## Analysis of paint pigments

Medieval oil paintings contained specific pigments to achieve the deep impressive color effects. A list of typical inorganic pigments and their chemical composition is:

<table>
<thead>
<tr>
<th>White pigments</th>
<th>Green pigments</th>
<th>Blue pigments</th>
<th>Black pigments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony white</td>
<td>Basic copper sulfate</td>
<td>2CuCO₃·Cu(OH)₂</td>
<td>Antimony black</td>
</tr>
<tr>
<td>Lithopone</td>
<td>Chromium oxide</td>
<td>CoO·nSnO₂</td>
<td>Sb₂O₃</td>
</tr>
<tr>
<td>Permanent white</td>
<td>Chrysocolla</td>
<td>CoO·Al₂O₃</td>
<td>Black iron oxide</td>
</tr>
<tr>
<td>Titanium white</td>
<td>Cobalt green</td>
<td>Co₂(PO₄)₂</td>
<td>Carbon or charcoal black</td>
</tr>
<tr>
<td>White lead</td>
<td>Emerald green</td>
<td>Cu(CH₃COO)₂·3Cu(AsO₃)₂</td>
<td>Cobalt black</td>
</tr>
<tr>
<td>Zinc white</td>
<td>Guignment green</td>
<td>Cr₂O₃·nH₂O + H₂BO₃</td>
<td>Ivory black</td>
</tr>
<tr>
<td>Zirconium oxide</td>
<td>Malachite</td>
<td>CuCO₃·Cu(OH)₂</td>
<td>Manganese oxide</td>
</tr>
<tr>
<td>Chalk</td>
<td>Verdigris</td>
<td>Cu(CH₃COO)₂·nCu(OH)₂</td>
<td></td>
</tr>
<tr>
<td>Gypsum</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Yellow pigments</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aureopigmentum</td>
<td>As₂S₃</td>
<td>Azurite</td>
<td>Antimony black</td>
</tr>
<tr>
<td>Cadmium yellow</td>
<td>CdS</td>
<td>Cerulean blue</td>
<td>Sb₂O₃</td>
</tr>
<tr>
<td>Chrome yellow</td>
<td>2PbSO₄·PbCrO₄</td>
<td>Cobalt blue</td>
<td>Black iron oxide</td>
</tr>
<tr>
<td>Cobalt yellow</td>
<td>K₂[Co(NO₃)₆]·1.5H₂O</td>
<td>Cobalt violet</td>
<td>Carbon or charcoal black</td>
</tr>
<tr>
<td>Lead–tin yellow</td>
<td>Pb₃SnO₃/Pb₈Sn₃SiO₇</td>
<td>Egyptian blue</td>
<td>Cobalt black</td>
</tr>
<tr>
<td>Massicot</td>
<td>PbO</td>
<td>Manganese blue</td>
<td>Ivory black</td>
</tr>
<tr>
<td>Naples yellow</td>
<td>Pb(SbO₃)₂/Pb₅(SbO₄)₃</td>
<td>Prussian blue</td>
<td>Manganese oxide</td>
</tr>
<tr>
<td>Strontium yellow</td>
<td>SrCrO₄</td>
<td>Smalt</td>
<td></td>
</tr>
<tr>
<td>Titanium yellow</td>
<td>NiO·Sb₂O₂·20TiO₂</td>
<td>Ultramarine</td>
<td></td>
</tr>
<tr>
<td>Yellow ochre</td>
<td>Fe₃O₄·nH₂O (20–70%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc yellow</td>
<td>K₂O·4ZnO·4CrO₃·3H₂O</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Red pigments</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cadmium red</td>
<td>CdS + CdSe</td>
<td>Antimony black</td>
<td></td>
</tr>
<tr>
<td>Cadmium vermilion</td>
<td>CdS + HgS</td>
<td>Black iron oxide</td>
<td></td>
</tr>
<tr>
<td>Chrome red</td>
<td>PbO·PbCrO₄</td>
<td>Carbon or charcoal black</td>
<td></td>
</tr>
<tr>
<td>Molybdate red</td>
<td>7PbCrO₄·2PbSO₄·PbMoO₄</td>
<td>Cobalt black</td>
<td></td>
</tr>
<tr>
<td>Realgar</td>
<td>As₂S₃</td>
<td>Ivory black</td>
<td></td>
</tr>
<tr>
<td>Red lead</td>
<td>Pb₃O₄</td>
<td>Manganese oxide</td>
<td></td>
</tr>
<tr>
<td>Red ochre</td>
<td>Fe₃O₄ (up to 90%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vermilion</td>
<td>HgS</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fake or Forgery?

