# Material Analysis

After the classical nuclear physics on the MeV scale lost much of its attractiveness about thirty years ago many of the existing small accelerator facilities have been used for applied physics. It turned out soon that several methods of nuclear research are extremely helpful in materials analysis and modification. Therefore, the field of MeV ion beam physics evolved fast and has found many applications for the compositional and structural characterization of surfaces. It also found its way into research fields such as geology, mineralogy, biology, medicine, environmental science, and archeology. The advantage of ion beam analytical methods is their ease of use, the nondestructiveness and the straightforward and completely quantitative interpretation of the experimental results. The high accuracy of the techniques is mainly due to the precision with which cross-sections of the involved atomic and nuclear processes are known. In the last three decades on the order of one hundred new small MeV accelerators have been installed for materials science applications.

## Analysis Methods

Particle beams are particularly suited for materials analysis because of their interaction with matter. During the bombardment of a sample elastic and inelastic scattering, nuclear reactions and electromagnetic excitation take place.

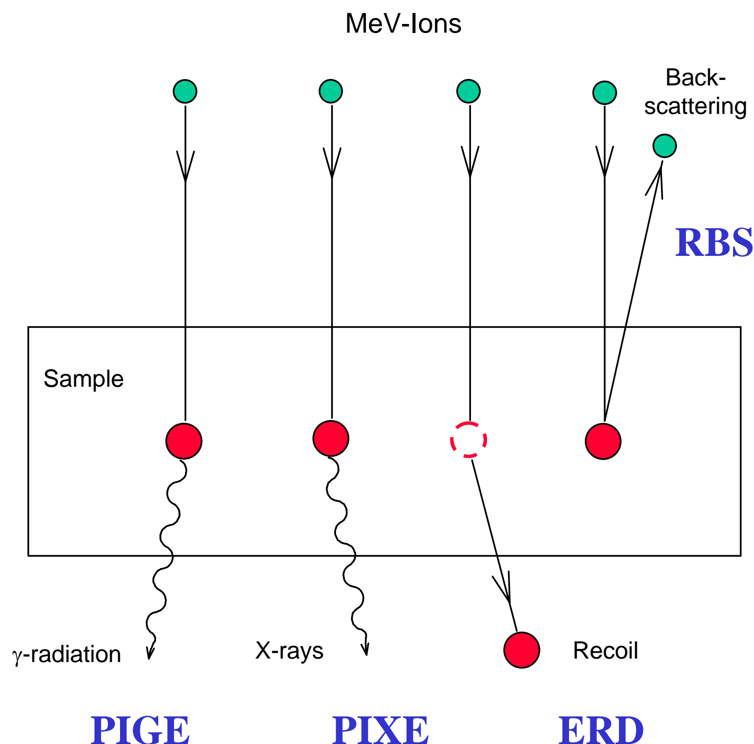



*Figure 1: Interaction between MeV ions and a material surface. Overview of processes relevant to ion beam analysis.*

From the number of observed events per incident beam particle the material composition can be deduced. Since most of the interaction processes are either very

simple to calculate (e.g. elastic scattering), or are very well explored during the many decades of nuclear research, the analysis is often straightforward and completely quantitative. The experimental equipment (apart from the accelerator) is relatively simple and in many cases consists of standard nuclear detectors with associated electronics.

## 1.) Rutherford Backscattering Spectrometry (RBS)

RBS is the most frequently used ion beam analysis method. It relies on the fact that the 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). This allows to profile the elemental composition of the sample close to the surface. Combined optimization of the mass and depth resolution shows that a $^4$He beam with approx. 2 MeV backscattered under an angle close to 180° is suitable for most problems.

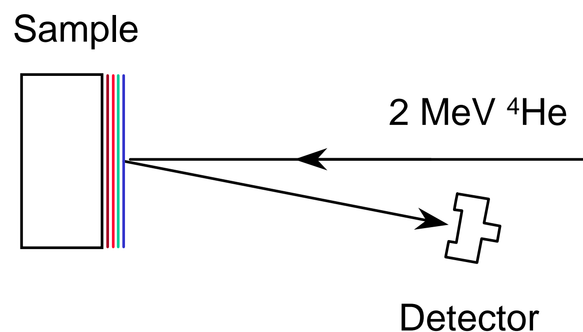
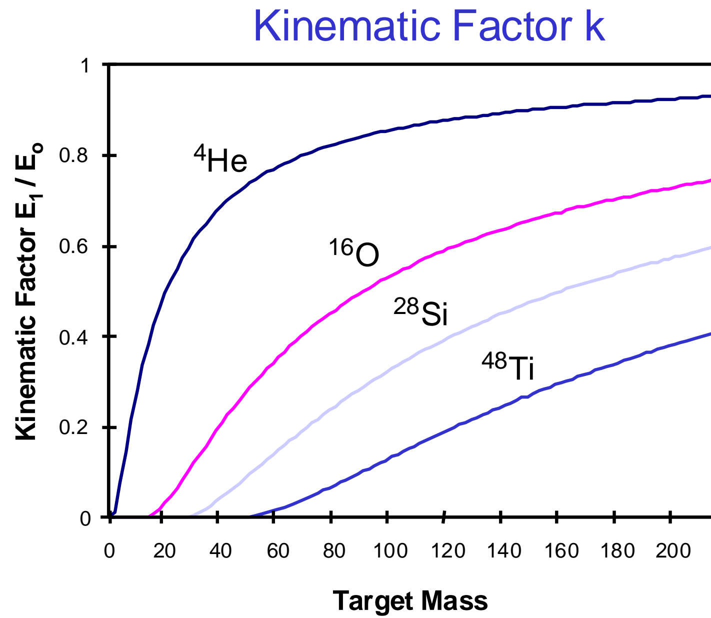



