3.2. Neutron activation of paintings

Possible applications:
- Pigment analysis by activation techniques
- Neutron radiography by neutron absorption ⇒ Autoradiography

Requires neutron irradiation of the entire painting using homogenous neutron flux followed by subsequent point by point raster activation measurement.
Technical approach with reactors

Neutron guide line is needed for providing sufficient neutron flux (~$10^{14}$ neutrons/cm$^2$/s) for activation of bulky materials outside the reactor core!
By taking advantage of the characteristic decay time of the activated radioactive isotopes $T_{1/2} > 10$ minutes, it allows differentiating between different pigments and identification of brush stroke and under-drawing.

The painting needs to be stretched and held in place during activity recording.
### Timescale and Radiation Sensitivity

<table>
<thead>
<tr>
<th>Chemical element</th>
<th>Associated pigment</th>
<th>Radioactive isotope formed during activation and its half-life</th>
<th>Time period after activation during which best images in autoradiographs are produced</th>
</tr>
</thead>
<tbody>
<tr>
<td>manganese</td>
<td>umber, dark ocher</td>
<td>Mn(^{66}), 2.6 hours</td>
<td>0–24 hours</td>
</tr>
<tr>
<td>copper</td>
<td>malachite, azurite, verdigris</td>
<td>Cu(^{65}), 5.1 minutes Cu(^{64}), 12.8 hours</td>
<td>0–20 minutes 1–3 days</td>
</tr>
<tr>
<td>sodium</td>
<td>glue, medium, canvas, ultramarine</td>
<td>Na(^{24}), 15.0 hours</td>
<td>1–3 days</td>
</tr>
<tr>
<td>arsenic</td>
<td>smalt, glass</td>
<td>As(^{76}), 26.5 hours</td>
<td>2–8 days</td>
</tr>
<tr>
<td>phosphorus</td>
<td>bone black</td>
<td>P(^{32}), 14.3 days</td>
<td>8–30 days</td>
</tr>
<tr>
<td>mercury</td>
<td>vermilion</td>
<td>Hg(^{203}), 48 days</td>
<td>more than 25 days</td>
</tr>
<tr>
<td>cobalt</td>
<td>smalt, glass</td>
<td>Co(^{60}), 5.3 years</td>
<td>more than 25 days</td>
</tr>
</tbody>
</table>

Chemical elements and associated pigments most frequently observed in autoradiography of seventeenth-century Dutch and Flemish paintings.

The following pigments generally do not cause distinct images in autoradiographs: chalk, lead white, ocher, lead-tin yellow, lakes, madders, and indigo.
Activation with subsequent X-ray and $\gamma$-ray detection

$^{63}$Cu($n,\gamma$)$^{64}$Cu, Cu(x)
$^{202}$Hg($n,\gamma$)$^{203}$Hg, Hg(x)

X-ray data provides pigment position
$\gamma$-ray data provides pigment characteristics
Anthony van Dyck, Saint Rosalie praying for the Plague stricken of Palermo 1624
Pigment identification by analysis of time dependence for characteristic activity 3rd run

- 3rd autoradiograph
  - 4-4.75 hrs (after irradiation)

- $^{54}$Mn $t_{1/2}$ 2.6 hr

- umber = Fe$_2$O$_3$+MnO+clay minerals

- ground, preliminary sketch

- exposure reveals Mn position, brushstrokes
Pigment identification by analysis of time dependence for characteristic activity 6\textsuperscript{th} run

- 6\textsuperscript{th} autoradiograph
  - 2 - 4 d after irrad.

- $^{64}$Cu $t_{1/2} = 12.8$ hr
  - azurite
    - $CuCO_3,Cu(OH)_2$

- $^{24}$Na $t_{1/2} = 15$ hrs
  - ultramarine
    - sodium aluminosilicate
Pigment identification by analysis of time dependence for characteristic activity 8\textsuperscript{th} run

- 8\textsuperscript{th} autoradiograph
  - 8-20 d after irrad.

- $^{32}\text{P } t_{1/2} = 14.3 \text{ d}$

- bone black
  - $C + \text{Ca}_3(\text{PO}_4)_2$

- compositional difference between portrait and St. Rosalie sketch
  image separation possible
Young man in the background
Van Dyck Self-Portrait

Head also visible in X-ray radiograph

Self-Portrait of van Dyck 1622
St. Sebastian ca 1649

Painting in the Gemäldegalerie Berlin
original by Georges de la Tour (1593-1652)
French Court Painter

Original in Louvre, question about authorship
of copy, George de la Tour himself or by
his son Entienne de la Tour?

Neutron radiated $10^9$ n/cm²s

Neutron induced $\gamma$ activity is
recorded in two different time
steps: e.g.
1 day for $^{64}\text{Cu}$ ($T_{1/2}=12.8h$),
5 days for $^{203}\text{Hg}$ ($T_{1/2}=46.6d$)
and $^{32}\text{P}$ ($T_{1/2}=14.2d$)
X-ray radiograph

Painter used white lead for brightly lit areas.
(white lead was the only medieval white paint available.)
Comparison to x-ray radiograph

X-ray radiograph (white lead paint is main absorber for x-rays → visible)

Neutron activation (lead is not activated → invisible)
1 day: Azurite distribution ($^{64}\text{Cu}$)

Azurite ($2\text{CuCO}_3\cdot\text{Cu(OH)}_2$) is mainly visible in mourners veil. Contour of body is reinforced with ivory black $\text{C}+\text{Ca}_3(\text{PO}_4)_2\ (^{32}\text{P})$
The long-lived activity of $^{203}\text{Hg}$ (vermillion HgS) is clearly recognizable in the red dress and the lighter flesh colors. Also the body contour shows as $^{32}\text{P}$ decay.
The Depiction of St. Sebastian

Analysis gives evidence that painting is original copy by Georges de la Tour himself!

- Paint stroke similar to the one used in other paintings
- Clear outline and lack of overlap between painted areas indicates the use of cartoons which is also typical for Georges de la Tour
The ultimate painting by Rembrandt van Rijn 1606-1669
The Man with the Gold Helmet

Gemäldegalerie, Berlin, Germany

Rembrandt used “Cinnebar” in all his paintings except this one. A different paint stroke technique is revealed by the $^{32}\text{P}$ analysis $T_{1/2}=14.3$ d. The results indicated that this very famous Rembrandt painting was not painted by Rembrandt $\Rightarrow$ Rembrandt school?