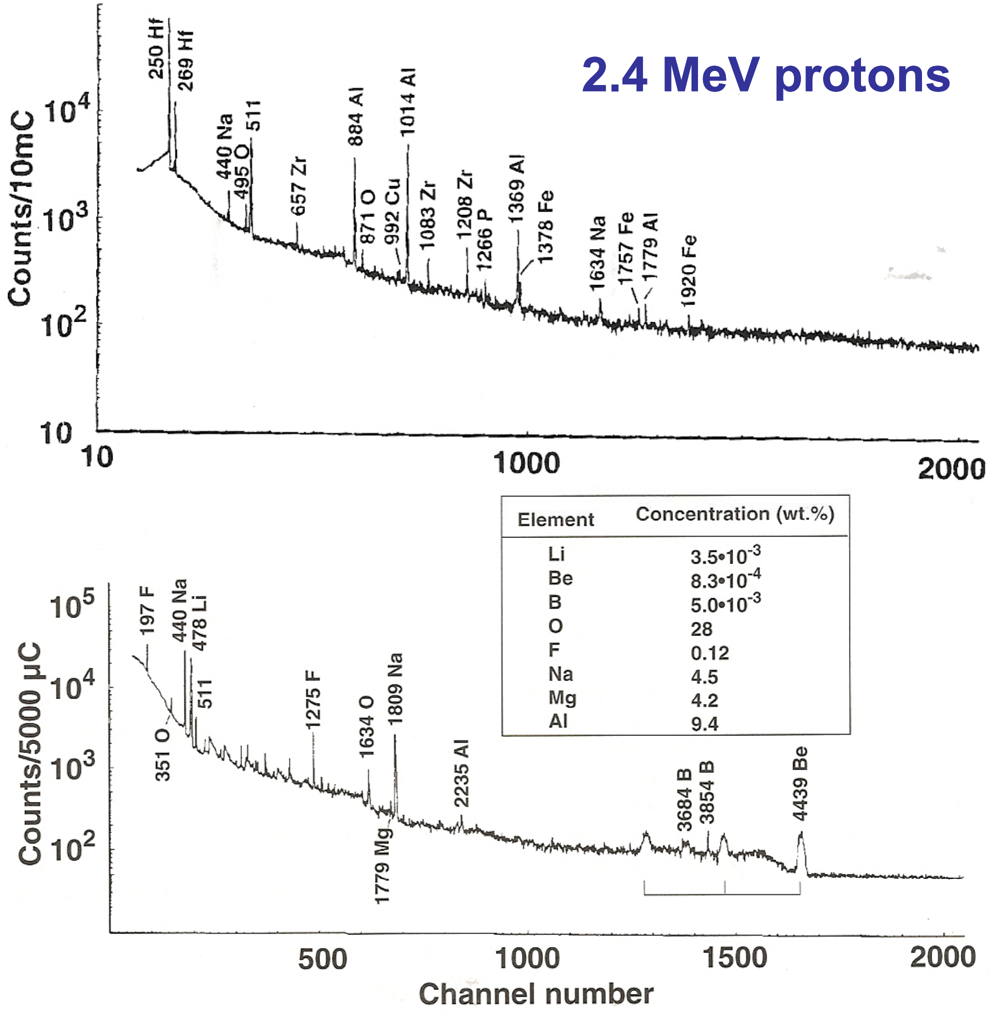
Typical sensitivities: 1:10^4 in atomic proportion

Nuclear Reaction Analysis (particle-gamma) or PIGE

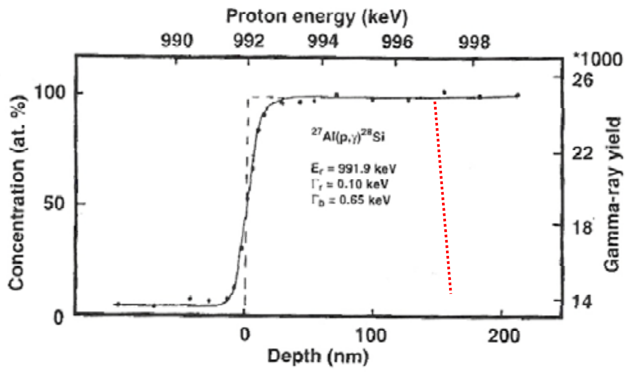
- ***Use of a γ-ray detector (preferably HPGe)***
- ***Use of standards in identical conditions:***

