The Abdus Salam International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization

IAEA International Atomic Energy Agency

SMR/1843-4

X-Ray Emission Techniques for Forensic Applications

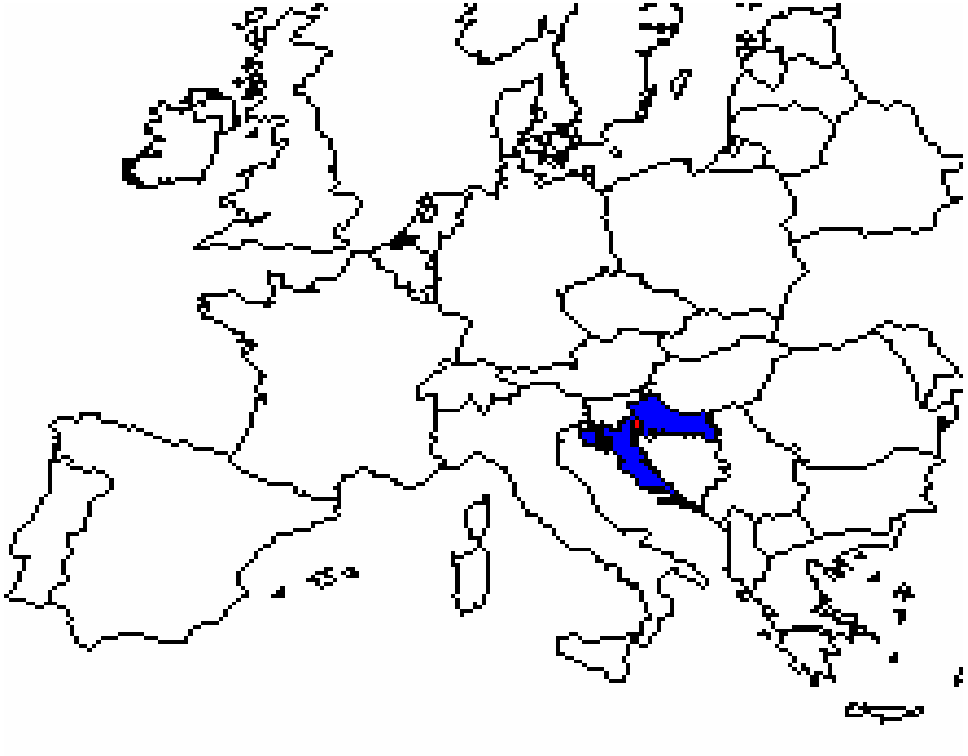
28 May - 1 June, 2007

Ion Beam Analysis-methodology and forensic applications

I. Bogdanovic Radovic
Rudjer Boskovic Institute,
Zagreb, Croatia.

Ion Beam Analysis - methodology and forenzic applications

I. Bogdanović Radović



Laboratory for Ion Beam Interactions

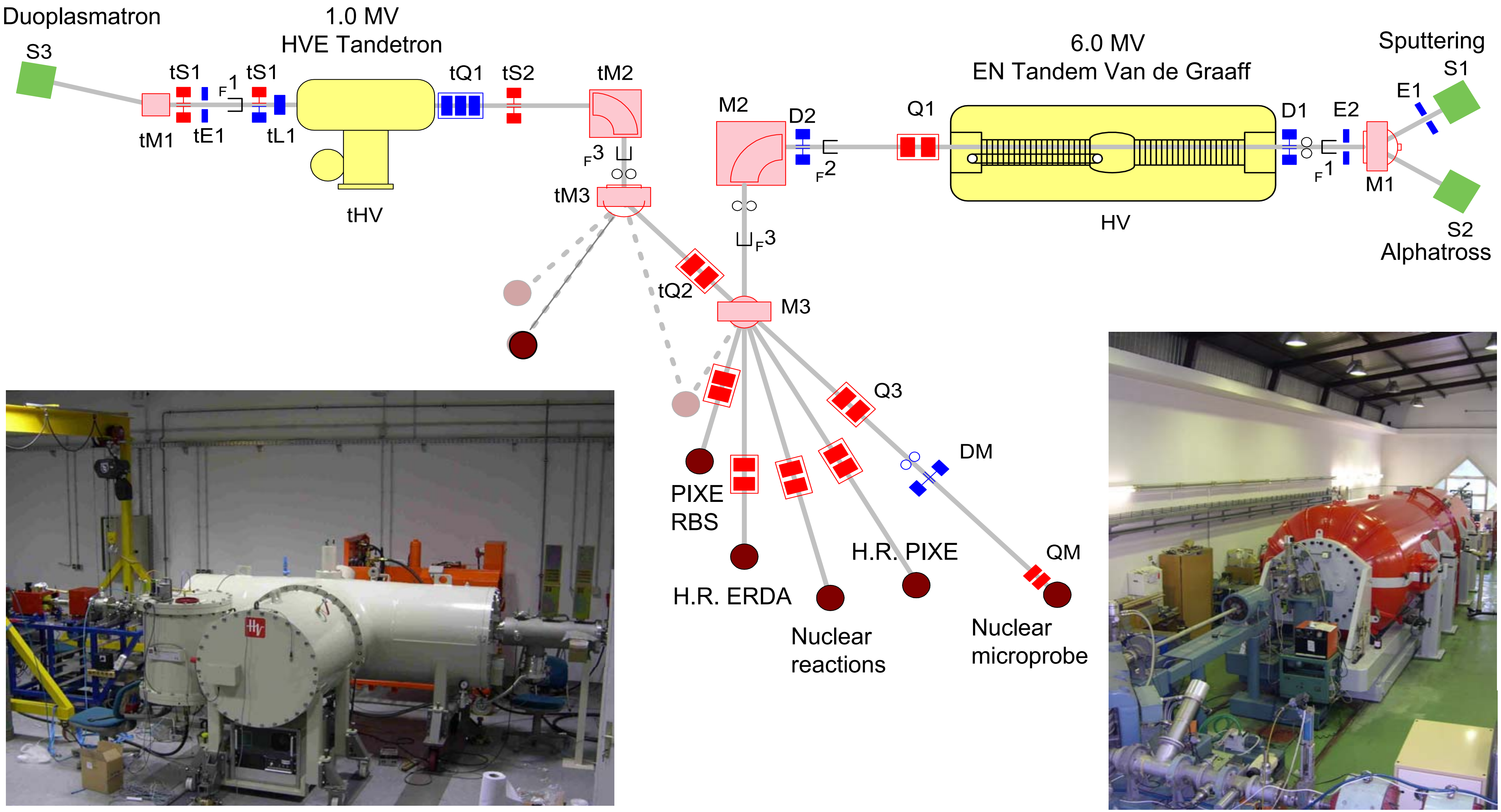
Department for experimental physics Ruđer Bošković Institute, Zagreb, Croatia

Outline

- Laboratory for ion beam interactions
- Ion Beam Analysis (IBA) - methodology
- IBA - Examples

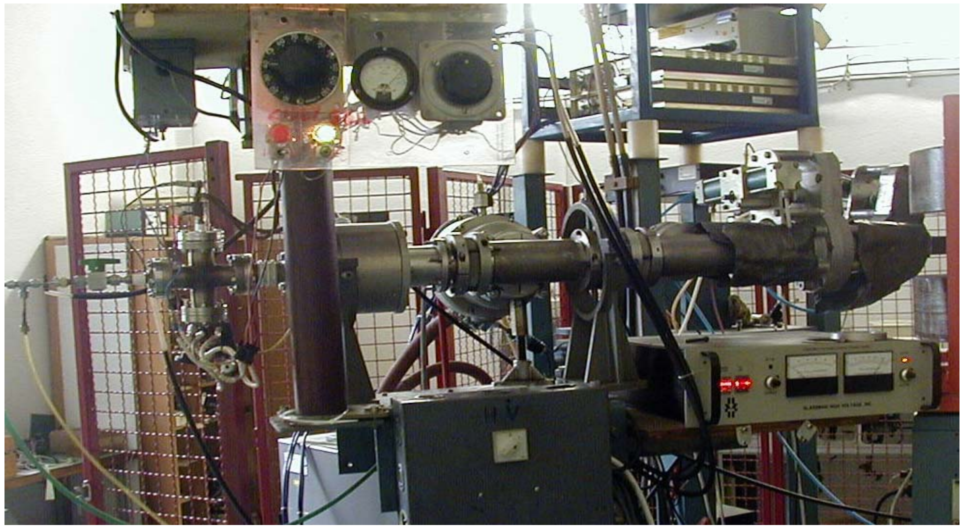
- **Laboratory for ion beam interactions**
- **Ion Beam Analysis (IBA) - methodology**
- **IBA - Examples**

LIBI - Laboratory for Ion Beam Interactions



6.0 MV EN Tandem Van de Graaff

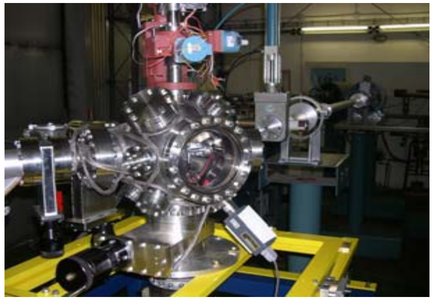
- 1963 – 1984 Rice University, Houston, Texas
- Since 1987 in routine operation in Zagreb
- Two ion sources – Alphatros (H, He), sputtering (Li, C, O,….)
- Five beam lines

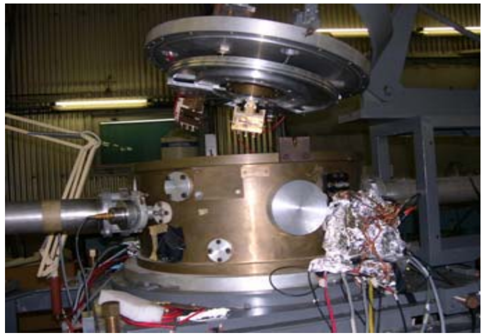


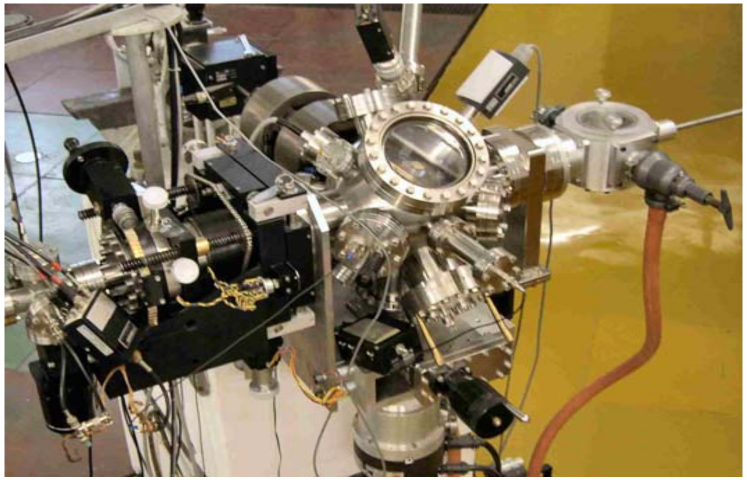
Beam lines

- Existing beam lines of EN Tandem accelerator

    1. IAEA line– well calibrated chamber for PIXE/RBS/PIGE
    2. TOF ERDA
    3. Nuclear reactions chamber
    4. High resolution PIXE / ion implant.
    5. Nuclear microprobe