*Figure 2: Experimental setup for RBS*

The detection of backscattered particles can be done with simple silicon surface barrier detectors. In principle all elements from Be to U can be detected, though the sensitivity depends largely on the combination of elements and the sequence of layers in the target. RBS is suited best for the detection of heavy elements on light substrates. In this case sensitivities between 10 and $10^{-4}$ monolayers can be reached. The accessible depth for profiling is a couple of µm with a depth resolution of the order of 10 nm at the sample surface. With special detection systems monolayer depth resolution can be achieved. The analysis of the experimental spectra is made easy by commercially available software. The accuracy of the results is of the order of 1 %.

**Target mass discrimination:** The identification of a certain atomic mass in the target is made via the kinematic factor k:

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




where E is the ion energy, $M_1$ the mass of the incident ion, $M_2$ the mass of the target atom and $\theta$ the scattering angle. Thus, the backscattered energy is equivalent to a mass scale.

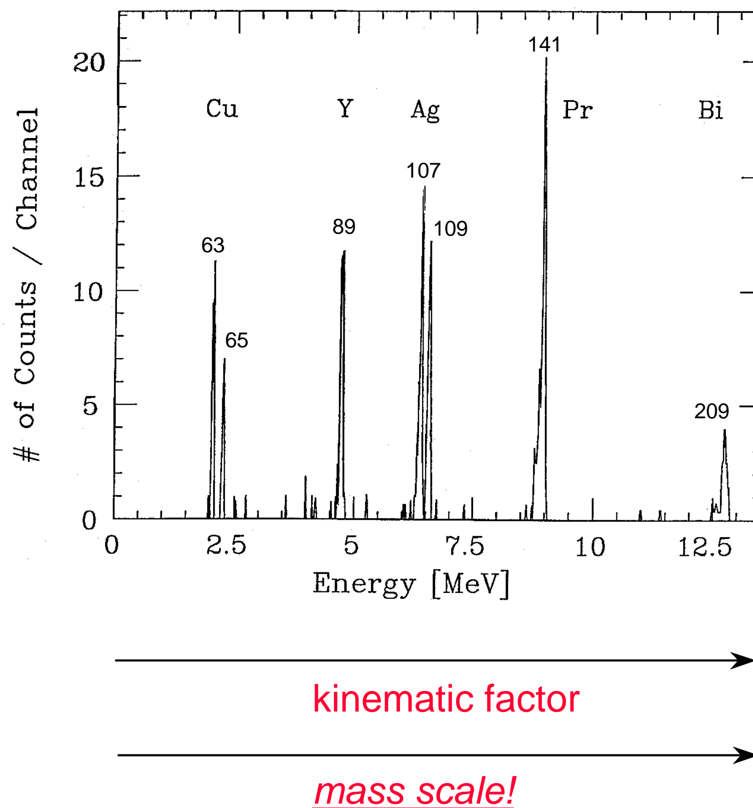
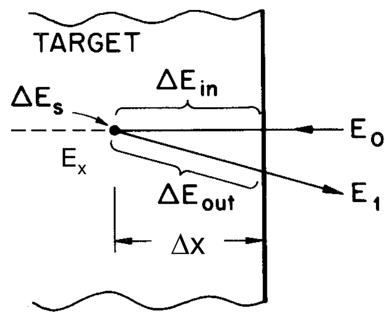



*Figure 4: RBS example demonstrating mass discrimination. Projectile: 25 MeV $^{35}Cl$; target: thin layers of Cu, Y, Ag, Pr, Bi. Isotopes of Cu and Ag are resolved.*

**Depth scale:** The signal from an atom at the sample surface will appear in the energy spectrum at a position $E_1 = k \cdot E_o$. The signal from atoms of the same mass below the sample surface will be shifted by the amount of energy lost while the projectiles passed through the sample, both before ($\Delta E_{in}$) and after a collision ($\Delta E_{out}$).