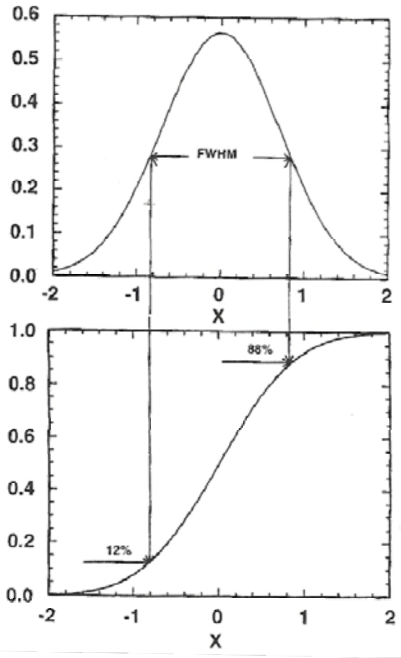
$$C_{i,s} = (C_{st}\, S_s\, Y_{i,s}) / (S_{st}\, Y_{i,st})$$

- ***Dealing with the problem of different stopping powers between standard and target***
- ***Lack of generally accepted computer simulation code***
- ***Lack of accurate/evaluated cross section data for γ-inducing nuclear reactions in literature***

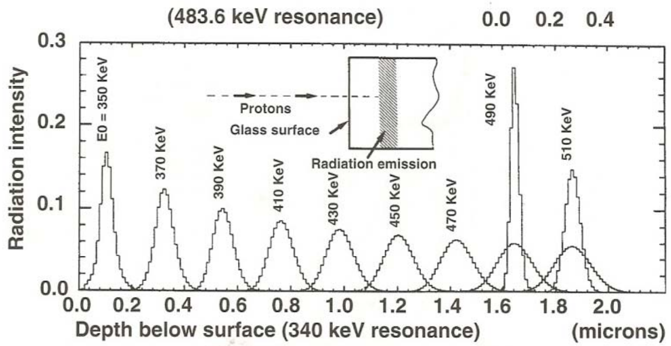


Element	Concentration (wt.%)
Li	$3.5 \cdot 10^{-3}$
Be	$8.3 \cdot 10^{-4}$
B	$5.0 \cdot 10^{-3}$
O	28
F	0.12
Na	4.5
Mg	4.2
Al	9.4

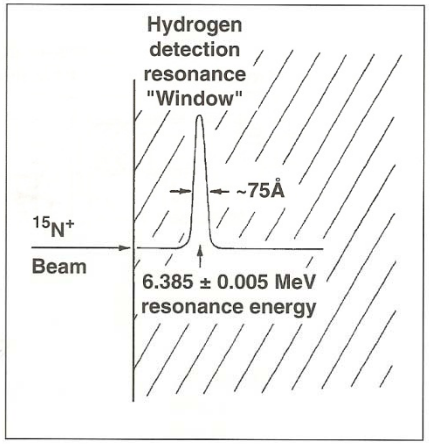




Demonstration of the mechanism:



The depth resolution:



- *Changes in the beam energy*
- *Use of narrow, strong, isolated resonances for superior depth profiling of light isotopes not always possible*

Extra NRA (particle-gamma) Characteristics:

POSITIVE

- ✓ *Excellent for hydrogen profiling, fluorine and aluminum (MDL~1-10 ppm)*
- ✓ *Quite satisfactory for carbon, nitrogen, oxygen, magnesium, silicon*
- ✓ *Relatively easy to implement, due to the standards used*
- ✓ *Excellent for machine calibration (accelerator tuning)!*

NEGATIVE

- ➲ *HPGe detectors are very expensive, fragile, and need liquid nitrogen cooling!*
- ➲ *Usually very time-consuming studies*
- ➲ *Very element-specific technique*
- ➲ *Overlap of resonances might occur if the sample is relatively thick*
- ➲ *Efficiency calibration of the HPGe detector is a requirement!*

Ion Beam Analysis Profiling Techniques: Summary, Present Situation, Future Perspectives

SUMMARY

1. Rutherford backscattering (RBS) is ideal for depth-profiling of heavy elements on lighter substrates.
2. Elastic recoil detection analysis (ERDA) is excellent for depth-profiling of very light elements in thin films (for very small depths < 1 μm).
3. Nuclear reaction analysis (NRA), is excellent for high resolution depth-profiling of specific isotopes.

PRESENT SITUATION

1. A lot of work is being done in channeling, EBS and NRA (cross section measurements and evaluations).
2. Micro-beams and measurements in air (Louvre) have enhanced IBA capabilities.

FUTURE PERSPECTIVES

1. New techniques are always evolving (e.g. HR-RBS, TOF-ERDA).
2. Channeling analytical algorithms?
3. CAN WE SOLVE ALL THE PROBLEMS??? NO (BUT MANY YES…)