2.5. Depth-profiling with PIXE

PIXE opens with the opportunity for depth profiling an additional dimension in art and artifact analysis. Sequences of layers can be analyzed to probe the preparation procedure and the preparation techniques.

Bethe-Bloch Formula

For heavy charged particles:

\[- \frac{dT}{dx} = \frac{4 \pi e^4 z^2}{m_e v^2} NB \]

where

\[ B = Z \left[ \ln \frac{2 m_e v^2}{I} - \ln \left( 1 - \frac{v^2}{c^2} \right) - \frac{v^2}{c^2} \right] \]

with the following definitions:

- \( v \): velocity of the charged particle
- \( z e \): charge of the charged particle
- \( N \): number density of absorber atoms
- \( Z \): atomic number of absorber atoms
- \( m \): electron rest mass
- \( e \): electron charge
- \( I \): A parameter, treated as experimentally determined, representing average excitation and ionization potential
- \( B \): is known as the stopping number (atomic number scaled for stopping)
Depth scanning with protons

Schematic drawing of the superposition of many Bragg peaks to produce a flat Spread Out Bragg Peak (SOBP).

Numerous applications, particularly in radiation treatment applications.
Simple Approximation Formula for Range Calculations

\[ R_A \ [cm] \approx 3.2 \cdot 10^{-4} \cdot \frac{\sqrt{A_A}}{\rho_A} \cdot R_{\text{air}} \ [cm] \]

\( \rho_A \equiv \text{density in \([g/cm^3]\)} \)

\( A_A \equiv \text{atomic number of absorber} \)

Example: range \( R_{208} \) of 3 MeV protons in Lead (A=208, \( \rho=11.35 \text{ g/cm}^3 \))

\[ R_{208} \approx 3.2 \cdot 10^{-4} \cdot \frac{\sqrt{208}}{11.35} \cdot 13 \ [cm] \]

\[ R_{208} \approx 5.29 \cdot 10^{-3} \text{ cm} = 53 \mu m \]
3 MeV protons on Nickel/Iron layer

Confirm the observed range of the 3 MeV proton beam in Nickel! A=58, ρ=8.9 g/cm³

\[ R_{58} \approx 3.2 \cdot 10^{-4} \cdot \sqrt{58} \cdot \frac{13}{8.9} [cm] \]

\[ R_{58} \approx 3.5 \cdot 10^{-3} \text{ cm} = 35 \mu m \]

observed is about 32 \mu m
Beam Stopping in Reality

7 MeV beam energy
R≈60 cm

0.3 MeV beam energy
R≈1 cm
PIXE: experimental set-up

- beam exit: thin Kapton foil
- moveable mirror inflects laser on beam axis
- two detectors at 135°
- shielding against radiation from exit foil
- xy table
- camcorder surveys and documents beam spot
Depth profiling of the “14 Nothelffer” by Lucas Cranach the Elder

The red robe of the holy Christopherus

Depth distribution of Hg and Pb indicates that the deeper layer of the coat was painted with minium Pb$_3$O$_4$ and the surface layer with vermilion HgS.

The spectrum shows the three L-transitions for Hg & Pb at two different energies.
HgS depth profile

Calculate the range of the 2 MeV and the 4 MeV proton beam in HgS; assume pure Hg! (A=200, ρ=13.6 g/cm³). The thickness of the HgS layer corresponds to the 50% Hg X-ray intensity. R_{air}(2 MeV)=8 cm, R_{air}(4 MeV)=22 cm

\[ R_{Hg}(2 \, MeV) \approx 3.2 \cdot 10^{-4} \cdot \frac{\sqrt{200}}{13.6} \cdot 8 \, [cm] = 2.7 \cdot 10^{-3} \, cm = 27 \, \mu m \]

\[ R_{Hg}(4 \, MeV) \approx 3.2 \cdot 10^{-4} \cdot \frac{\sqrt{200}}{13.6} \cdot 22 \, [cm] = 7.3 \cdot 10^{-3} \, cm = 73 \, \mu m \]

HgS thickness corresponds to about 50 \( \mu m \)
Art History Motivation:

19th century painting

- many copies of Allori, even by himself
- this copy: unknown artist 19th century??
- high quality of painting: (brushstroke...) ⇒ much older?

Judith with the head of Holofernes

Christofano Allori (1615)
Pitti Palace, Firenze

trust collection, Berlin

copy of Allori:
indirect dating

• analytical task: identification of pigments used (indirect dating by pigment chronology)
• paint layers > 100 µm thick ⇒ high proton energies necessary
• 15 different spots analysed on the painting
• on all but one spot: only lead, iron, calcium
19th century or much older?

- stylistic evaluation not sufficient
- more “solid” arguments: chronology of pigments

- collaboration with restaurateurs/art historians
copy of Allori: yellow colour

- Fe, Pb, Ca
- from Fe $K_{\alpha}/K_{\beta}$: iron on top of lead
  $\Rightarrow$ most probably yellow ochre
- no Cd, Cr ... $\Rightarrow$ modern pigments can be excluded
- No Sb, As $\Rightarrow$ Naples Yellow and Auripigmentum can be excluded
copy of Allori blue colour

- the only spot without Fe ⇒ Prussian Blue excluded (after 1735)
- no Co, Cu ⇒ Smalt, Cobalt Blue, and Azurite excluded
- ⇒ either ultramarine (Na, Al) or indigo (organic) both “invisible” for PIXE (in air), both used since antiquity
PIXE in the analysis of metal surface structure

Because of the large stopping power of high Z material (metals) for charged ion beams, protons cannot penetrate deeply into metal material. Nevertheless PIXE emerged as a very successful method for studying metal surface layers to learn about ancient metal treatment techniques.

e.g. surface analysis of gilded metal artifacts like this drinking cup.
The thickness of gold gilding

Gold has the atomic number $A=198$ and a density of $\rho=19.3 \text{ g/cm}^3$.

$$R_{\text{Au}}(4 \text{ MeV}) \approx 3.2 \cdot 10^{-4} \cdot \frac{\sqrt{198}}{19.3} \cdot 22 \text{ [cm]} = 5.1 \cdot 10^{-3} \text{ cm} = 51 \mu\text{m}$$

A gold gilding of up to 50 $\mu$m thickness can be investigated. To penetrate through thicker layers higher beam energy is required!

(example $E_p = 10 \text{ MeV, } R_{\text{air}} = 115 \text{ cm}$):

$$R_{\text{Au}}(10 \text{ MeV}) \approx 3.2 \cdot 10^{-4} \cdot \frac{\sqrt{198}}{19.3} \cdot 115 \text{ [cm]} = 2.7 \cdot 10^{-2} \text{ cm} = 270 \mu\text{m}$$
Penetration through surface layers (lacquer, patina, …)

- range of 4 MeV protons in plastic: 
  \[ \sim 0.25 \text{ mm} \]

\[ \Rightarrow \text{use of 68 MeV protons:} \]
- energy loss in 1 mm plastic \((\rho \gg 1 \text{ g/cm}^3)\): \(\sim 1 \text{ MeV}\)
- small lateral straggling