2.4. Particle Induced X-Ray Emission (PIXE)

The previous section concentrated on X-ray fluorescence. This section discusses a different X-ray production technique that can lead to the development of 2-D/3-D elemental imaging.

Technique is based on the use of 2-6 MeV particle accelerators.
The PIXE arrangements

Typically proton beams; protons transmit energy to the inner-shell electrons, ionize atoms with subsequent X-ray de-excitation.
PIXE Spectrum

Same energies as in the previous section, only the electron excitation mechanism is different!
X-Ray Energies as before!

**Characteristic X-Ray Energies**

<table>
<thead>
<tr>
<th>Atomic Number</th>
<th>X-ray energy [keV]</th>
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<tbody>
<tr>
<td></td>
<td>Ka</td>
</tr>
<tr>
<td></td>
<td>Kb</td>
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<tr>
<td></td>
<td>La</td>
</tr>
<tr>
<td></td>
<td>Lb</td>
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</tbody>
</table>

\[ E_x = (Z - 1)^2 \cdot 13.6 \text{[eV]} \cdot \left(1 - \frac{1}{n_i^2}\right) \]

\[ E_x = (Z - \sigma)^2 \cdot 13.6 \text{[eV]} \cdot \left(\frac{1}{2^2} - \frac{1}{n_i^2}\right) \]
Sensitivity of PIXE

PIXE shows superior peak-background sensitivity than electron beam induced or X-ray fluorescence methods. This reduces the samples size and improves sensitivity to 0.5 - 5 ppm value range.
Micro-beam techniques

Proton beam is focused onto a mm spot-size and then scanned in x-y direction across the sample
micro-beam line applications

Mapping of gold globules grown on crystal surfaces

Mapping of Deuterium concentration in human hair.
External PIXE beam applications

Micro beam penetrates thin Ni exit window. Distance in air depends on initial energy. The range for 2.5 MeV protons in air is $\Rightarrow 10$ cm.
Applications in Art & Archaeology

Gold jewelry artifacts,
• pottery,
• ancient record books,
• painting material
• writing material in Medieval & Renaissance manuscripts,
• Dinosaur bone and eggshell fossil,
• Human and Neanderthal man bone
• obsidian tools,
• human bones,
• rock varnish.

Because of limited depth-profile of method mostly applications in surface studies!
Tracing Material Origins

The red stone eyes of the statue of the Parthian goddess of love Ishtar were originally thought by Louvre curators to be made of colored glass.

PIXE analysis showed that the inlays were rubies. $\text{AL}_2\text{SiO}_4(F,\text{OH})_2+(\text{Cr,Fe rich})$

Where did the rubies come from?

Trace element content currently used as a fingerprint in archaeology

Comparison of Fe versus Cr content in Ishtar rubies with rubies from various provenances shows strong indication that rubies did originate from Burma. Ancient trade connections between near and far east empires!
Systematic study of Ruby impurity concentrations with PIXE

Thailand and Burma are the main supplier of natural rubies. The color of Thailand ruby is violet to deep crimson, of Burma ruby from pinkish to blood red. PIXE analysis of 60 rubies indicated that lighter color of Burma rubies results from higher impurity concentration on Chromium or Vanadium.
Native American and European Copper

Copper made objects have been found in 1400-1500 AD ‘pre-colonization’ settlements along the Ohio River valley. PIXE analysis of the relative Ag, Sb and Pb content revealed origin from native sources (A) or European (trade) sources (B).
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:

\[
-\frac{dT}{dx} = \frac{4\pi e^2 z^2}{m_0 \nu^2} NB
\]

where

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

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
- \( m \) 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)
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, r=11.35 g/cm\(^3\))

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

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

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

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

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

observed is about 32 μm
Beam Stopping in Reality

- 7 MeV beam energy
  - \( R \approx 60 \text{ cm} \)
- 0.3 MeV beam energy
  - \( R \approx 1 \text{ cm} \)