2.7. Profiling of Materials

XRF technique is limited by X-ray absorption
PIXE technique is limited by proton absorption

High energy XRF synchrotron radiation provides a more intense X-ray source to overcome absorption losses

High energy PIXE results in larger particle penetration depths for probing higher density material and deeper material layers
X-ray Fluorescence of Cast Bronze for Restoration

A Renaissance masterpiece, Benvenuto Cellini’s Perseus (1545) holding the head of Medusa", a work (first suggested by Duke Cosimo I de Medici) now in the Loggia dei Lanzi at Florence. The casting of this bronze group caused Cellini much trouble and anxiety, but it was hailed as a masterpiece as soon as it was completed. Because of damage due to air pollution the bronze figure was restored in 1996 – 2000.

Bronze Alloy Composition

Cu alloy
3.6% Sn
6.0% Pb
1.0% Sb
< 1% Fe
< 1% Ag

Absorption in Patina
Absorption in Patina

\[
\frac{I}{I_0} = e^{-\mu \cdot d}
\]

http://www.csrri.iit.edu/mucal.html

For Cu x-rays, \(E_x=8.2\ \text{keV}\); \(\mu=469\ \text{cm}^{-1}\)
For Sn x-rays, \(E_x=25.2\ \text{keV}\); \(\mu=59.7\ \text{cm}^{-1}\)

\[
d = \frac{1}{\mu} \cdot \ln \left( \frac{I_0}{I} \right); \left[ \frac{I}{I_0} \right]_{Cu} = 0.25; \left[ \frac{I}{I_0} \right]_{Sn} = 0.80
\]

\(d_{Cu} = 0.003\ \text{mm} = 3\ \mu\text{m}\);
\(d_{Sn} = 0.003\ \text{mm} = 3\ \mu\text{m}\)

High intensity source \(I_0\) translates into the possibility for larger depth analysis!
Details in alloy composition

Cu-Au composition

Bronze
Cu-Sn composition
Synchrotron Radiation

When high-energy particles are in rapid motion, including electrons forced to travel in a curved path by a magnetic field, continuous high intensity, strongly forward peaked, polarized synchrotron radiation is produced. Synchrotron radiation is the brightest artificial source of X-rays.
Homework Problem

Calculate the Flux $F$ of the bending magnets synchrotron radiation as a function of energy!

$$F = \frac{3 \gamma^6 \phi_m}{16 \pi^3 \varepsilon_0 \sigma_z \sigma_y \hbar c} \frac{I e \Delta \omega}{\omega} \gamma^2 *$$

$$\exp \left[ - \frac{1}{2} \left( \frac{z^2}{\sigma_z^2} + \frac{z'^2}{\sigma_z'^2} \right) \right] \left[ \left( \frac{1}{\gamma^2} + \psi \ast^2 \right)^2 K_{2/3}^2(\zeta) + \left( \frac{1}{\gamma^2} + \psi \ast^2 \right) \psi \ast^2 K_{1/3}^2(\zeta) \right] d\psi dz dz'$$
A typical beam line and detection arrangement

collimating mirror
- heat rejection
- vertical collimation
- bandpass filter

sagittal focusing
- double crystal monochromator
- monochromatization
- harmonic rejection
- horizontal focusing

refocussing mirror
- vertical refocussing

sample

source

slit

Slit

X-Ray

Sample holder

Sample

Ge SSD

XRF

X,Z stage

Detector

Controller

driftchamber det.

collimator

poly CCC
+ Si(Li) det.

polycap. halfiense
Synchrotron Technology
Synchrotron light source distribution - world wide and growing-
The Sky Disk from Nebra is a work of the smith's craft. From a rough-cast flan of soft bronze, a smith beat out the disc until it was 32 cm in diameter, which was no easy task.

In their metalworking technique too, the Nebra finds, with their metal inlays, are almost unique in central Europe. The Nebra hoard consists of about 4 kg of bronze and 50 g of gold: a substantial amount. There are copper deposits in the region around Nebra, but the results of the analyses point to a different source, and to extensive long-distance trade connections. The clues lead into other parts of Europe, such as England and Austria.
The Sky Disc was not created in a single round of work. It was altered again and again over four different time periods and each different generation of smiths left a particular metallurgic signature on the cult object.
Charged particle interaction with Air

The focused beam of accelerated protons leaves the vacuum tube through a thin HAVAR® exit window and strikes the object which is positioned on air. Along the proton path in matter Coulomb interactions and nuclear reactions take place with atoms of the material under analysis. That causes energy loss by Coulomb interaction and scattering of beam particles with the atmospheric medium. This excites atoms and causes them to emit X-radiation at energies characteristic for the particular chemical element.
Energy loss and 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

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

with the following definitions:

\[v\] velocity of the charged particle
\[ze\] charge of the charged particle
\[N\] number density of absorber atoms
\[Z\] atomic number of absorber atoms
\[m_e\] 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)
Beam Stopping in Reality

7 MeV beam energy
\[ R \approx 60 \text{ cm in air} \]

0.3 MeV beam energy
\[ R \approx 1 \text{ cm in air} \]
Simple Approximation Formula for Range Calculations

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

\( \rho_A \) = density in [g/cm\(^3\)]

\( A_A \) = atomic number of absorber

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

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

\[ R_{208} \approx 5.29 \cdot 10^{-3} \, cm = 53 \mu m \]
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

SRIM simulation

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

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

observed is about 32 μm
High energy beams (68 MeV protons)


Egyptian Coffin Mask

- gilded wood
- Queen Satdjehuti 1600 B.C.
- excavated about 100 years ago, private ownership
- status excellent - repaired?
- sensitive object, difficult to position

- investigated on 21 points
- on nearly all points:
  > 92 % Au, ca. 6% Ag, 1% Cu, (river gold) at least 1.5 µm
- thickness and composition → original gilding
  mask now in the Staatlichen Sammlung ägyptischer Kunst, München
Identification of a Chinese bowl

• both reports based on art historical expertise
• indirect dating: identification of pigments (Cr in green: after 1850)

Report 1 (Japan):
500 years old
Ming Dynasty (1368-1644)
1 Mio. €

Report 2 (Berlin):
100 years old
Qing Dynasty (1644-1911)
max. 25 000 €

Chinese Bowl

- porcelain extremely sensitive
- high-energy protons: small risk of damage due to low proton intensity and small \( dE/dx \)
- on bowl: Pb (flux) and Cu (pigment)
- modern porcelain: Cr (pigment)

- green colour no information
- yellow colour measured: modern pigment detected

→ report 2 could be confirmed