$E_x$ = energy before scattering

$$\Delta E_{in} = \left(\frac{dE}{dx}\right)_{in} \cdot \Delta x$$

$$\Delta E_s = (1-k) \cdot E_x \qquad \text{(kinem. loss)}$$

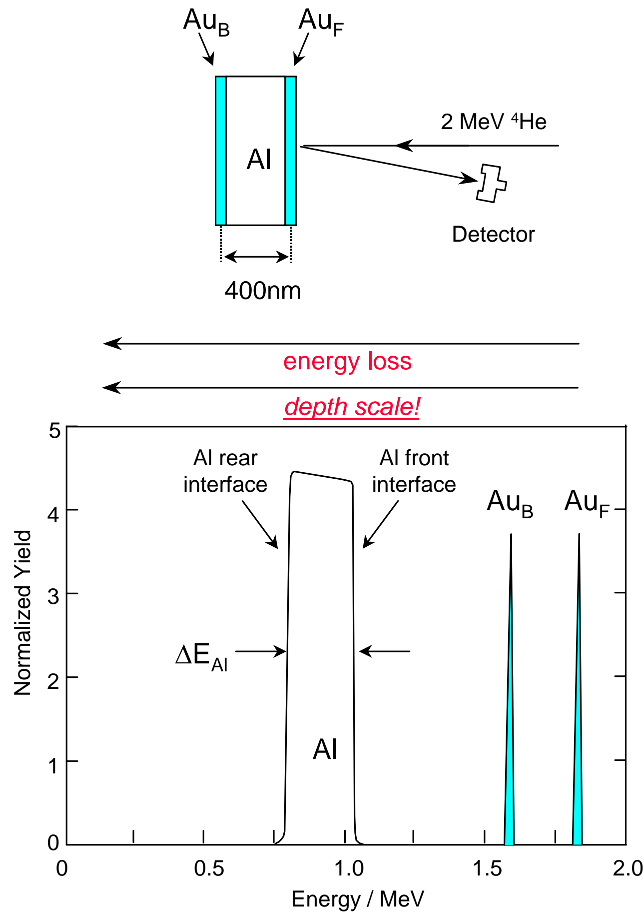
$$\Delta E_{out} = \left(\frac{dE}{dx}\right)_{in} \cdot \frac{\Delta x}{\cos\theta}$$

Detected energy $E_1 = E_o - \Delta E_{in} - \Delta E_s - \Delta E_{out}$

$$\approx kE_o - \underbrace{\left[\left(\frac{dE}{dx}\right)_{in} \cdot k + \left(\frac{dE}{dx}\right)_{out} \cdot \frac{1}{\cos\theta}\right]}_{S} \cdot x$$

Close to the surface there exists a linear relation between the measured energy $E_1$ and the depth *x* at which the scattering took place:

$$E_1(x) = kE_o - S \cdot x$$




Thus an RBS spectrum is an overlay of the depth profiles of all individual atomic species present in the target material.

Cross section: If the projectile energy is chosen properly (above electronic screening, below Coulomb-barrier) the scattering yield follows the well known Rutherford cross-section which is basically inverse proportional to the projectile energy and proportional to the square of the atomic number of the target atom.

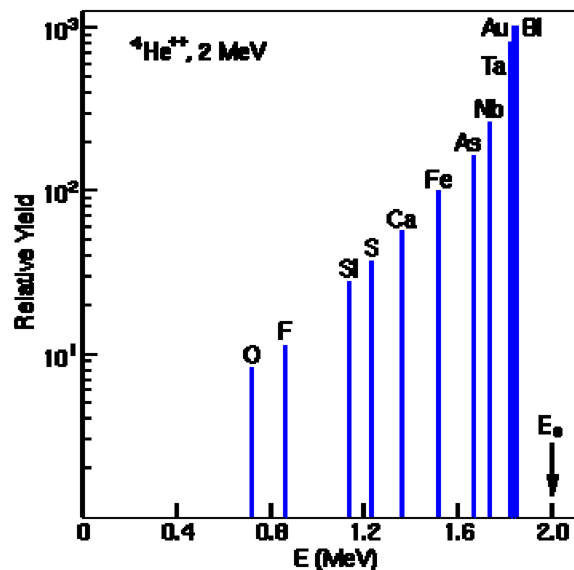


*Figure 7: Comparison of scattering yields as a function of the target atomic number.*

**Main features of RBS:**

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

## 2.) Elastic Recoil Detection Analysis (ERDA)

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.

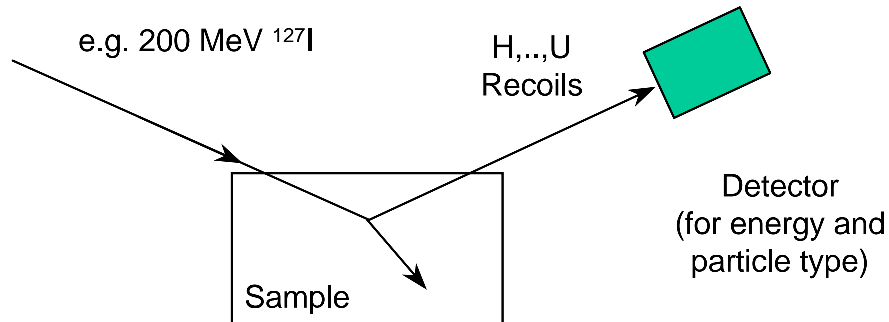



*Figure 8: Experimental setup for ERDA*

In order to discriminate between forward scattered projectiles and different types of recoiling particles absorber foils or mass discriminating detectors have to be used. The great advantage of ERDA with a mass (or nuclear charge) discriminating detector is that the depth profiles of all light target elements can be obtained simultaneously well separated from each other.