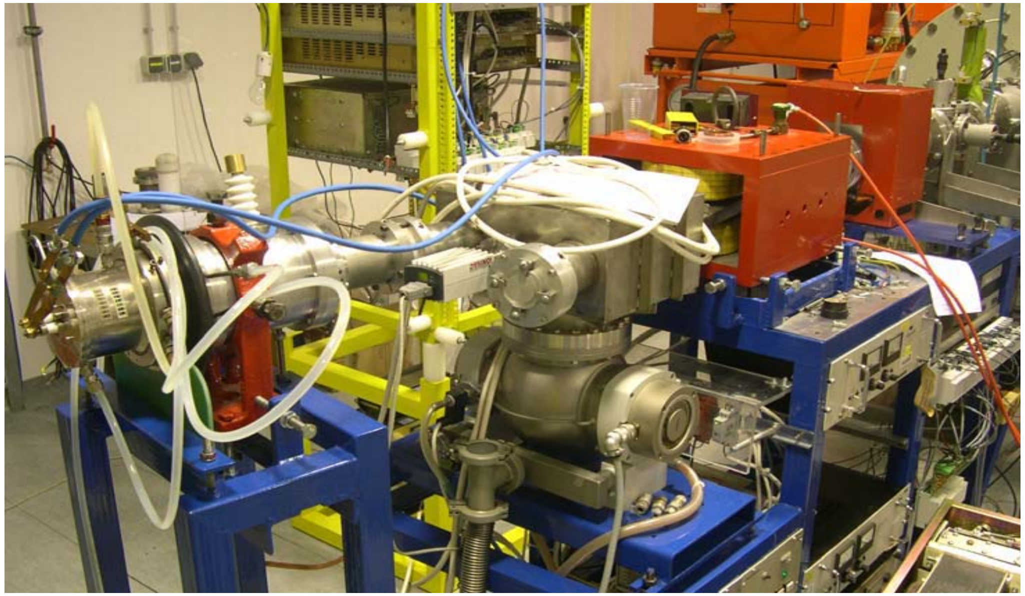


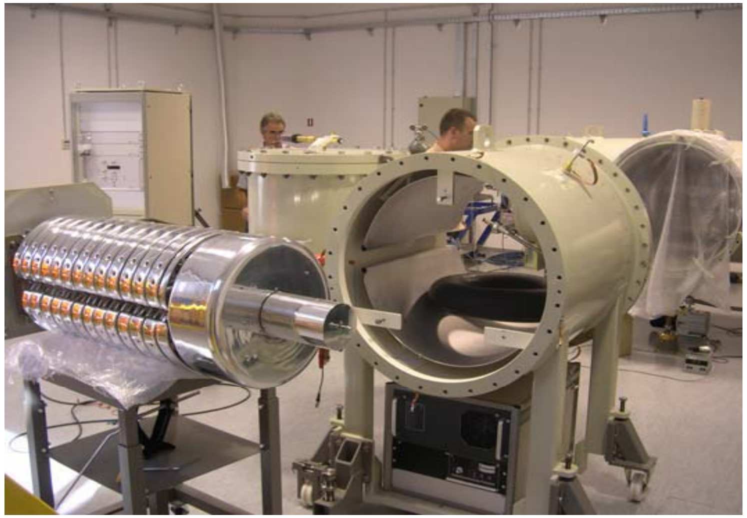




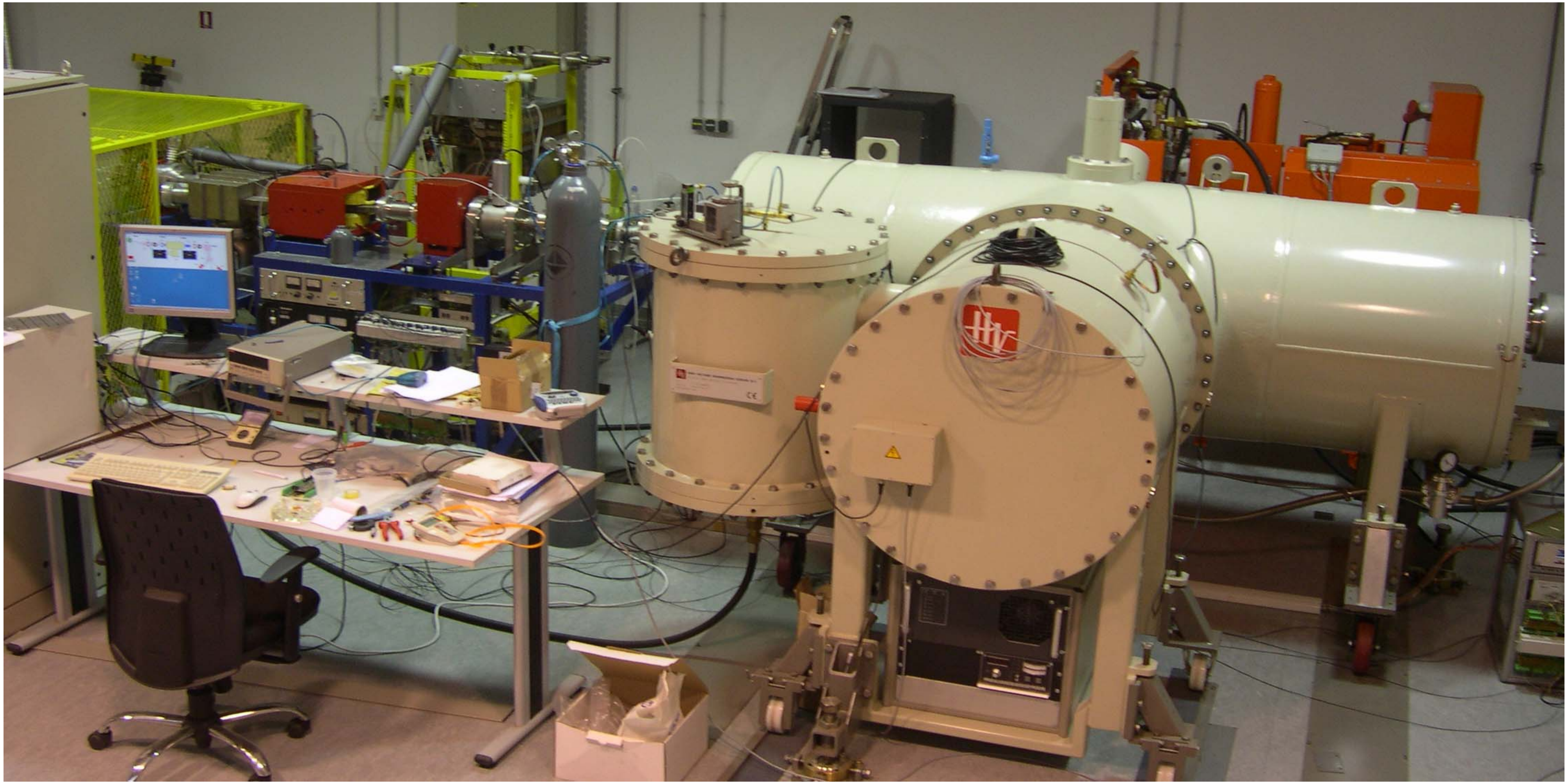
1.0 MV Tandetron

- High Voltage Engineering, The Netherlands
  (funded by Ministry of science of Croatia and IAEA)
- Direct extraction duoplasmatron ion source
- Sputtering ion source (planned for 2007)
- Terminal voltage range 0.1 – 1.0 MV, high stability,
  beam currents up to 50 μA



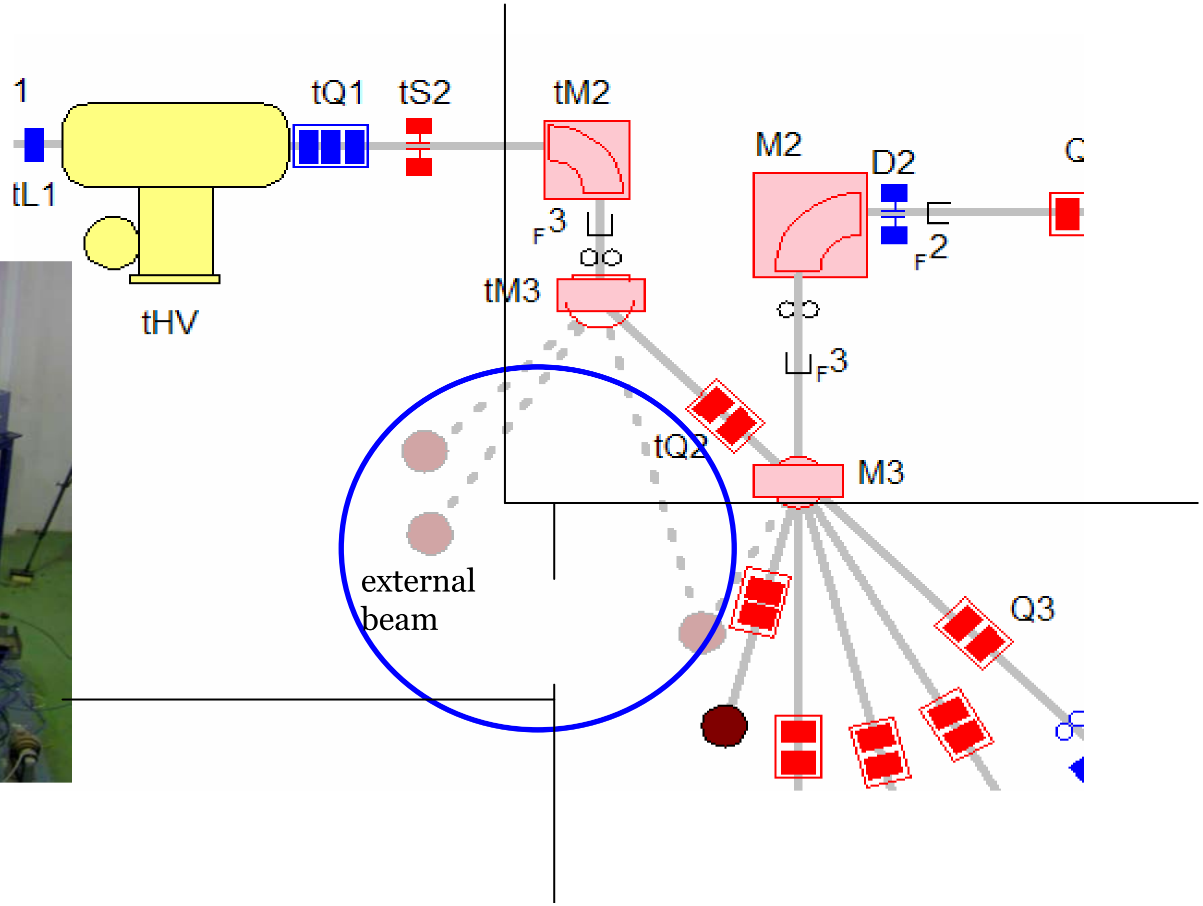


1.0 MV Tandetron



Tandetron beam lines

- External beam for cultural heritage objects (operational)
- New microprobe for heavy ions / low energies (planned)
- Two beams chamber for materials modification (planned)



Research highlights

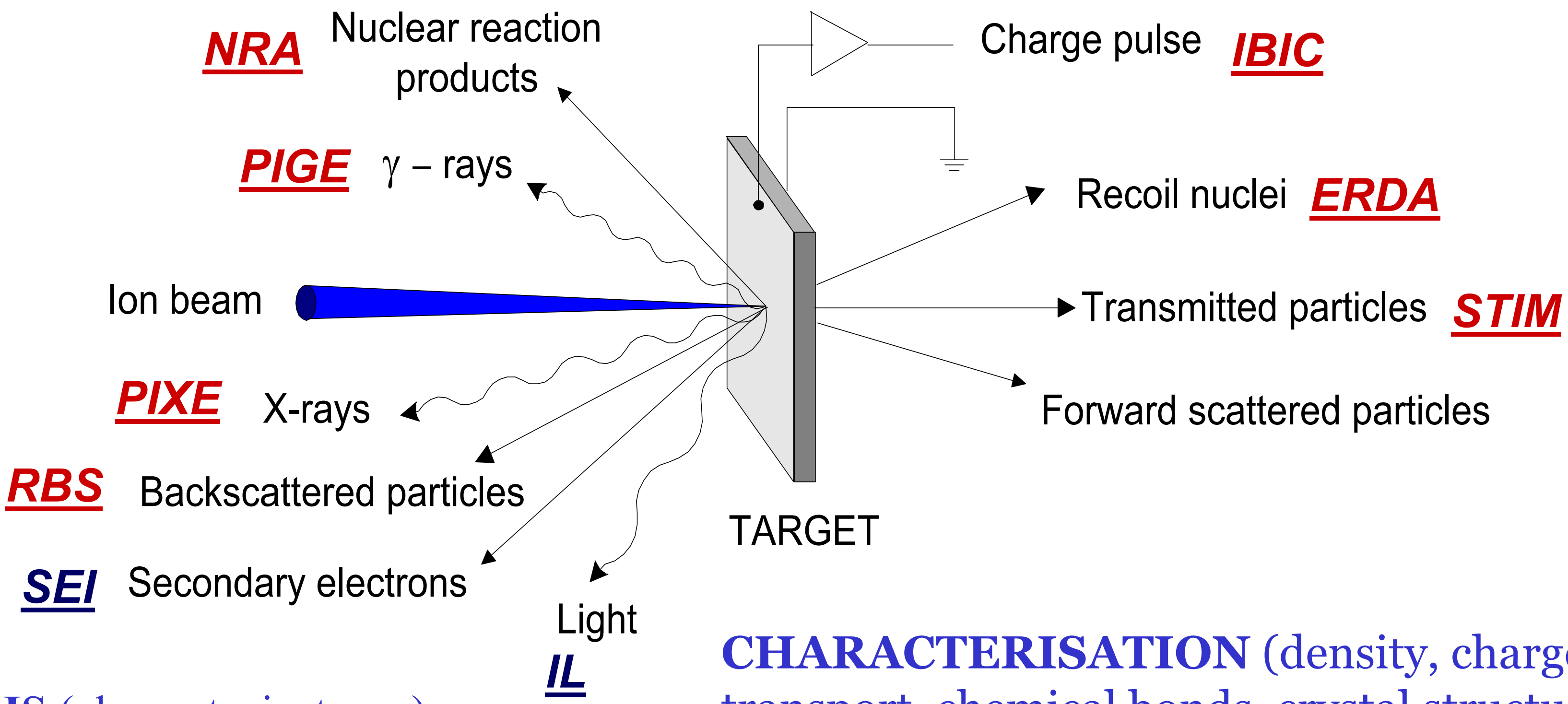
- **Basic research in nuclear and atomic physics**
  1. Light nuclei nuclear reactions
     (Laboratory for nuclear reactions - Đ. Miljanić et al)
  2. Inner shell ionisation, chemical effects
  3. Elastic scattering of light ions, data base
- **Materials science and applications**
  1. Transport of charge carriers – characterisation/modification
  2. Analysis of thin films (RBS &ERDA) with nm depth resolution
  3. Modification of insulators
- **Analytical applications**
  1. Cultural heritage objects – HRZ
  2. Technological projects (cement, solar cells)
  3. Air polution monitoring
  4. Other analytical services

- Laboratory for ion beam interactions

- **Ion Beam Analysis (IBA) - methodology**

- IBA - Examples

Ion Beam Analysis - methods



ANALYSIS (elements, isotopes) with **MeV ION BEAMS** - (nA, pA)

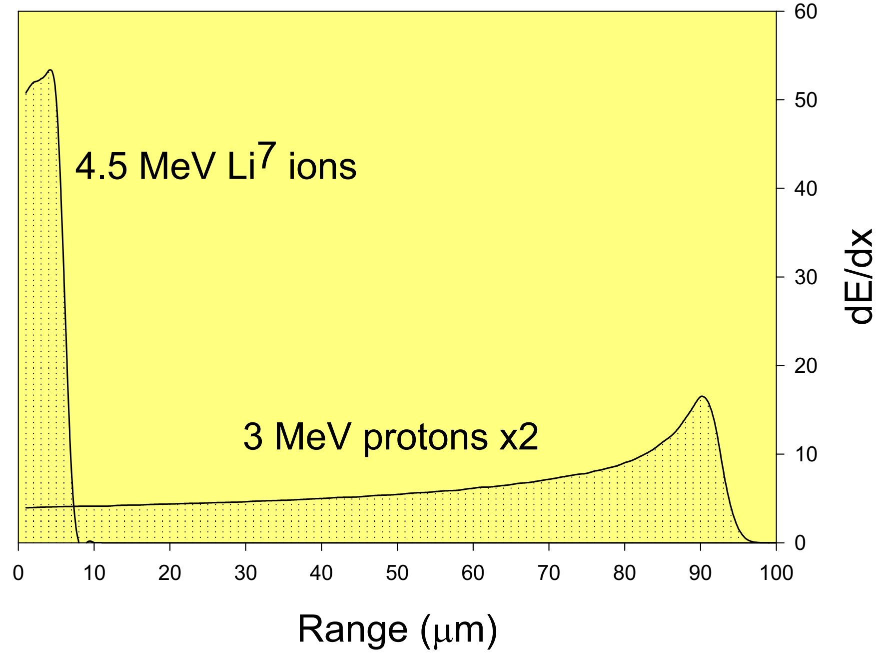
- <u>elements</u> - x-rays (**PIXE**)
  - backscattering (**RBS**)
  - recoil (**ERDA**)
- <u>isotopes</u> - nuclear reactions
  γ - rays (**PIGE**)
  particles (**NRA**)

CHARACTERISATION (density, charge transport, chemical bonds, crystal structure, morphology,...) with **MeV SINGLE IONS** - (fA)

- density - transmitted ions (**STIM**)
- charge transport - charge pulse **(IBIC**)
- crystal structure - **channelling** (RBS)
- morphology - secondary electrons (**SEI**)
- chemical bonds - light, x-rays **(IL, PIXE**)

Stopping of ions in matter

- By changing the ion energy and ion species, ion beam analysis can be performed at different surface layer thicknesses.
- Ranges of different ions in silicon are given as example:
  - 1.5 MeV p - 30 μm,
  - 3.0 MeV p - 90 μm
  - 6.0 MeV p - 290 μm
  - 3.0 MeV Li^6 - 6.5 μm
  - 3.0 MeV O^{16} - 2.7 μm

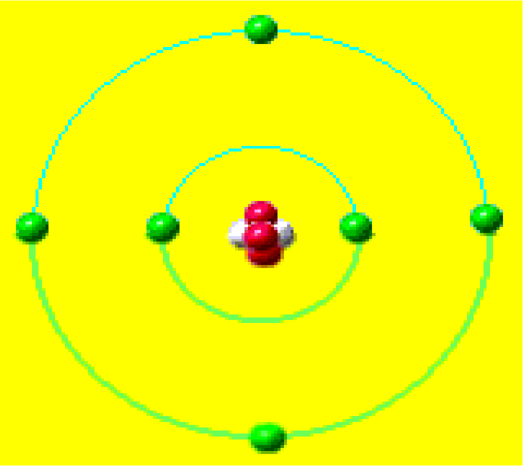


- Different IBA techniques can be therefore used to probe different sample depths.
- Only some techniques are depth sensitive.