The art market is flooded with fake paintings of 20th century artists such as ... Matisse, Modigliani, Picasso ...

X-ray spectrum indicated the use of cerulean blue CoO\(\cdot n \cdot \text{SnO}_2\) a pigment Modigliani did not use in any other of his paintings \(\Rightarrow\) forgery?
Breviarium van den Bergh

Breviarium Van den Bergh has been illuminated 1510 by three different artists: • Simon Bening, • Gerard Horenbout, • Jan Provoost. Comparison of color content lead to identification of the artist responsible for each illumination.

Comparison of • dark green and light green

Different ways to paint green

Jan Provoost painted light green with a mixture of blue (azurite), white lead, and yellow, all other samples contained green copper pigments.

For dark green sample again close similarity between both samples except Pb. Sample from different miniature contained large Ca component and less As.
Discovery & Analysis of Medieval Scriptures
The content of ink

Ink preparation was an extremely important and difficult chemical technique. Ink had to maintain color and stability with time.

15th century manuscript by Raphael de Mercatellis (1437-1508)

Ferro-gallus ink prepared with an addition of tin and iron. The recipe allows the dating of the manuscript.

FeSO₄ + gallotannic acid

FeSO₄ + glucose

gallic acid

15th century manuscript by Raphael de Mercatellis (1437-1508)
The relative high Fe, Zn content is characteristic for Mercatellis and allows for a unique identification of his manuscripts. In addition the analysis shows that vermilion, HgS, is not part of the red ink composition.
The K-transition in iron-gallus ink

The observed x-ray spectrum lines correspond to the energy of K-transitions. Calculate the difference between the characteristic X-ray transitions for iron and zinc and compare it with the previous spectrum.

Data for Fe; Z = 26

- **K-edge**: 7.11200 keV
- **L-edges**: 0.842000, 0.719900, 0.706800 keV
- **Kα₁, Kβ₁**: 6.40300 7.05700 keV

Data for Zn; Z = 30

- **K-edge at**: 9.65900 keV
- **L-edges at**: 1.19600, 1.04400, 1.02100 keV
- **Kα₁, Kβ₁**: 8.63800 9.57100 keV

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

for Fe: Z = 26

\[ E_x = (25)^2 \cdot 13.6 [eV] \cdot \left(1 - \frac{1}{2^2}\right) = 6.37 \text{ [keV]} \]

for Zn: Z = 30

\[ E_x = (29)^2 \cdot 13.6 [eV] \cdot \left(1 - \frac{1}{2^2}\right) = 8.58 \text{ [keV]} \]
The Brittleness of old Documents
Authenticity of iridescent Art Nouveau Glass Ware

Tiffany Glass, USA
Loetz Glass, Austria
Strini Art Grass, USA
Jack Ink Glass, Austria

Iridescence is optical effect of light dispersion, interference and diffraction when viewing object from different angles.

Thin SnO$_2$ layer increases iridescence effect

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Statistical Analysis for Comparison

Bulk and surface analysis of K\textsubscript{\textalpha} lines from Mg, K, Si, Ag, Zn, Se, and L\textbeta lines from Pb with correlation of intensity.

X-ray analysis of SnO\textsubscript{2} layer

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.
Cellini’s Perseus

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.csrrri.iit.edu/mucal.html

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

\[
d = \frac{1}{\mu} \cdot \ln \left[ \frac{I_0}{I} \right]; \quad \left[ \frac{I}{I_0} \right]_{Cu} = 0.25; \quad \left[ \frac{I}{I_0} \right]_{Sn} = 0.95
\]

\[d_{Cu} = 2.96 \cdot 10^{-3} \text{ cm} = 0.03 \text{ mm};\]
Details in alloy composition

Cu-Au composition

Bronze

Cu-Sn composition
Advanced Techniques in XRF

Laser guidance
poly-capillary optics
spatial resolution 100 μm
lateral resolution
X-ray fluorescence has a wide range of application in art and archaeology. It is superior to radiography since it allows to determine the chemical constituency of archaeological artifacts or art samples in a nondestructive manner. This method provides opportunities of analysis beyond the absorption method of X-ray radiography. The method is based on X-ray induced emission of characteristic X-ray radiation from the sample material. Typically only medium or heavy mass elements can be detected by measuring either the characteristic energies of the K-transitions – for low Z Elements - or L-transitions - for large Z elements - with Si(Li) detectors or crystal diffraction gratings.