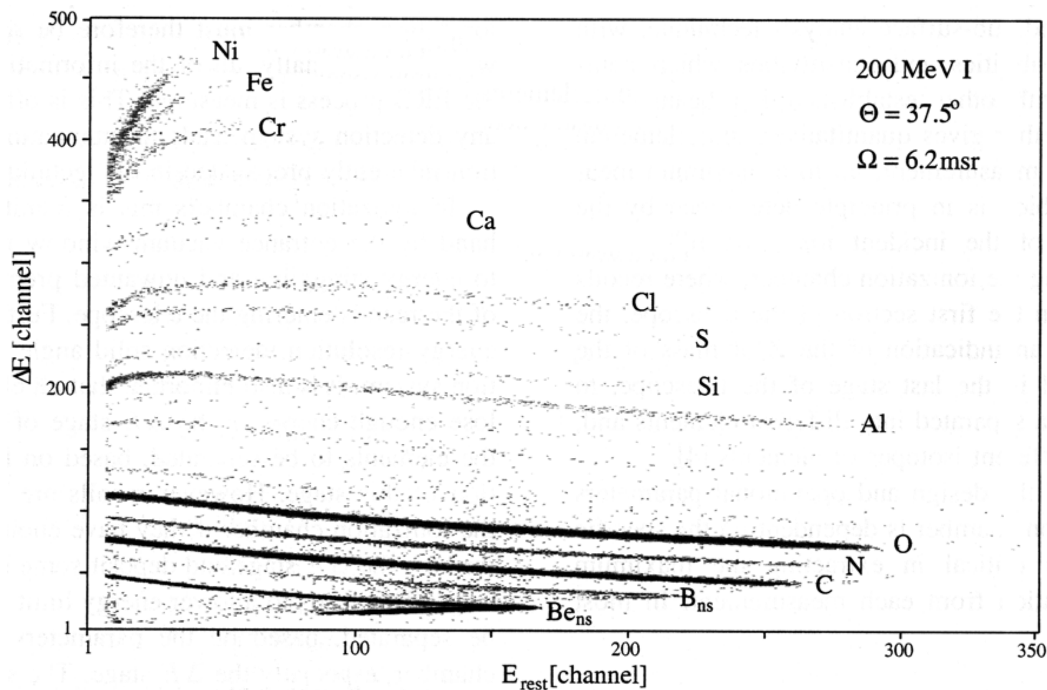
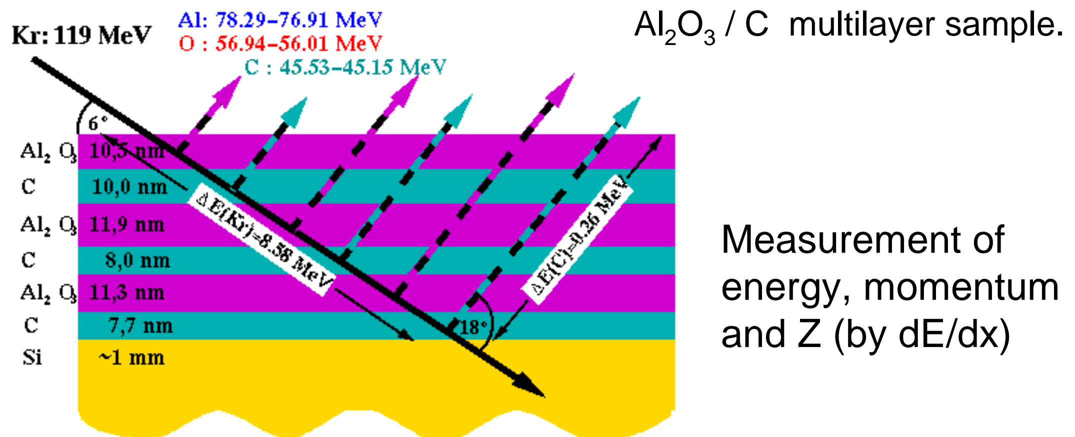
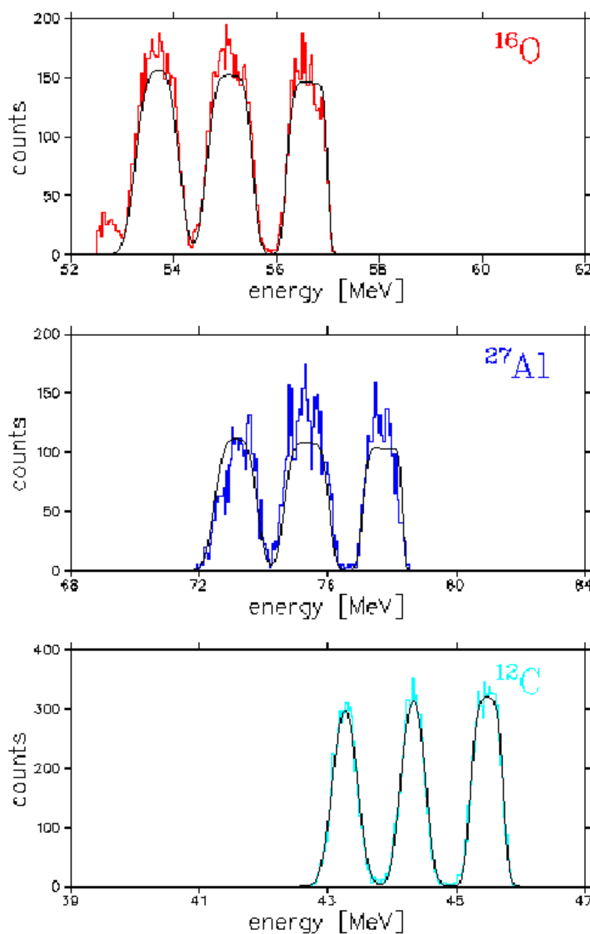


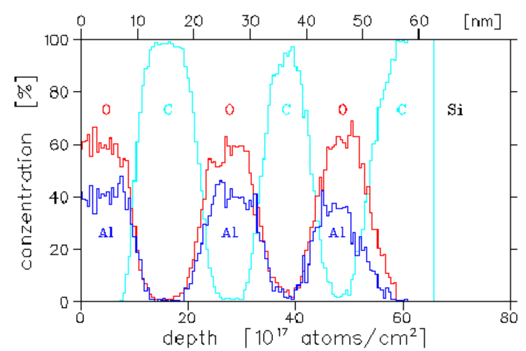

*Figure 9: ERDA spectrum from gas ionisation chamber with splitted electrode. Measures energy loss rate and total energy. Allows Z-identification. (JET first wall carbon sample (from V.M. Prozesky et al. NIMB 118 (1996) 327).*

Ionization chambers, combined silicon and time-of-flight detectors and combined magnetic and/or electrostatic spectrometers can be used. ERDA is one of the few fully quantitative hydrogen profiling methods.