1. PIXE – physical principles

- ion loses energy by exciting e^- in the atoms
- ejected inner shell e^- (K, L….) – unstable atom
- $t < 10^{-15}$ s - vacancy filled with outer e^-
- energy conservation – one way emission of characteristic x-rays

- characteristic x-rays are characteristic of the element and therefore can be used to identify elemental composition



- concentrations of almost all elements in the sample down to approximately 1 ppm (part-per-million)

PIXE

-excitation- 2-3 MeV proton beam

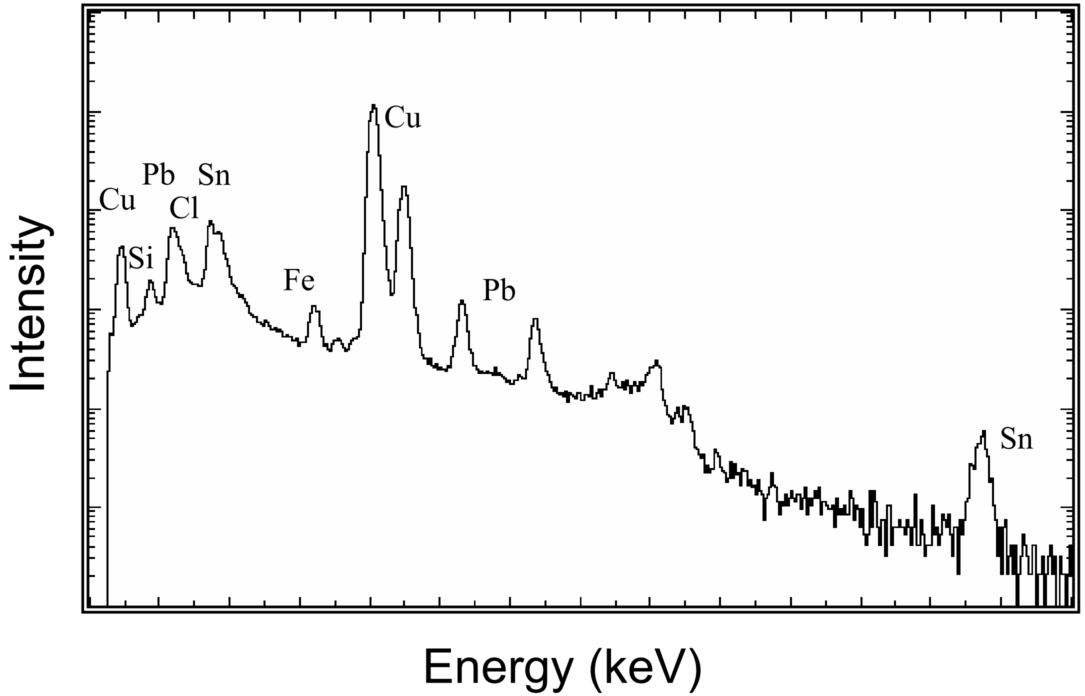
-X-ray detection by energy dispersive semiconductor detectors Si(Li)

- analysed elements from Na to U (K and L x-rays)

- nondestructive, multielemental, requires small samples

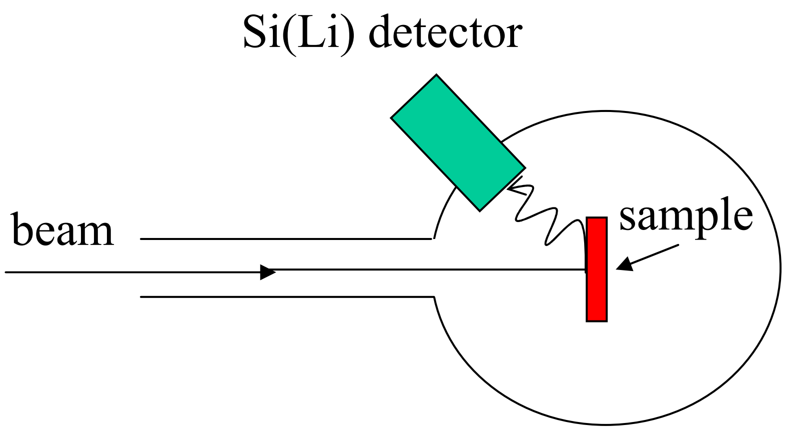
- PIXE is **not good** for depth profiling of elemental concentrations

- higest sensitivity for 20 < Z < 40 and Z > 75

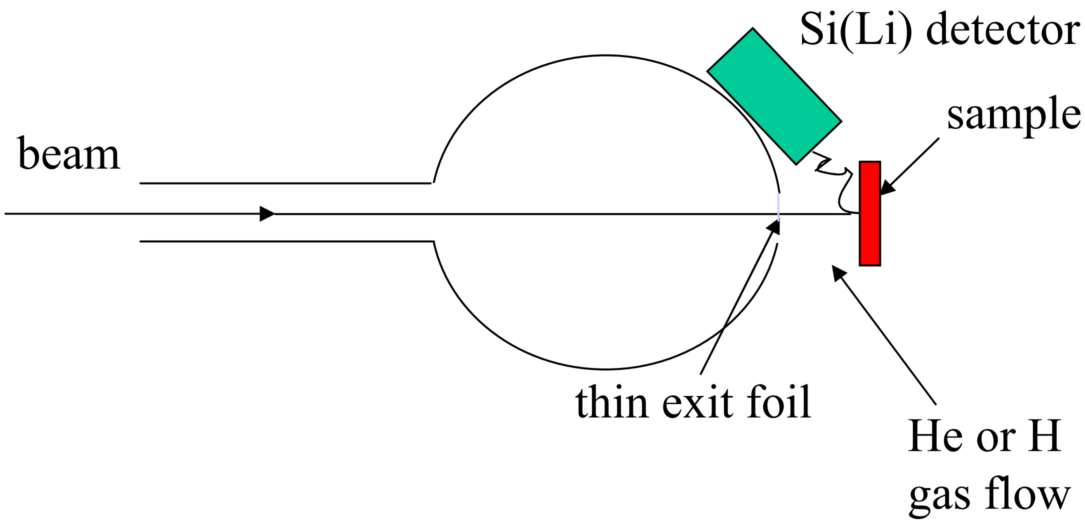


PIXE spectrum obtained from an archeological sample (Apoxiomenos).

Standard PIXE setup in vacuum:



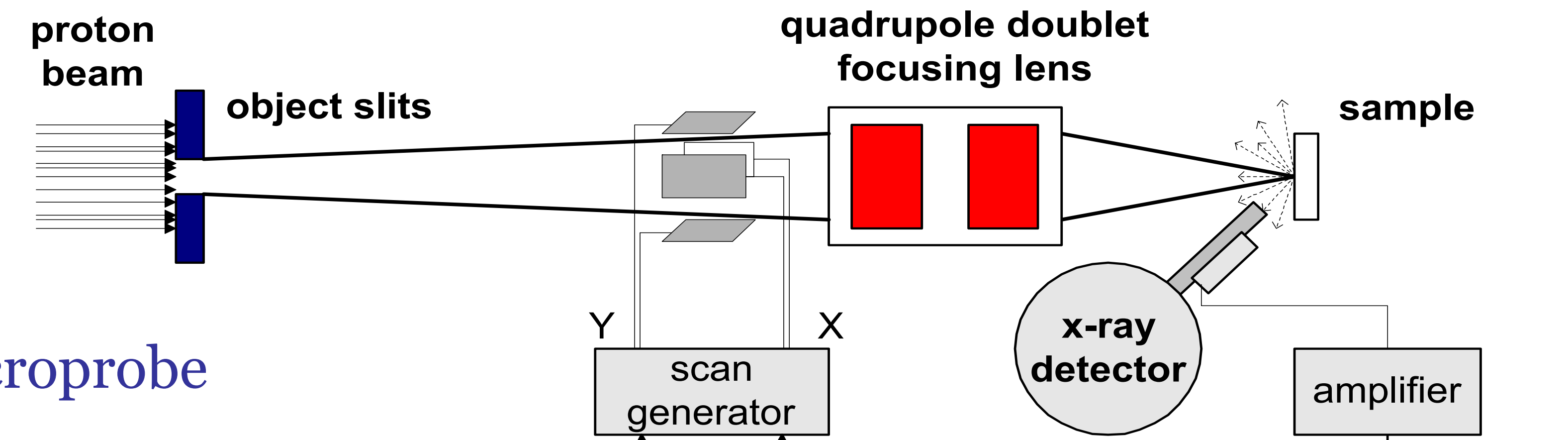
External beam PIXE setup:



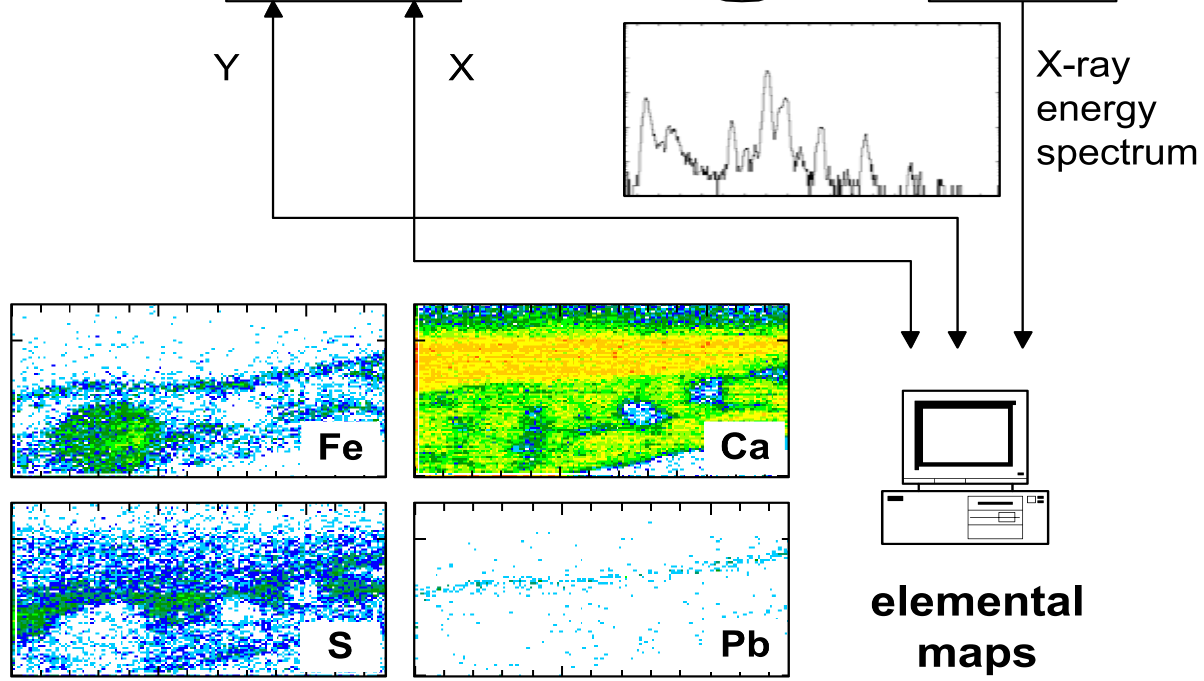
- **in vacuum** analysis reduce:
  1. x-ray absorption (important for low energy x-rays)
  2. beam spread due to scattering problems: sample size and integrity

- external beam:
- useful for art and archeology
- in situ analysis of objects without sampling
- non destructive (reduced risk of beam damage)
- less risk of dehydration (papyrus, paintings, etc.)
- main problems: degradition of beam quality (energy loss, energy spread and angular divergence in exit window and air)

Microbeam PIXE imaging of elemental distributions



Nuclear microprobe PIXE:
proton beam is **<u>focused</u>** and **<u>scanned</u>** to produce **<u>images</u>** of elemental distributions

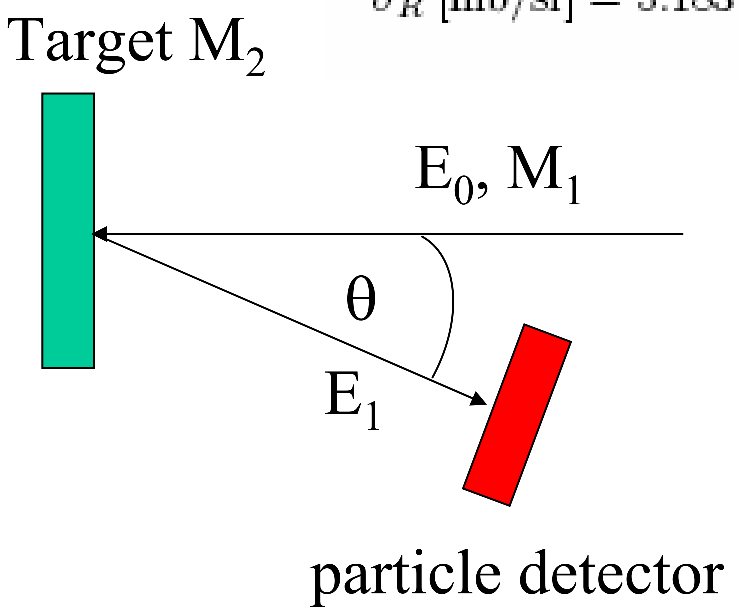


2. RBS - Rutherford Backscattering

- energy of an elastically backscattered particle depends on the **mass** of the target atom **(kinematic factor)** and on the **depth** at which the scattering took place (**energy loss** on the way to and from the point of interaction).

scattering on Coulomb potential:

$$\sigma_R\ [\mathrm{mb/sr}] = 5.1837436 \times 10^6 \left(\frac{Z_1 Z_2}{E\ [\mathrm{keV}]}\right)^2 \frac{\left\{\left(M_2^2 - M_1^2 \sin^2\theta\right)^{1/2} + M_2\cos\theta\right\}^2}{M_2 \sin^4\theta\ \left(M_2^2 - M_1^2\sin^2\theta\right)^{1/2}}$$

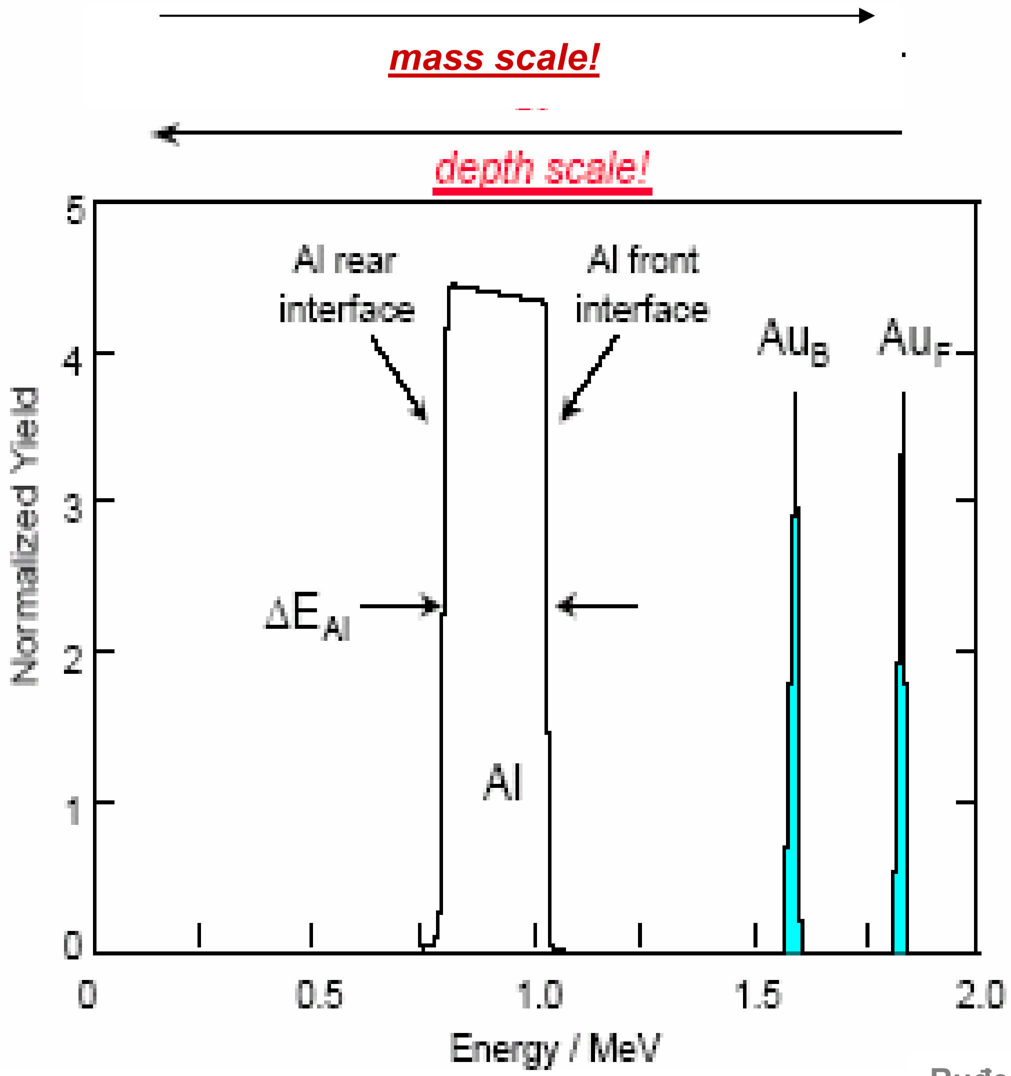


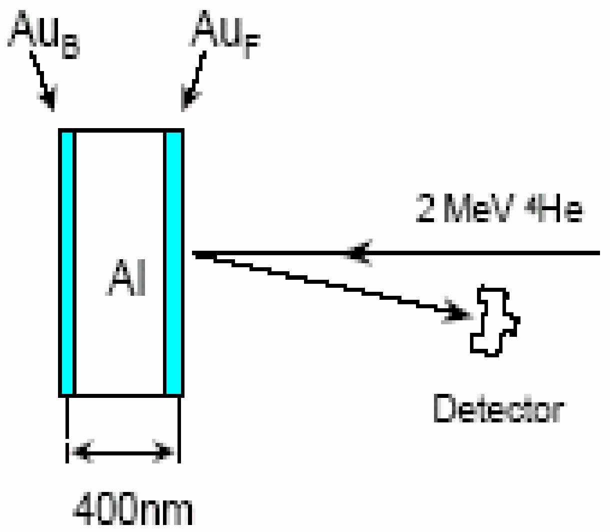
kinematic factor:

$$k = \frac{E_1}{E_0} = \left[\frac{\left(M_2^2 - M_1^2\sin^2\theta\right)^{\frac{1}{2}} + M_1\cos\theta}{M_2 + M_1}\right]^2$$