## Elemental depth profile:




From A. Blazevic et al. HMI Berlin

*Figure 10: ERDA example, demonstrating simultaneous measurement of all elemental profiles.*

**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

Simultaneous profiles of all elements
Accessible depth range ~ 1µm
Light elements detectable on heavy substrates

### 3.) Particle Induced X-ray Emission (PIXE)

The incident beam particles (normally protons) eject inner shell electrons from the target atoms which results in the emission of characteristic X-rays.

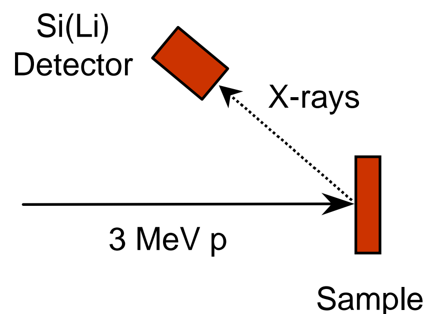



*Figure 11: Experimental setup for PIXE*

With a suitable x-ray detector (usually Si(Li) crystals) all elements heavier than C can in principle be detected. PIXE is the analogon to Energy Dispersive X-ray analysis (EDX) with electron microprobes. However, due to the complete absence of primary bremsstrahlung the sensitivity of PIXE is enhanced by about a factor of 100 compared to EDX and is of the order of ppm for most elements.

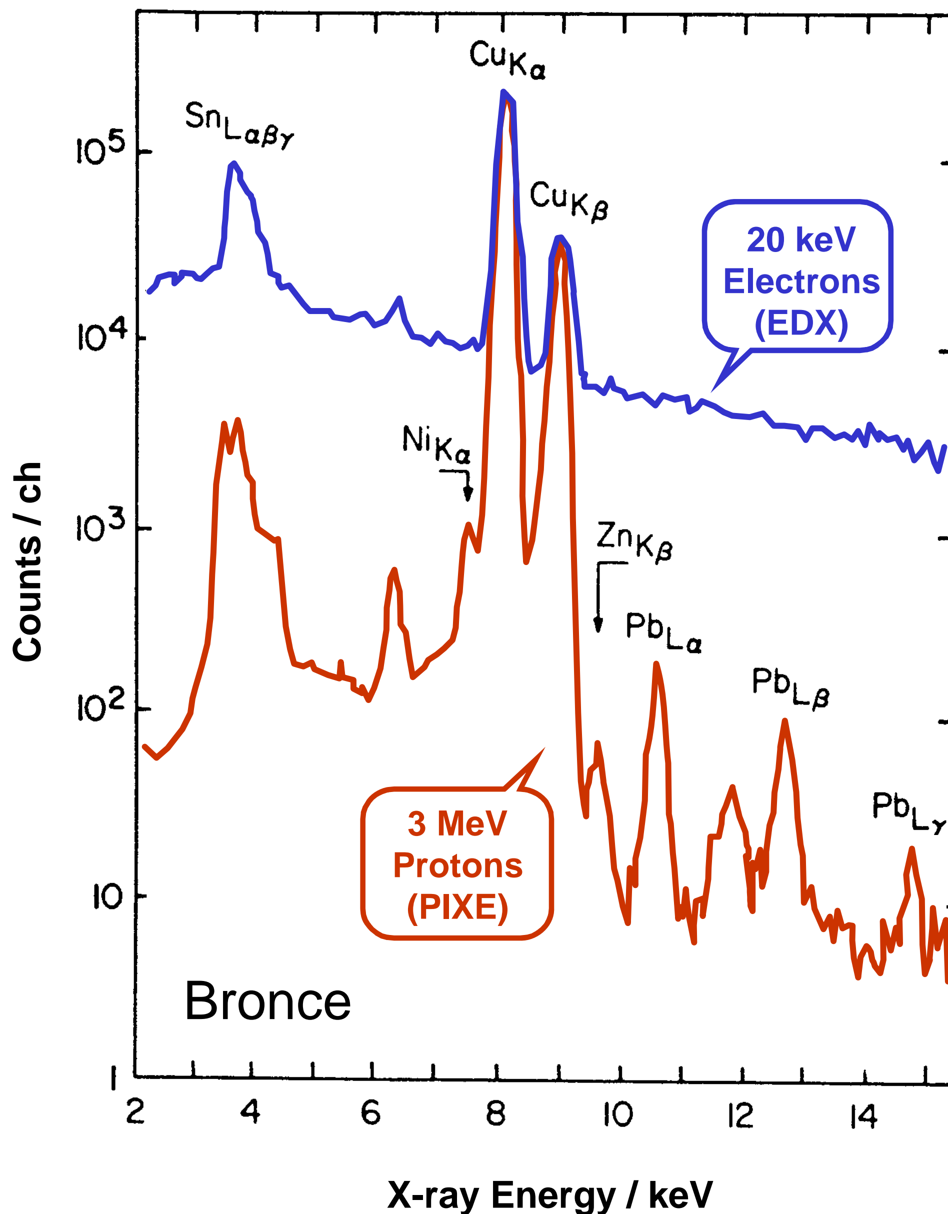



*Figure 12: Comparison of PIXE and EDX. PIXE is generally approx. 100 times more sensitive.*

PIXE is often used together with imaging nuclear microprobes for spatial elemental mapping with a lateral resolution down to a fraction of a µm.