RBS - Rutherford Backscattering

~ MeV light projectiles
p, α or Li



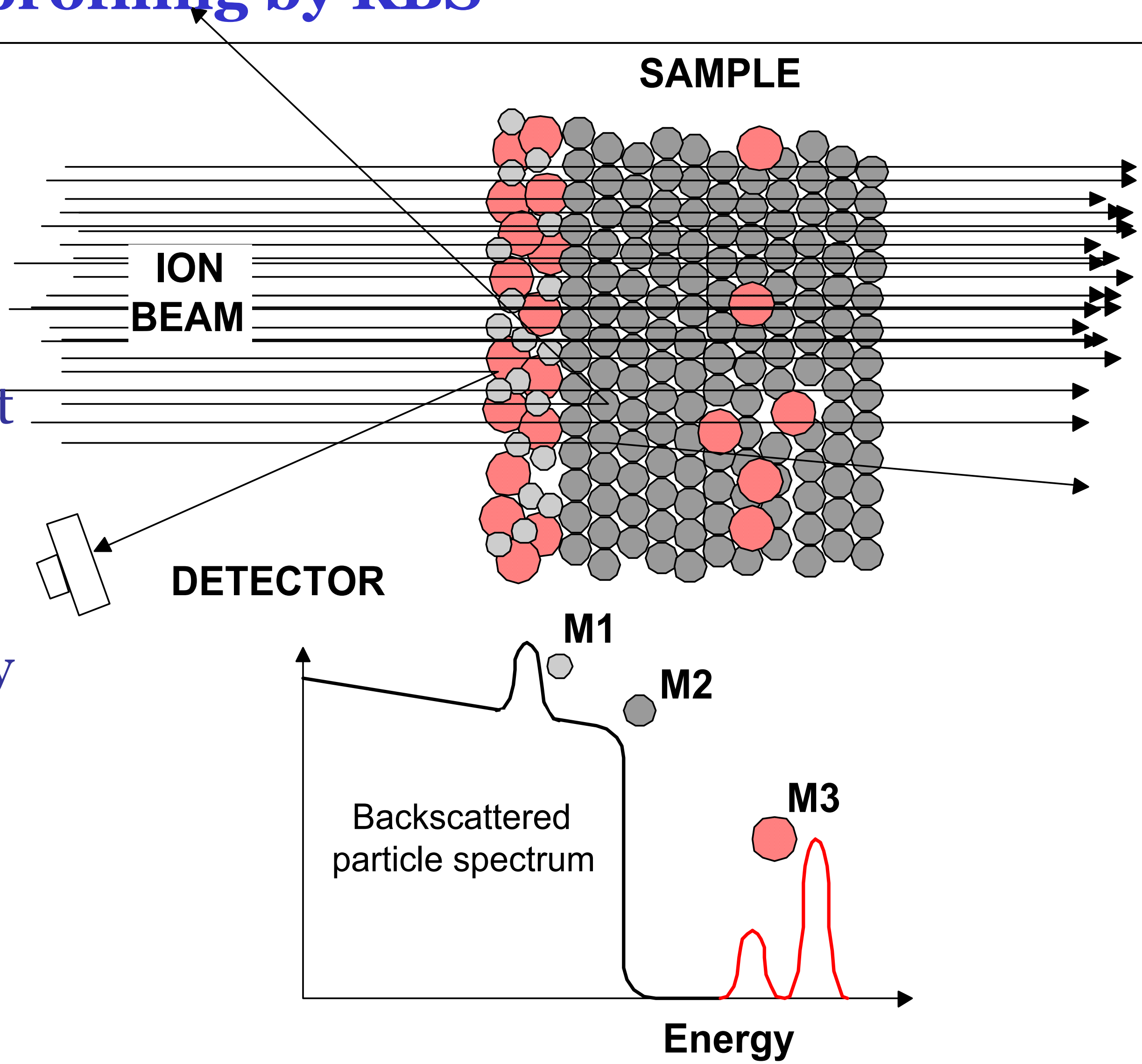


Principle of depth profiling by RBS

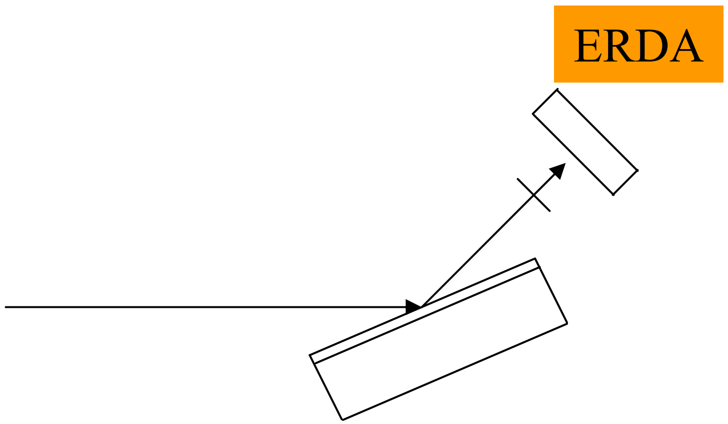
suitable for:
- very thin films

- determination of heavy elements in light matrices

problem:
- light elements in heavy matrices
- $\sigma \sim Z^2$
- non Rutherford cross sections at higher energies $\sigma/\sigma_{Ruth} >> 1$

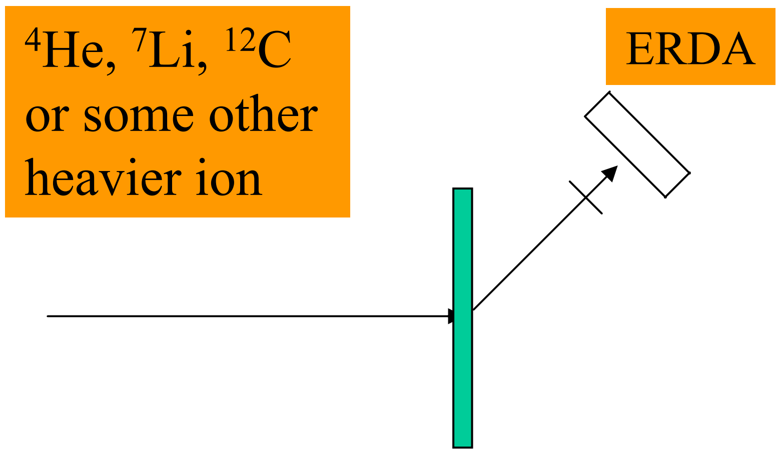


3. ERDA - Elastic Recoil Detection Analysis



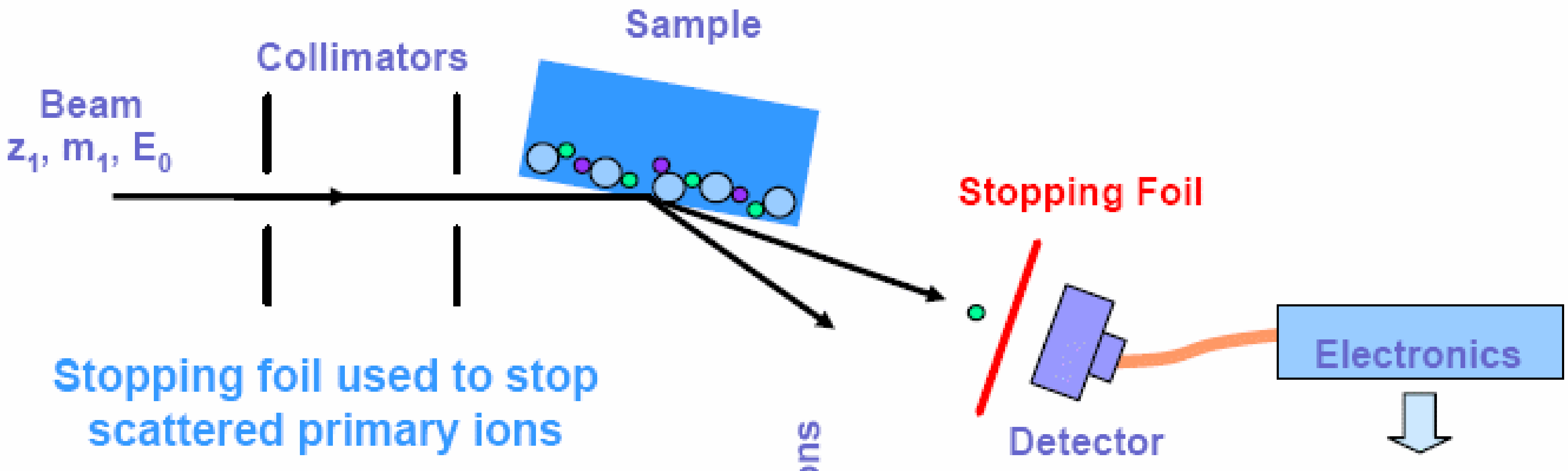
- Incident ion recoils target atom
- $Z_{ion} > Z_{atom}$

Important method for H detection



In order to discriminate between forward scattered projectiles and different types of recoiling particles, absorber foils or mass discriminating detectors have to be used.

ERDA basic concept

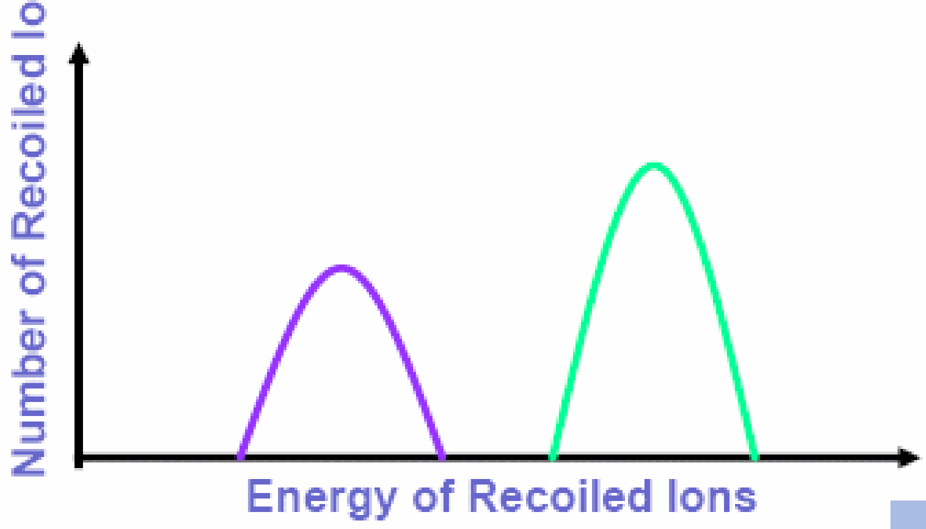


Stopping foil used to stop scattered primary ions

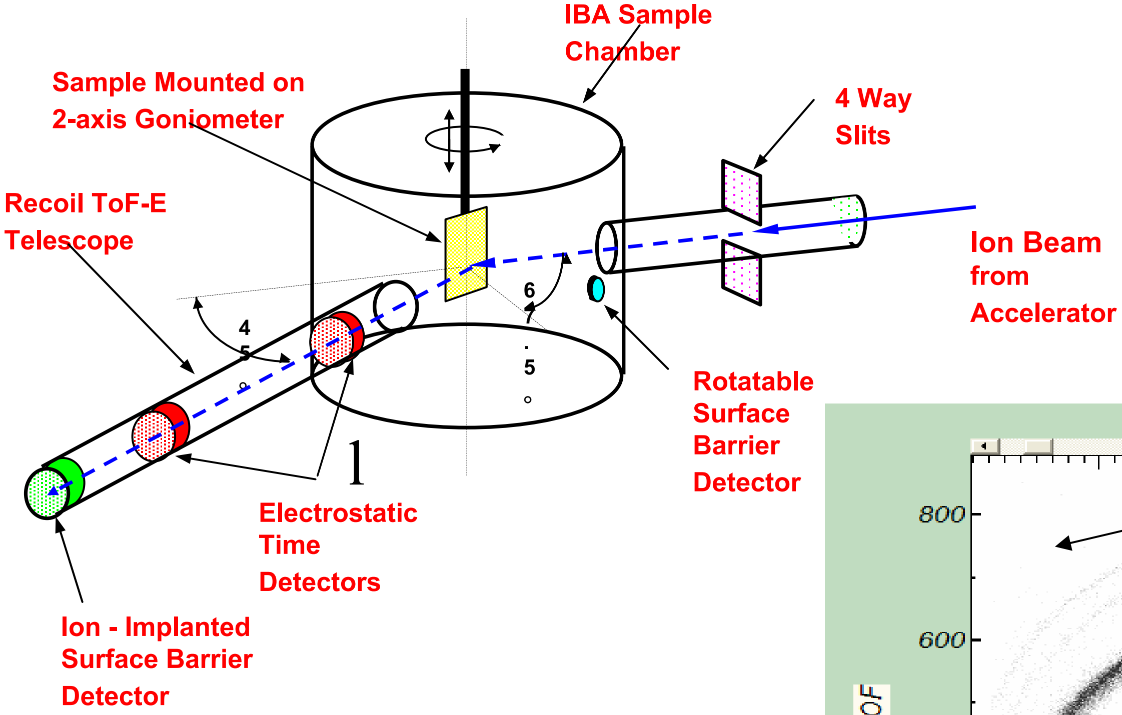
Detect recoils with mass less than that of the incident projectile ions

$$K' = \frac{4M_1M_2\cos^2\phi}{(M_1+M_2)^2}$$

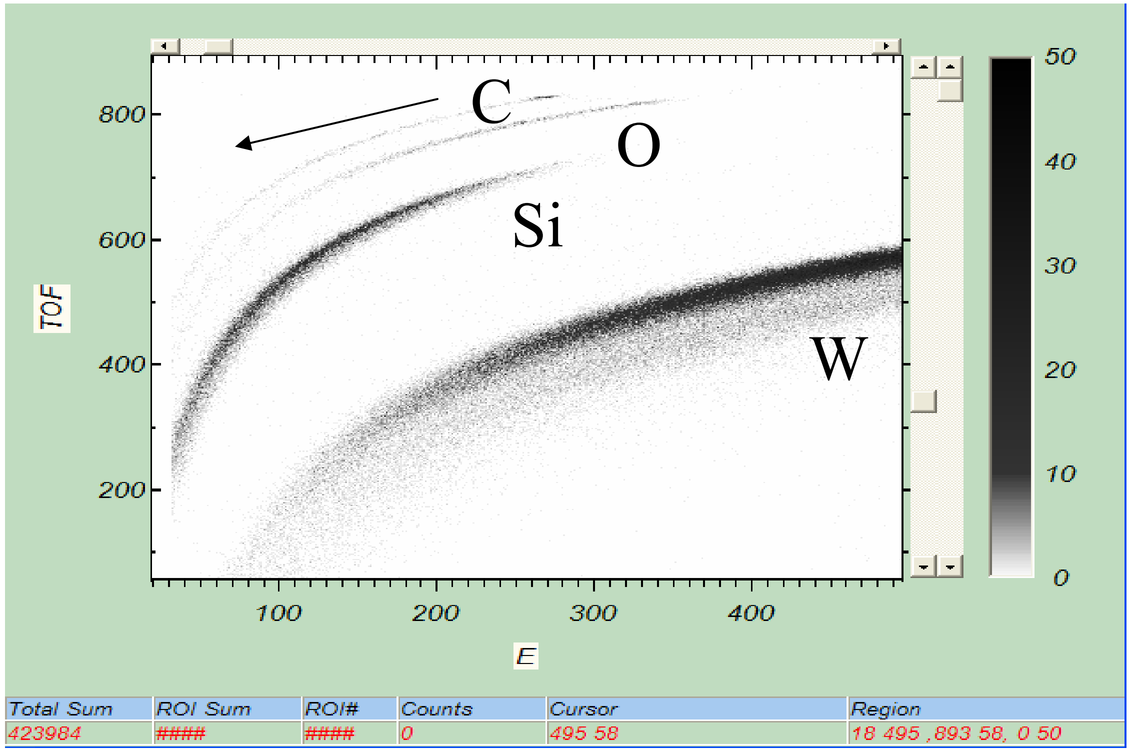
$$\left(\frac{d\sigma}{d\Omega}\right)_\phi = \left(\frac{Z_1Z_2e^2}{2E_0}\right)^2\left(\frac{M_1}{M_2}+1\right)^2\frac{1}{\cos^3\phi}$$



Time-Of-Flight ERDA



$$t = l(M_2/2E)^{1/2}$$



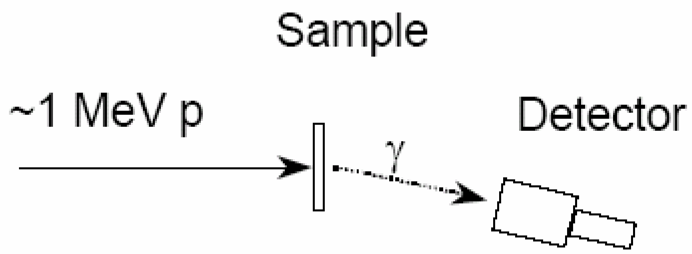
4. NRA -Nuclear Reaction Analysis

MeV ion beams - nuclear reactions in the target nuclei
NRA - analysis of H, Li, Be, B, C, N, O,F, Na, Al, P.
The yield of the prompt characteristic reaction products (γ, p, n, d, ^{3}He, ^{4}He, etc.) is proportional to the concentration of the specific elements in the sample.

Examples of nuclear reactions suitable for NRA

$^7Li(p,\alpha)^4He$	E_p » 3 MeV, σ » 3 mb/sr, Q = 17.3 MeV
$^{12}C(d,p)^{13}C$	E_d » 1-3 MeV, Q = 2.7 MeV
$^9Be(^3He,p)^{11}B$	E_{He} » 1-5 MeV, Q = 10.3 MeV
$^{31}P(\alpha,p)^{34}S$	E_α » 3 MeV, Q = 0.63 MeV
$^7Li(p,n)^7Be$	E_p » 2 MeV
$^1H(^{15}N,^{12}C)\alpha\gamma$	E_N = 6.4 MeV, resonance
$^{19}F(p,\alpha\gamma)^{16}O$	E_p = 340, 484, 872 keV, resonances
$^{27}Al(p,\gamma)^{28}Si$	E_p = 991 keV, narrow resonance

PIGE - Proton Induced γ-ray Emission



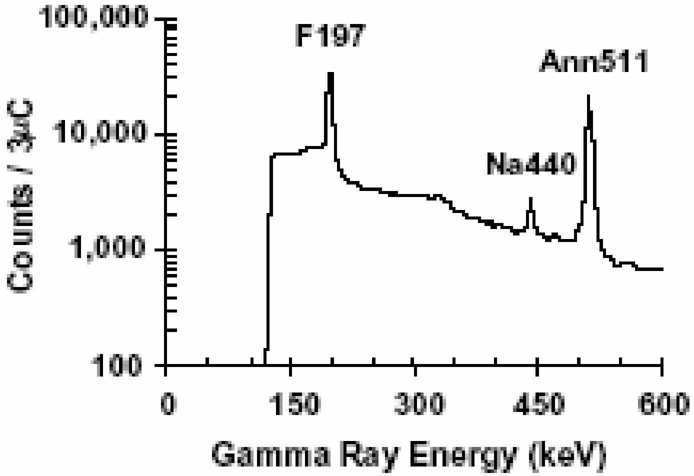
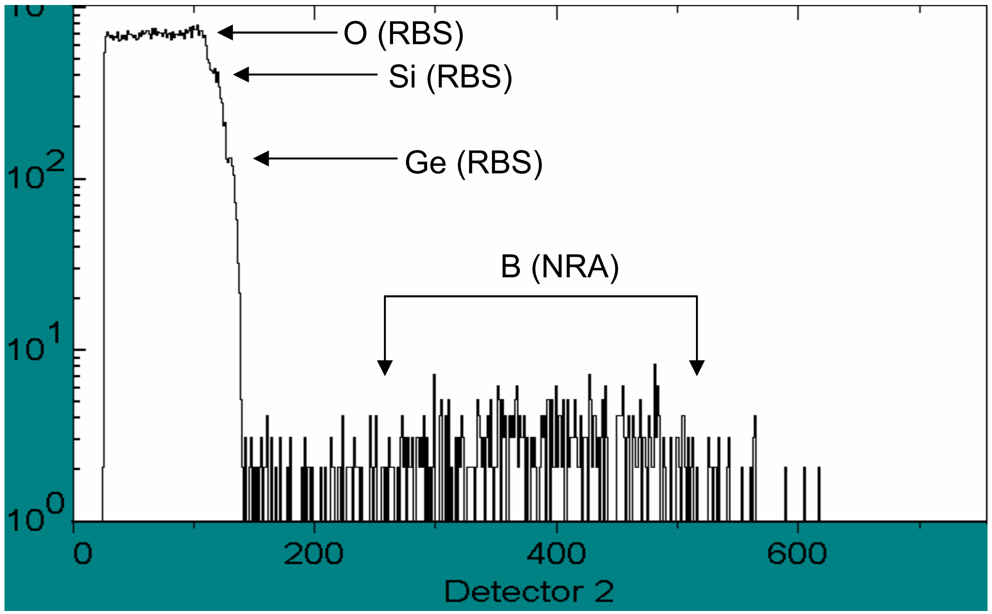


Fig. 2. A typical PIGE spectrum using 2.6 MeV protons for Teflon filters from the Cheju Island site in Southern Korea, exposed on 6 March 2002.

Minimum detectable limits for sodium and fluorine by PIGE were around 100 ng/m^3 of air sampled.

D.D. Cohen et al. / Nucl. Instr. and Meth. in Phys. Res. B 219–220 (2004) 145–152

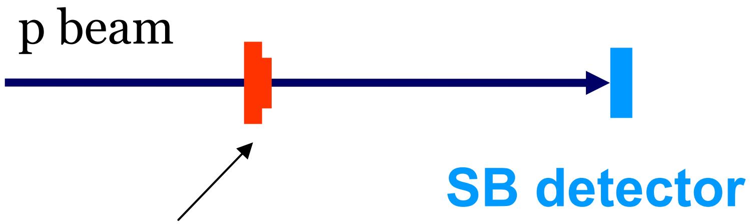
NRA -nuclear reaction analysis



$^{11}B\ (p,\alpha)\ ^8Be$
$Q = 8.582$ MeV

- same particle detector as for RBS
- RBS well separated from NRA part (for $Q > 0$)
- no noise in spectrum coming from high Z elements
- NRA cross sections smaller than RBS cross sections-
  higher currents!

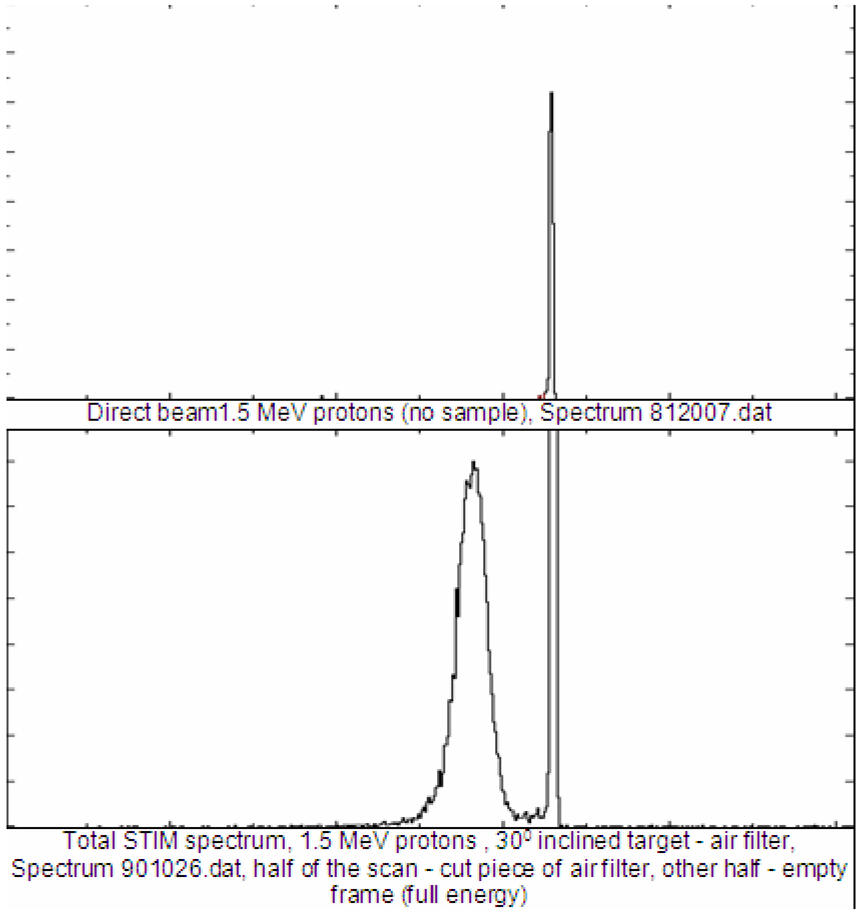
5. STIM – Scanning Transmission Ion Microscopy



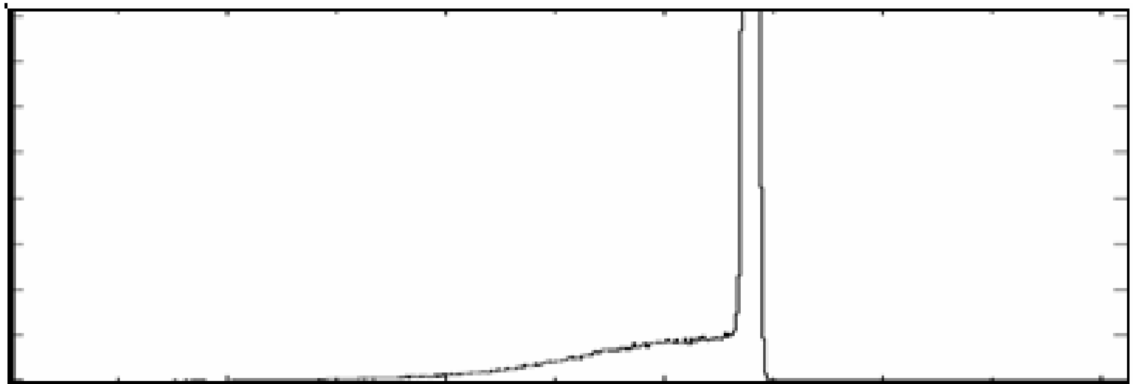
Thin transmission sample (μm)
(tissue, thin films, fly ash particles, etc.)

Principle of STIM method:

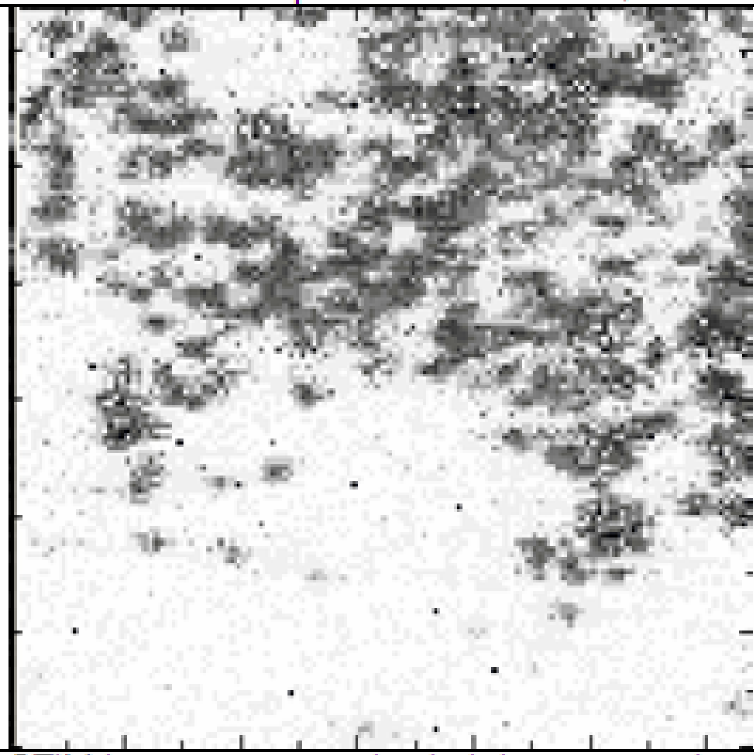
– passing through the sample particle lose energy
- by measuring energy loss in the transmitted beam we can obtain information about particle density/thickness.



STIM

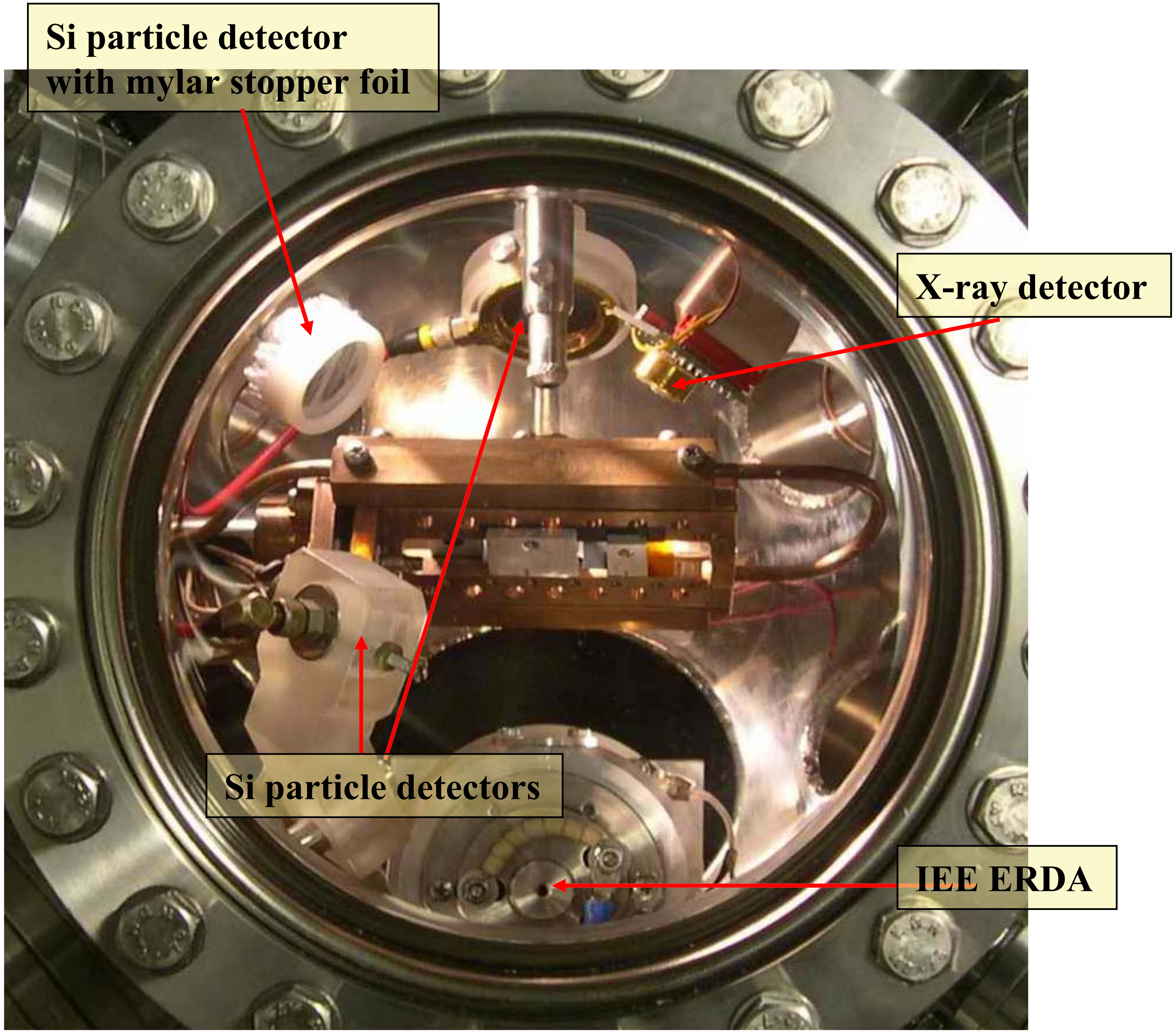


Total STIM spectrum, 1.5 MeV protons , mylar with spreaded algae
413 std. Spectrum 901037.dat,