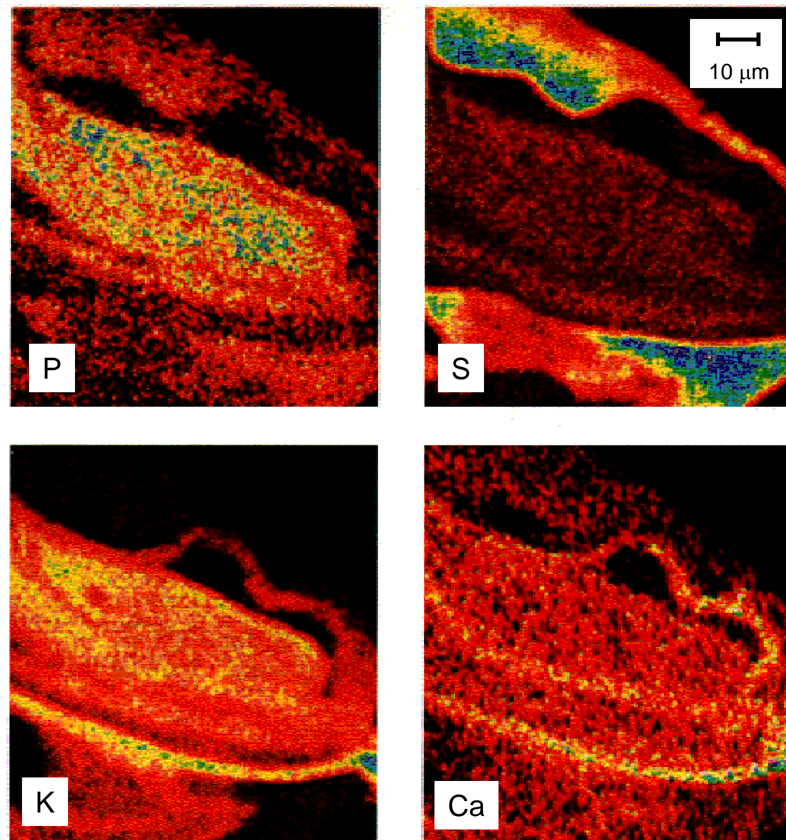



*Figure 13: Micro-PIXE: elemental mapping of a wheat cell*

In contrast to elastic scattering, PIXE offers no depth resolution unless the sample is cross sectionned and examined with a microbeam.

**Main features of PIXE:**

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

**4.) Nuclear Reaction Analysis (NRA)**

MeV ion beams can induce nuclear reactions in the target nuclei. In the energy range accessible to accelerators used for materials analysis (up to ~50 MeV) this is especially the case for light projectiles impinging on light to medium heavy atoms. The yield of the prompt characteristic reaction products ($\gamma$, p, n, d, $^{3}He$, $^{4}He$, etc.) is proportional to the concentration of the specific elements in the sample. If $\gamma$-rays are among the reaction products the detection becomes extremely simple since a conventional detector (NaI, BGO, Ge) can be positionned outside the vacuum system.

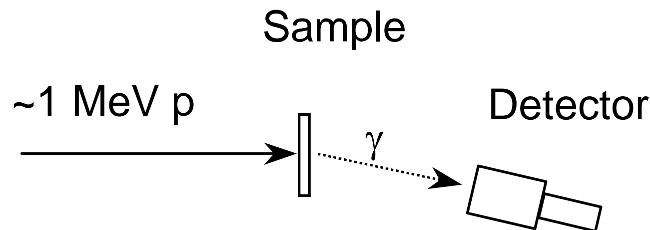



*Figure 14: Possible experimental setup for NRA*

Suitable reactions can be found for the analysis of virtually all elements up to mass 30. For heavier nuclei only scarce reactions exist. NRA is most often applied for the analysis of H, Li, Be, B, C, N, O, F, Na, Al, P. Detection limits range from $10^{-3}$ to $10^{-7}$. Absolute concentrations can be calculated easily with the help of simple standards (e.g. bulk material or compounds of the analysed elements). Reactions with narrow resonances (100 eV to 1 keV) can be found for many of the forementioned elements. These can be used for depth profiling with a resolution of the order of 10 nm by stepping up the accelerator energy and thus shifting the depth within the target at which the reaction takes place. The accessible depth can range up to a few µm. If reaction products are charged their energy spectrum can also be used for depth profiling.