STIM image, mean pulse height presentation,
algae spreaded on mylar
(white - full energy (ch.700), black - low energy (ch.500))
scan size 150 x 150 um

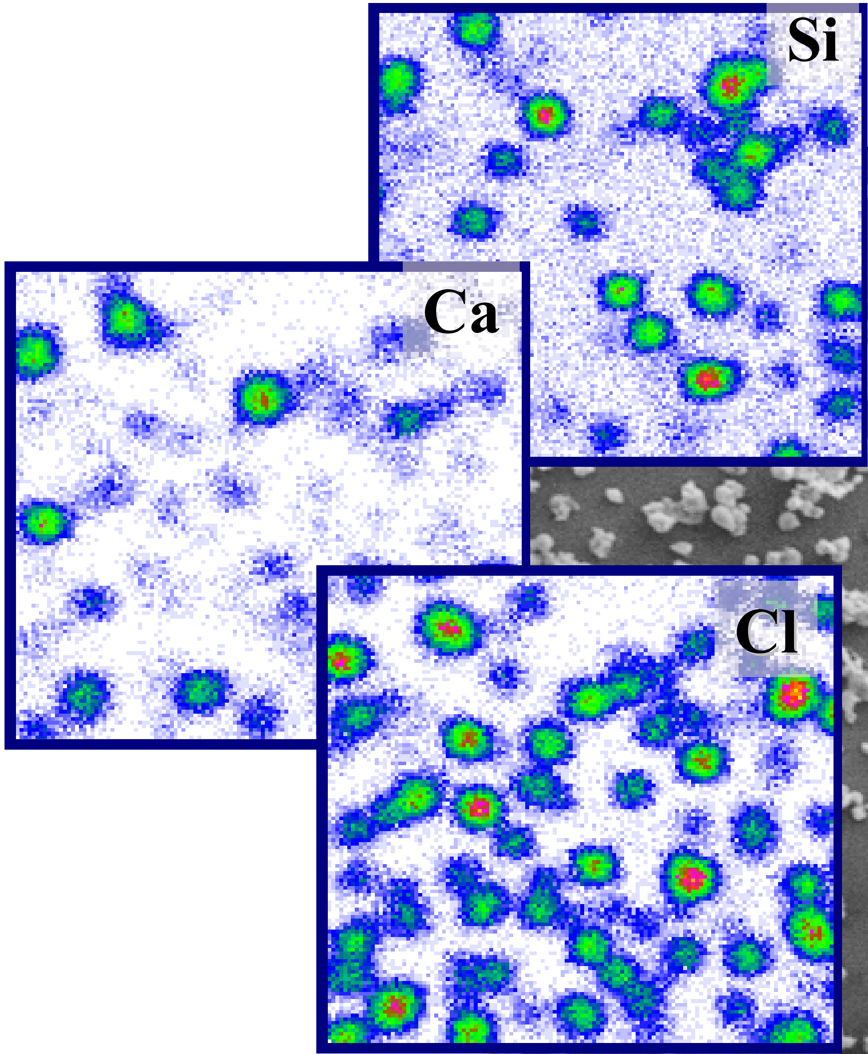
Microprobe setup for PIXE, RBS, ERDA and NRA

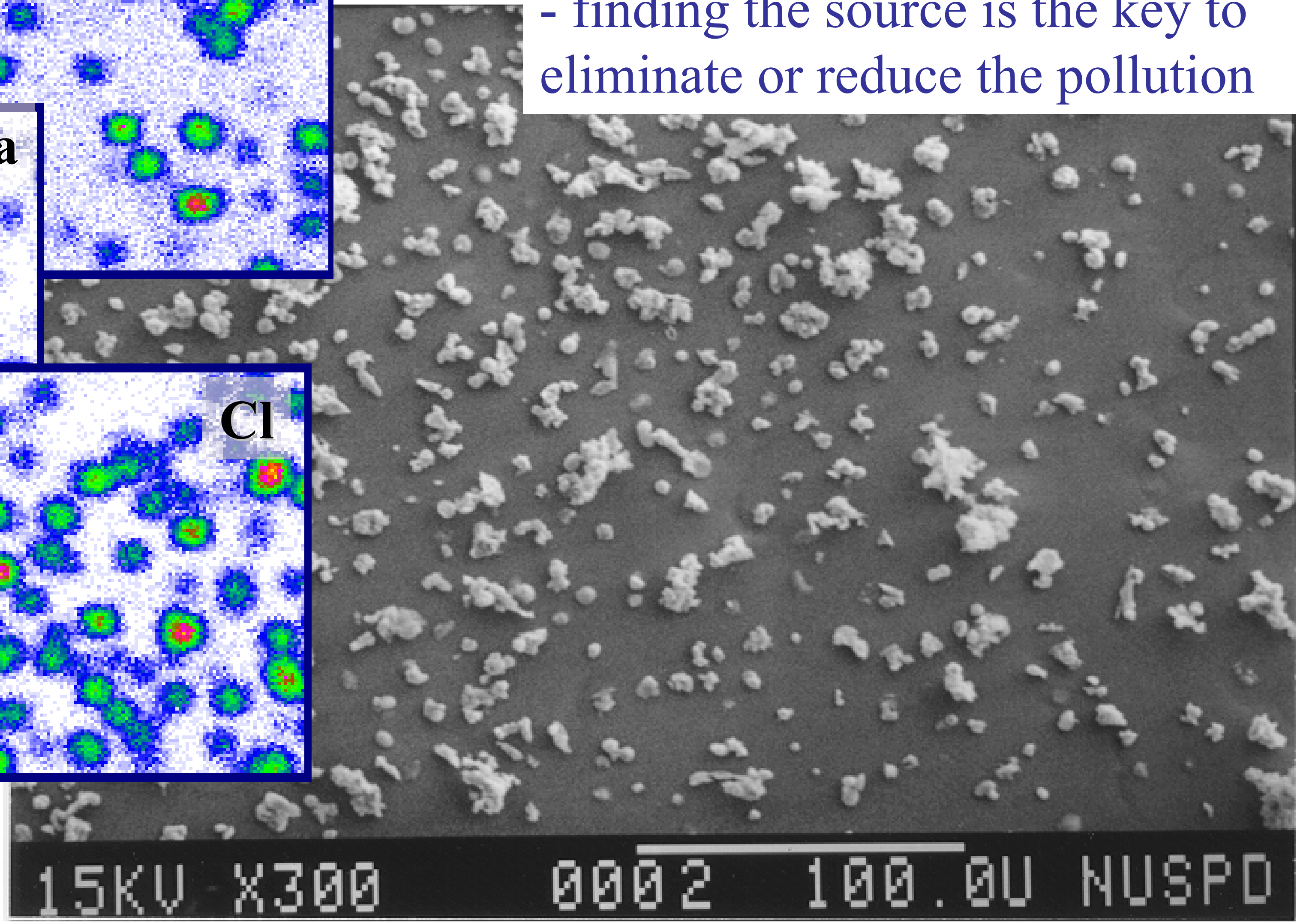


- **Laboratory for ion beam interactions**
- **Ion Beam Analysis (IBA) - methodology**
- **IBA - Examples**

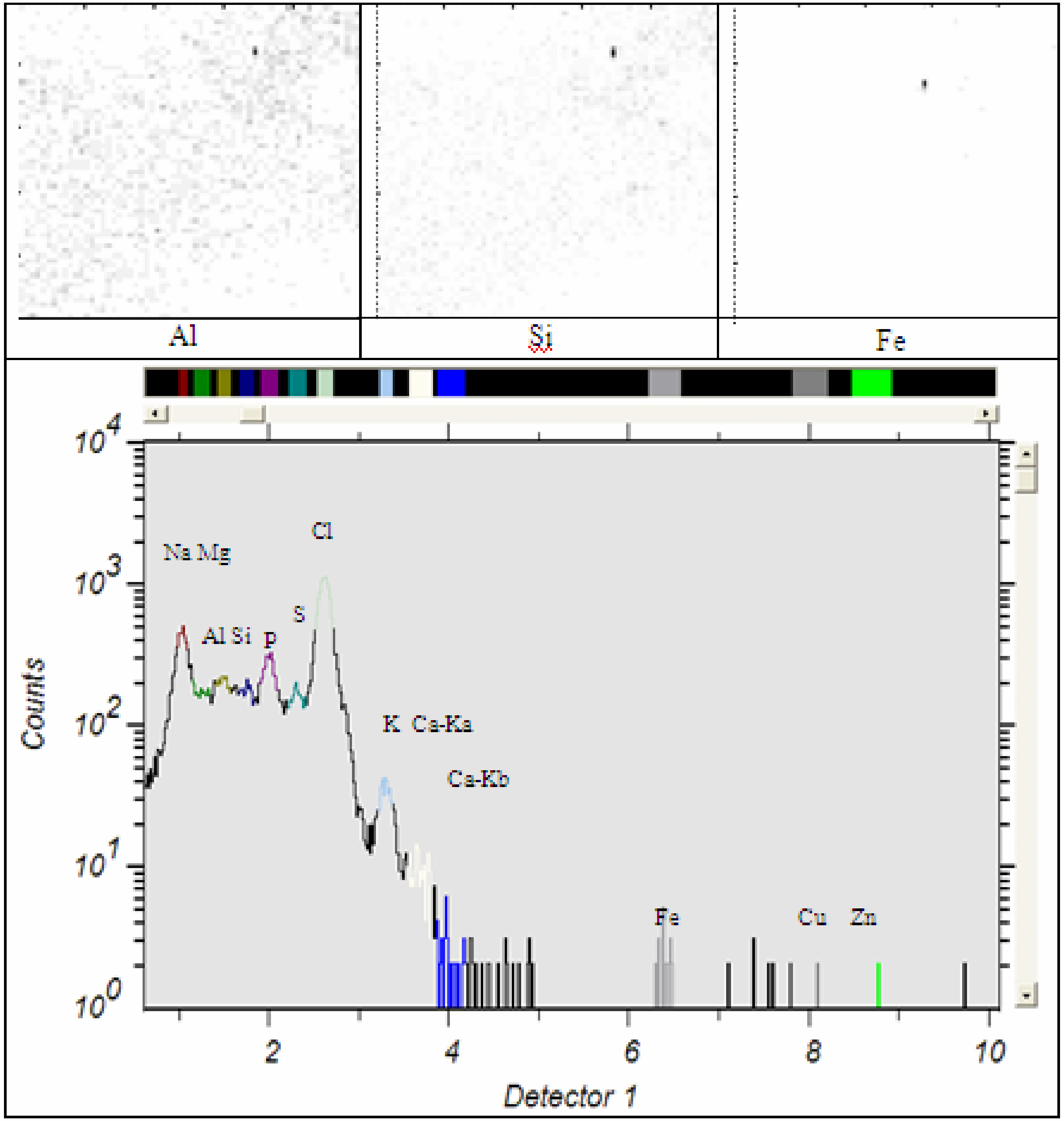
Nuclear microprobe imaging of air particulate matter (APM)

- to identify the sources of pollutant
- to 'map' pathways through the air
- finding the source is the key to eliminate or reduce the pollution



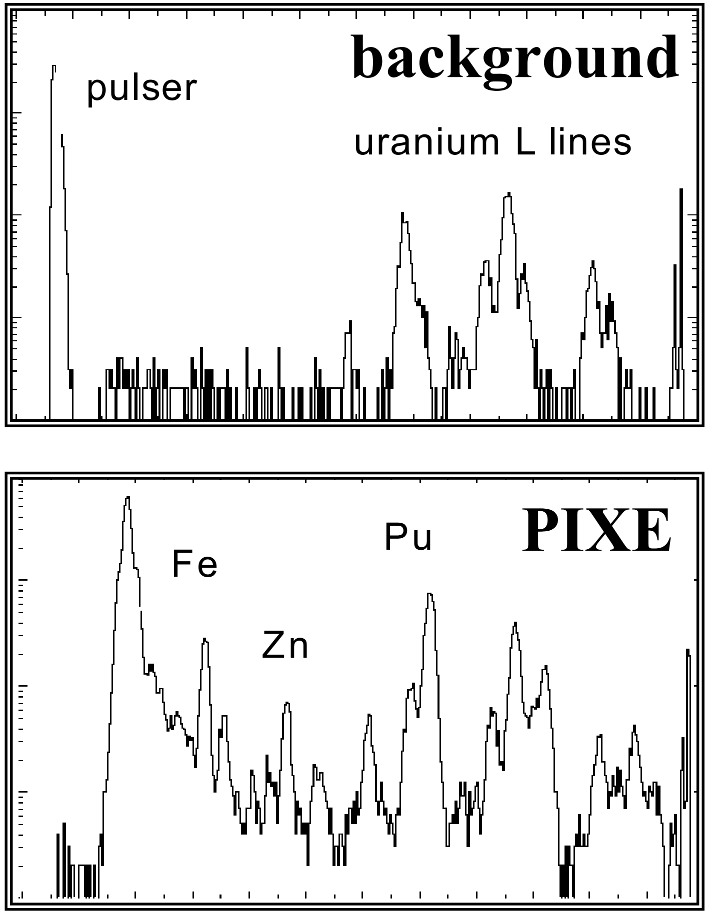


- qualitative imaging



For heavier elements (low background) as well as for lighter elements (high background) agglomeration of particular element can be seen in 2D map even for very low peak statistics.

μPIXE imaging of hot particles

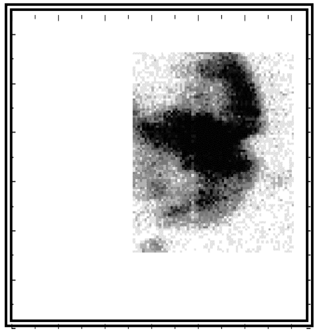


-U x-ray L lines (internal conversion) without the excitation source

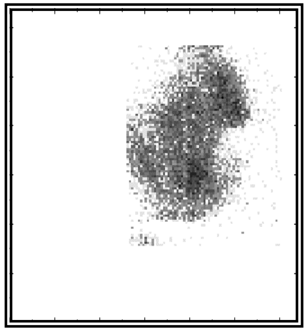
- high PIXE cross sections and high detection efficiency - good separation of peaks from the background

- samples between two Kapton sheets detection efficiency for low energy x-rays is low

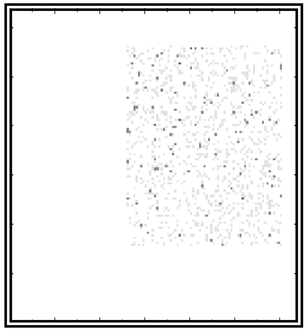
Sample #1



calcium (Kα)

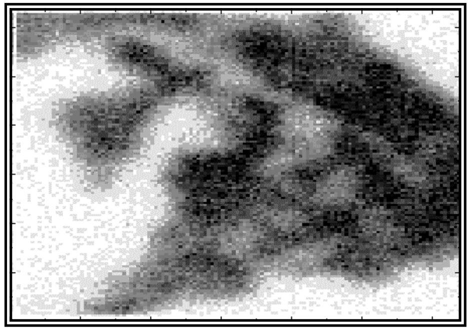


plutonium (Lα)

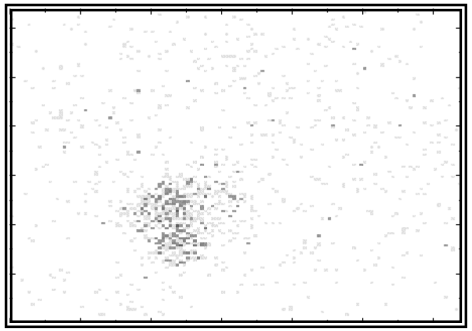


uranium (Lα)

Sample #2



Calcium (Kα)



Plutonium (Lα)

Sample #1

- homogeneously distributed Pu over the whole hot particle is visible

-the x-ray intensity maps with homogeneous intensity distribution can be used to distinguish between the"real" and the "background" peaks

Sample #2

-Pu distribution is localized and separated from Ca distribution

Analysis of art objects

External beam PIXE setup at the Ruđer Bošković Institute in Zagreb

- IBA can clarify the histories of archaeological artifacts and works of art by identifying elements present in trace quantities

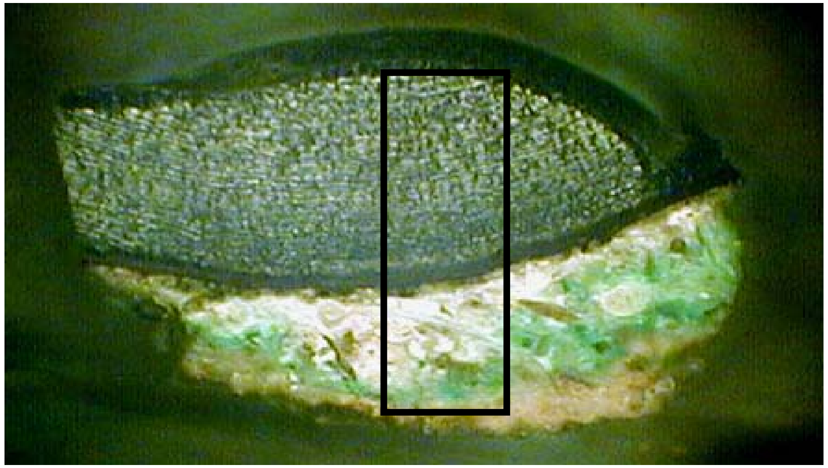
- external beam μPIXE

- numerous studies on paper, manuscripts and drawings to determine the nature of inks, pigments or metal points

Bronze sculpture – Apoximenos

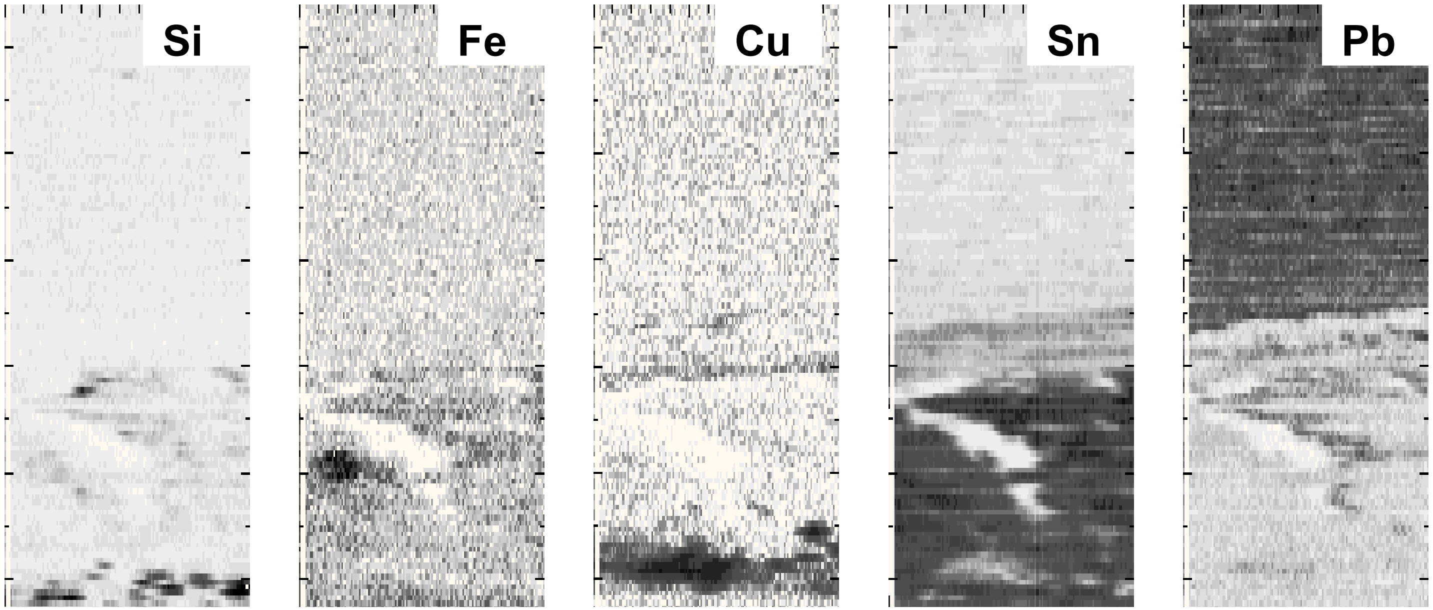
- Found in 1996 near Lošinj in Croatia, 45 m below sea surface between two rocks
- Analyses of state, construction, molding, organic material in sculpture
- X-ray
- PIXE, microprobe

Bronze sculpture – Apoximenos



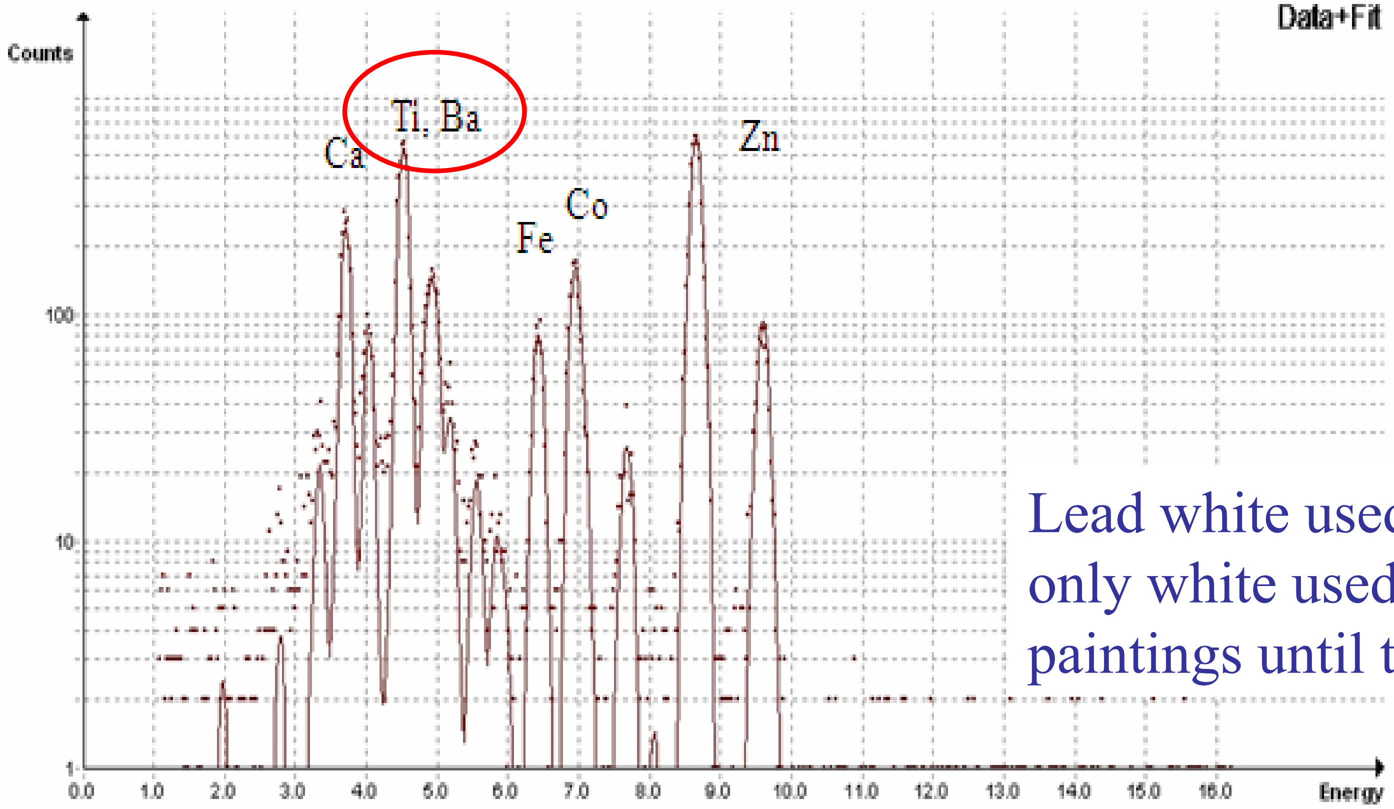
In vacuum micro PIXE of bonding interface (Greek or Roman?) (2. century b.c.)

Bronze with different amounts of Pb, Greek < Pb, Roman > Pb



Cu is leached by seawater that explain increased concentration of Pb at the surface --> Sculpture is of Greek origin

The authenticity of art objects



20 Ca	19.5 %	
22 Ti	16.3 %	
26 Fe	1.8 %	
27 Co	3.9 %	
30 Zn	25.5 %	
56 Ba	13.8 %	

Lead white used since antiquity, only white used in European paintings until the 19th century.

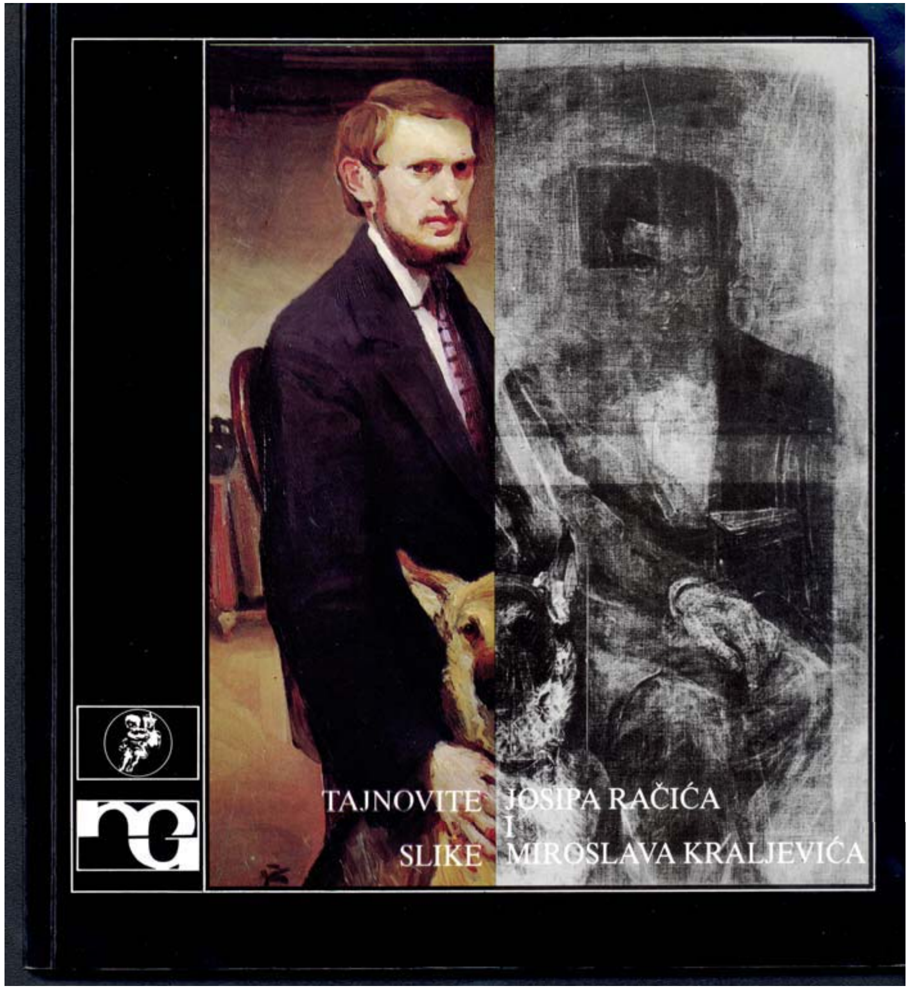
- In 19th century lead white ($2PbCO_3 \cdot Pb(OH)_2$) was replaced by zinc white ZnO and barium white ($BaSO_4$)

The use of titanium white - maximum age of the painting of about 100 years, as TiO_2 was discovered in 1908.

Project Račić-Kraljević

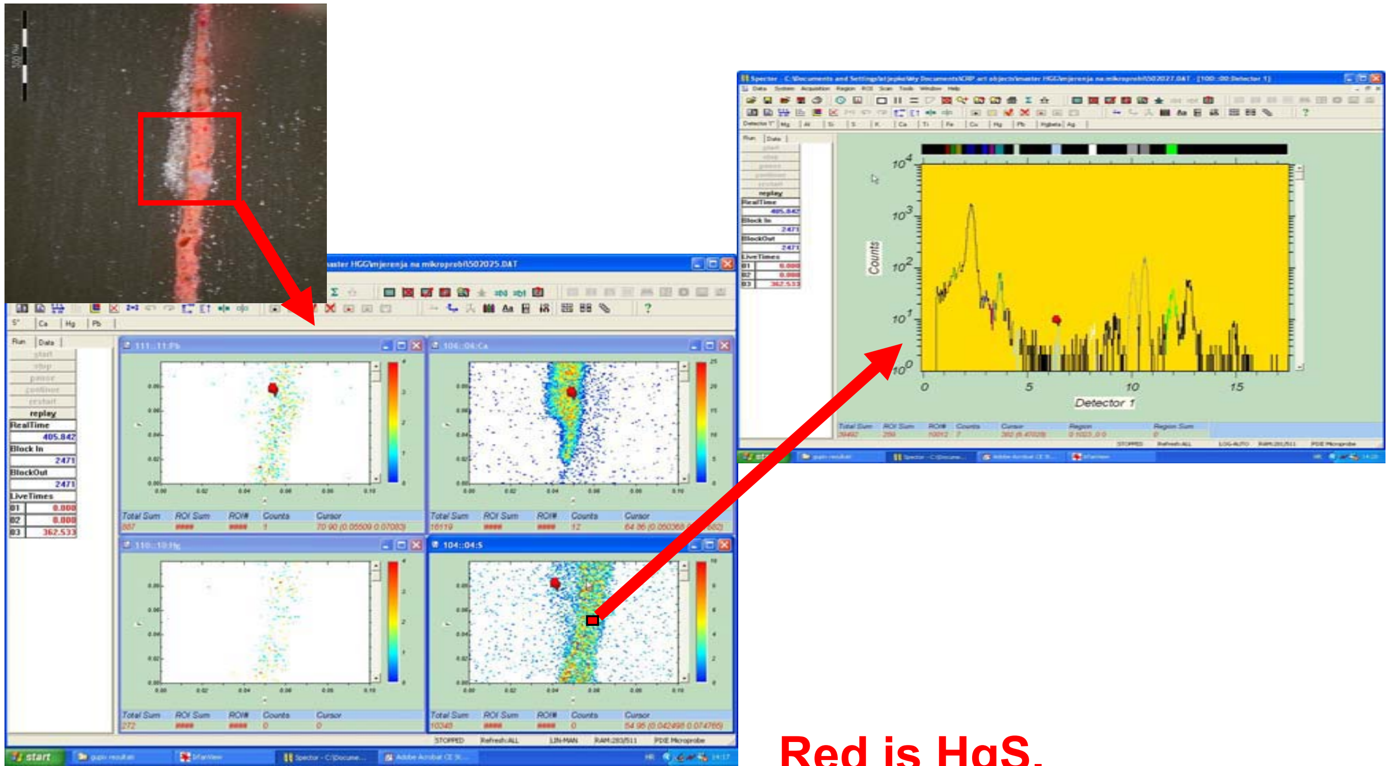
First sistematic scientific investigations of paintings by Croatian Conservation Institute done in 1986.