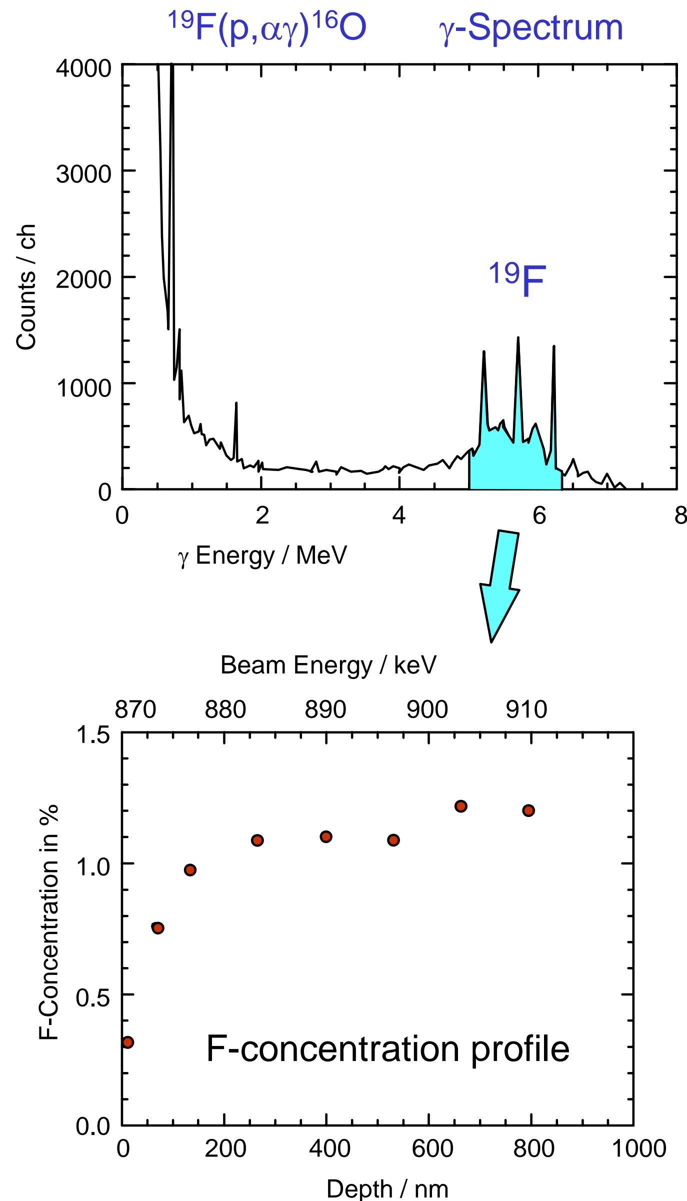



*Figure 15: Example for NRA-analysis of a plastic foil using a resonant (p,αγ) reaction. By stepping up the incident proton energy a depth profile of the fluorine concentration is obtained.*

If the reaction product is long-lived its decay can be measured after the irradiation with the particle beam. This analytical method is then called *Charged Particle Activation* (CPA) and is an analogon to Neutron Activation Analysis (NAA). Since the measurement of the decay products (mostly γ-rays) can be done after the beam has been turned off the background is much lower than for prompt radiation analysis. Therefore, detection limits as low as $10^{-12}$ can be reached (e.g. for C and N in Si).

<u>Examples of nuclear reactions suitable for NRA</u>:

| | |
|---|---|
| $^{7}Li(p,\alpha)^{4}He$ | $E_p$ » 3 MeV, $\sigma$ » 3 mb/sr, Q = 17.3 MeV |
| $^{12}C(d,p)^{13}C$ | $E_d$ » 1-3 MeV, Q = 2.7 MeV |
| $^{9}Be(^{3}He,p)^{11}B$ | $E_{He}$ » 1-5 MeV, Q = 10.3 MeV |

| | |
|---|---|
| $^{31}P(\alpha,p)^{34}S$ | $E_\alpha$ » 3 MeV, Q = 0.63 MeV |
| $^{7}Li(p,n)^{7}Be$ | $E_p$ » 2 MeV |
| $^{1}H(^{15}N,^{12}C)\alpha\gamma$ | $E_N$ = 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 |

**Main features of NRA:**

| | |
|---|---|
| Elements: | H - Al |
| Standard Conditions: | ~ 1 MeV proton beam ($^{15}$N, $^{19}$F, etc. for H-detection)<br>NaI, Ge, detector (Si detector for non-$\gamma$ reactions)<br>15 minutes per measurement<br>5 hours per profile. |
| Precision: | Composition: 5% relative<br>Absolute concentrations only by calibration standards |
| Sensitivity: | ppm to % depending on element<br>(ppb to ppt for CPA) |
| Depth Resolution: | 1 to 20 nm<br>Probed depth ~ µm |

**5.) Thin Layer Activation (TLA)**

For the measurement of corrosion rates and mechanical wear a thin layer in one or several spots at the surface of a machine part (e.g. shaft, joint, engine piston or cylinder) can be activated by an ion beam (p, d, $^{3}$He, $^{4}$He). By measuring the loss of activity during operation the abrasion rate can be deduced. Since exclusively $\gamma$-emmitters (e.g. $^{56}$Co) are used the measurements can often be done in-situ, i.e. the detector is placed close to the running machine and the wear is determined on-line. For steel a precision of 0.1 µm can be reached independently on the size of the machine part. A particular advantage of the method is the fact that surface wear and mechanical deformation do not interfere. Therefore, measurements can be done that are not possible in any other way. The needed activities are 3 to 300 kBq, so that the radiation hazard is negligible.