- among other techniques – XRF
- analysed almost all work of both painters – well known which pigments they have used
- in case of Račić there was one suspicious painting – pigment analysis proved that painting is a forgery



Hans Georg Geiger (HGG) – painter from 17th century

- 17th century cultural heritage in Croatia minimal
- Hans Georg Geiger was living and working between 1641 and 1680 in Slovenia and Croatia (Austrian Monarchy)
- he left 32 paintings (half in Croatia)
- most of his preserved works has not been signed
- almost all paintings in churches



Red is HgS.

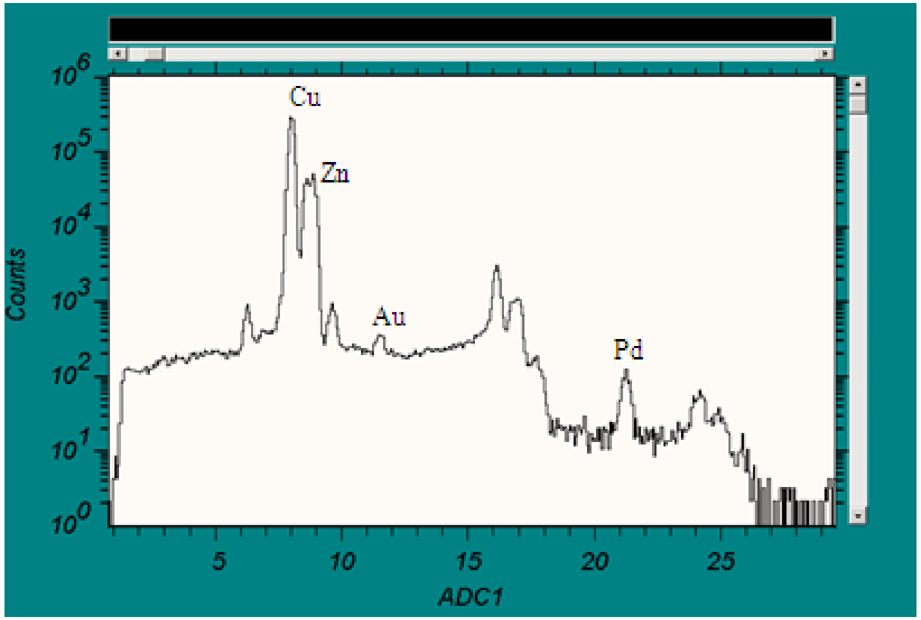
502027

Element	koncentracija u težinskim %	Greška u %
AlK	0.84	22.4
SiK	0.31	52.1
PK	0.60	34.6
SK	3.03	22.5
KK	0.21	54.1
CaK	2.19	7.5
CuK	0.22	32.6
HgLA	18.24	6.3
PbLA	52.83	3.7

HGG, ~30 samples analysed for the attribution purposes

Jewelry investigation

PIXE

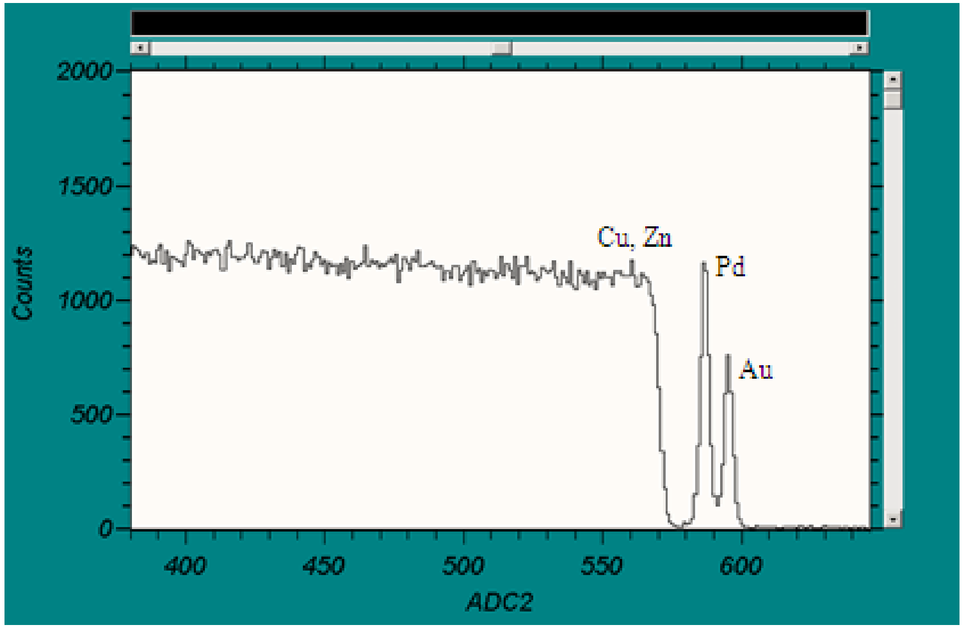


From PIXE spectra major elements present in the sample are seen: Cu, Zn, Pd i Au. Pt lines were not detected.

No information about depth distribution!

RBS

Sample layers:
- 102 nm Pd
- 23 nm Au
- bulk is CuZn alloy



Forensic examples from the literature

- traces of elements left by blades in bones
- trace element analysis of explosives

- case of cremation in which the nature of the remains was questioned

- cases of death by gunshot wound

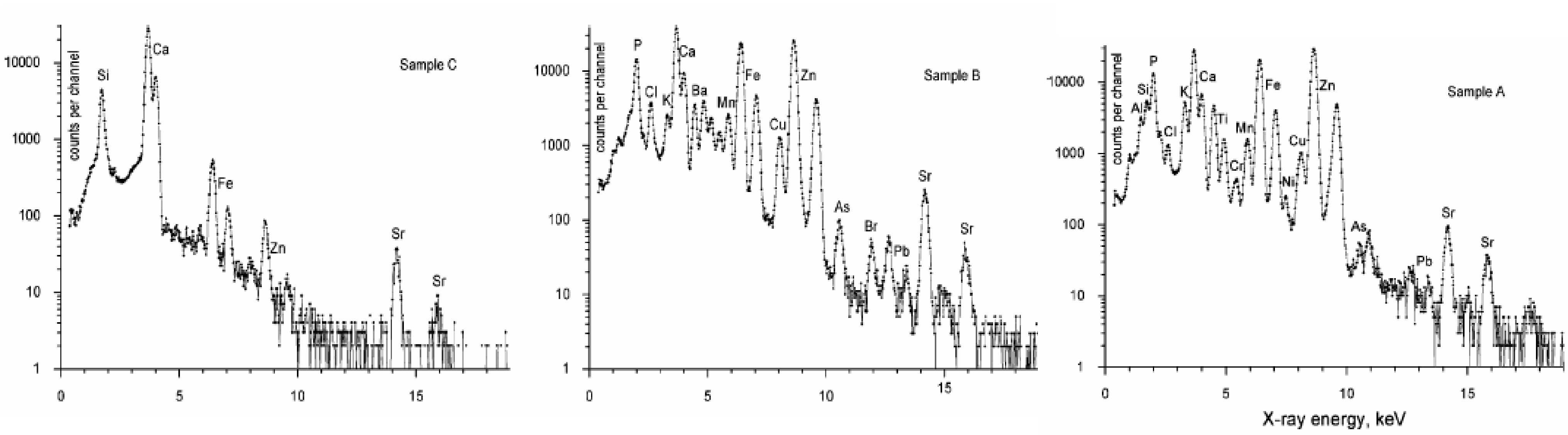
- identification of absorbed lubricants at a victim's clothing, shoes and gloves

-2007 PIXE Conference – B.L. Doyle et.al, Forensic analysis of particulates harvested from filters and other matrices at crime scenes or after terroristic acts

Elemental analysis of bone: proton-induced X-ray emission testing in forensic cases

M.W. Warren et al., Forensic Science International 125 (2002) 37

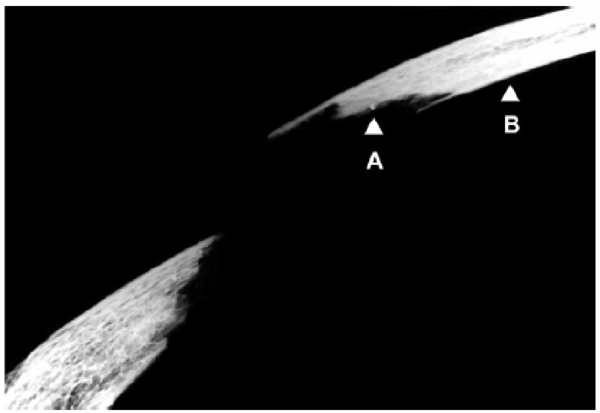
1.Case: Are cremated remains human?

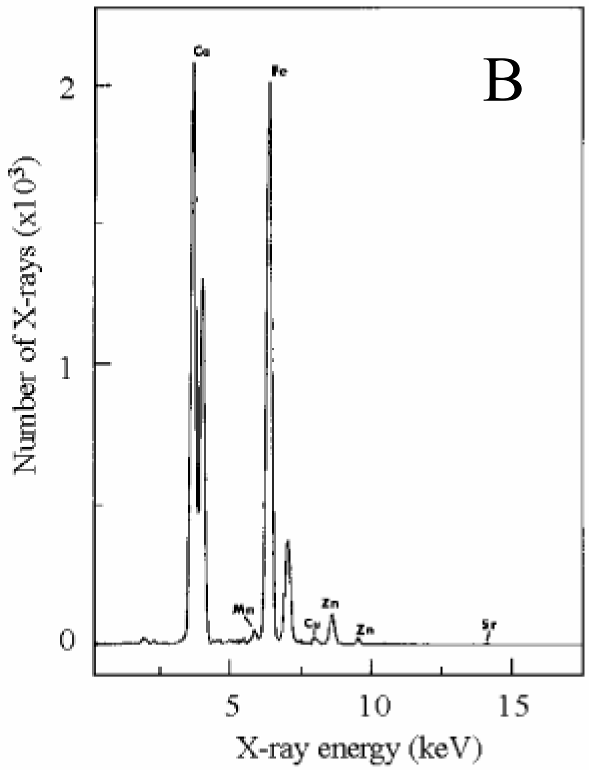


- lack of P (a major constituent in bone and teeth) and P/Ca ratio which does not represent ratio in the human body (0.44) leads to the conclusion that sample C does not represent cremated human remains

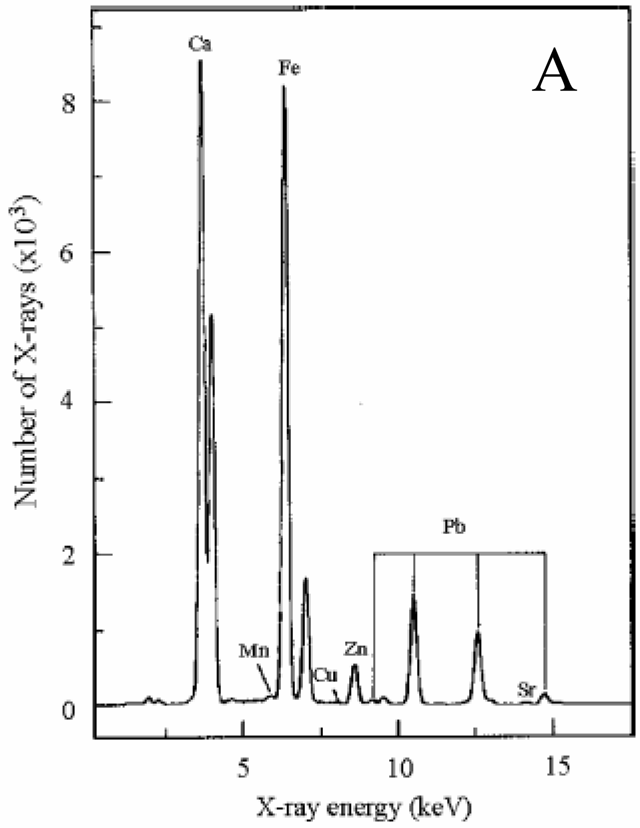
Sample C was identified as dolomitic limestone with an admixture of sand.

2.Case: Gunshot wound





(a)



(b)

- detection of such wounds in human skeletal remains, where the soft tissue diagnosis is no longer possible

-Pb traces were determined near suspicious place

- clear evidence of gunshot

PIXE – a new technique for the trace element analysis of high explosives

D.W. Lane , D.C. Wicks, Nucl. Instr. And Meth.161 (2000) 792

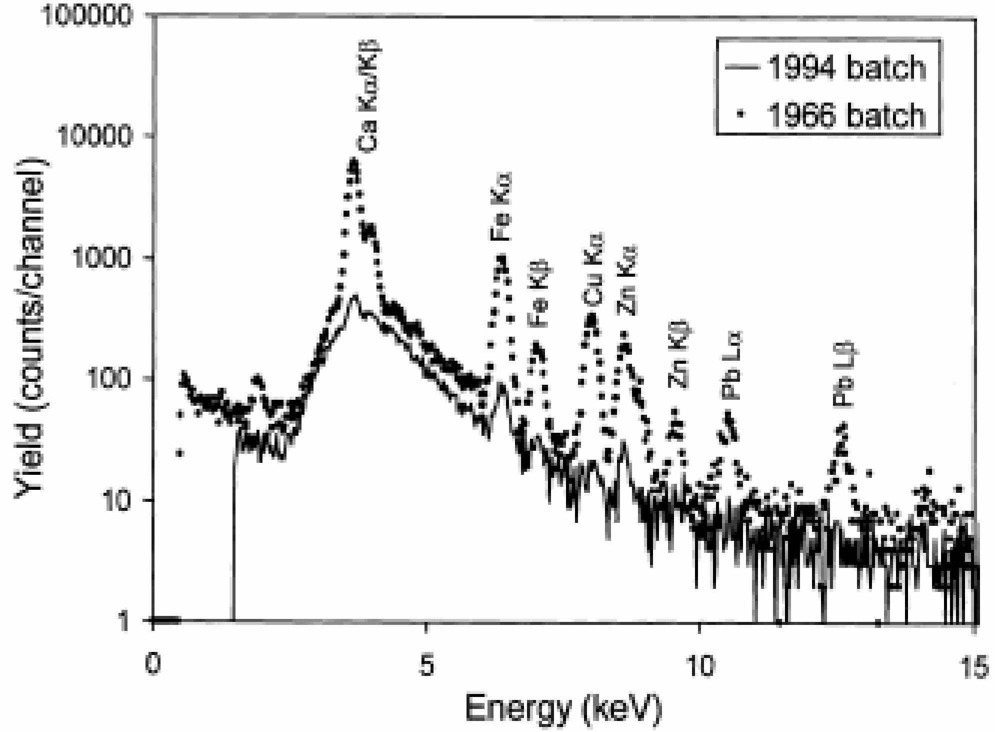


Fig. 1. PIXE spectra from two different batches of PE4 plastic explosives.

-they have analysed PE4 and ash from PE4 for 10 different production batches
dating from 1966 and 1994

-sudden drop in trace element concentrations occurred around 1985

- a statistically meaningful result at the 5% confidence level was only
achieved for Ca, Fe, Cu, Zn and Pb

Summary and conclusions

- IBA techniques can be succesfuly used for the identification and quantification of elements and their depth distribution in different materials such as paints, inks, tissues, hair, bone, air particulate particles, etc. and therefore can be used in forensic science.

-among IBA techniques most used are PIXE and μPIXE

- methods are multielemental, non-destructive and require small amount of sample for the analysis (important for forensic evidences!)