## 6.) Channeling

Channeling is the steering of an ion beam through the open spaces between rows or planes of atoms in a crystal. In a perfect crystal the number of scattering events of the beam particles with atoms in the lattice is reduced by approximately a factor of 100 if the beam is exactly aligned with a crystal axis. This number is very sensitive to the concentration and site of crystal imperfections and impurity atoms. Channeling can therefore be used for the determination of the concentration and structure of defects, amorphization profiles, impurity atom location, surface and interface configuration, lattice strain and deformation and overall quality of crystals and crystalline layers. The measured quantity in channeling is the number of 'close encounters' of the energetic ions in the beam with the target atoms at a certain depth in function of the crystal orientation. Detection methods are almost any of the above mentioned analysis techniques: RBS, ERDA, PIXE, and NRA. Among the advantages of the method are its high depth sensitivity (~10 nm resolution), the ability to look at a chosen atomic species in the crystal (even at very low concentrations and in thin layers) and the simple and unambiguous determination of the lattice site of atoms in many cases. It is one of the most important tools in submicron crystallography. In addition to the usual detection systems a precise goniometer for the adjustment of the sample is required.

## 7.) Micro Beam Methods

MeV charged particle beams can be focused to spot sizes around 1 μm with nA currents. Therefore, the ion beam analysis methods PIXE, RBS, ERDA, and NRA can be used in a surface imaging mode ('nuclear microprobe'). Since with RBS, ERDA and NRA depth information can be gained at each point of the surface, truly 3-dimensional maps of the sample can be obtained, nondestructively. Since a few years beam diameters below 100 nm can be achieved, though with much lower beam currents. These beams can be sent through thin samples to produce a density contrast image by the measurement of the energy loss of the particles. This method is called Scanning Transmission Ion Microscopy (STIM).

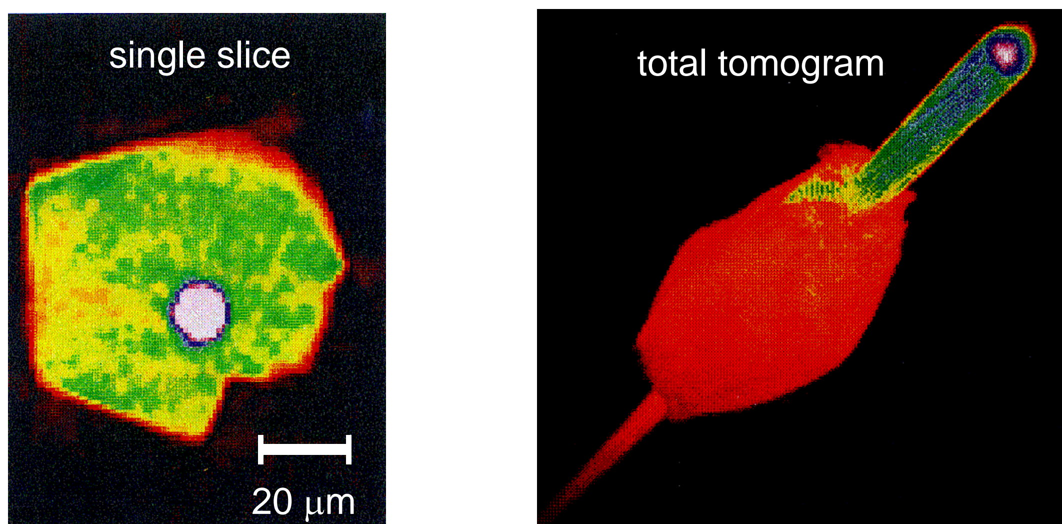



*Figure 16: Proton microbeam tomogram of a diamond particle on a needle (see text below).*

If the sample is rotated and shifted during the analysis a tomogram of the object can be produced showing its 3-dimensional density distribution with a spatial resolution in the micron range (Ion Microbeam Tomography (IMT)). It is possible to apply STIM to thin crystalline membranes under channeling conditions to obtain a 2-dimensional map of the crystal quality with a resolution of approx. 100 nm (Channeling Contrast Microscopy (CCM)). The information is gained via the dependence of the energy loss on the defect concentration in an aligned crystal.
By operating an ion microprobe in a 'single particle mode' (extremely low current) the electrical properties of integrated circuits can be probed (Ion Beam Induced Current, IBIC).

## Text books and other sources of information


'Fundamentals of Surface and Thin Film Analysis'
*L.C. Feldman, J.W. Mayer*
North Holland 1986.

'Handbook of Modern Ion Beam Materials Analysis'
*J.R. Tesmer, M. Nastasi*
MRS, Pittsburgh 1995.

'Backscattering Spectrometry'
*W.K. Chu, J.W. Mayer, M.A. Nicolet*
Academic Press 1978.

'The Stopping and Range of Ions in Solids '
*J.F. Ziegler, J.P. Biersack, and U. Littmark*
Pergamon Press, New York, 1985.

'Materials Analysis by Ion Channeling'
*L.C. Feldman, J.W. Mayer, S.T. Picraux*
Academic Press 1982.

TRIM/SRIM: http://www.srim.org

RUMP: http://www.genplot.com/

Charles Evans: http://www.cea.com/cai/rbstheo/cairtheo.htm


This manuscript can be found in similar form here:
https://cas.web.cern.ch/cas/Proc-Unpubl/Pruhonice.htm