2.2 X-ray absorption & fluorescence

X-ray absorption is classical spectroscopy technique originating from absorption line analysis of solar chromo-sphere spectrum.

Technique has been utilized for a wide range from visible, UV and X-ray light by absorption of light or X-ray spectrum in vapor.

Disadvantage: probe must be chemically prepared & vaporized.
X-ray fluorescence is based on the excitation of material & subsequent X-ray emission - fluorescence -

Only characteristic lines for material are emitted
Analysis of X-ray energies

Advantage of X-ray fluorescence is the unique determination of element characteristic X-ray radiation, $K_\alpha$, $K_\beta$, or $L_\alpha$, $L_\beta$, $L_\gamma$ lines.

Critical component for X-ray fluorescence studies is the necessity for high energy resolution in the X-ray spectrum to separate energetically the characteristic X-ray lines of different elements.
Characteristic x-Ray Energies

The characteristic X-ray energies correspond to the energies of the K or L transitions in the atom:

\[ E_x = h \cdot \nu = h \cdot c / \lambda = \Delta E = E_n(i) - E_{K/L}(f) \]

or it corresponds to the difference of the absorption edge energies:

\[ E_x = E_{K,L} - E_n \]

Data for Pb; Z = 82
atomic weight = 207.210;
density = 11.3400

Absorption edges
K-edge: 88.0060 keV
L-edges: 15.8600, 15.1980, 13.0350 keV
M-edge: 3.85000 keV

Characteristic energies
K\(\alpha_1,K\beta_1\): 74.9570 84.9220 keV
L\(\alpha_1,L\beta_1\): 10.54900 12.6110 keV

Analyzing the strength of characteristic x-ray transitions gives the abundance of element in sample: good energy resolution is required
The Lithium drifted Silicon (SiLi) detector

When an X-ray strikes the detector, it will generate a photoelectron within the body of the Si. As this electron travels through the Si, it generates electron-hole pairs. The electrons and holes are attracted to opposite ends of the detector with the aid of a strong electric field. The size of the current pulse thus generated depends on the number of electron-hole pairs created, which in turn depends on the energy of the incoming X-ray. Thus, an X-ray spectrum can be acquired giving information on the elemental composition of the material under examination.
- taking data - using a simple XRF approach

Am x-ray source

Cu $K_\alpha = 8.04\text{keV}$; $K_\beta = 8.91\text{keV}$

Au $L_\alpha = 9.71\text{keV}$; $L_\beta = 11.44\text{keV}$
The reflection of x-rays with a certain wave-length $\lambda$ on crystal lattice with spacing $d$ is described by the Bragg Law: $2 \cdot d \cdot \sin \theta = \lambda_0$. This means that the maximum intensity for the reflected X-ray with wavelength $\lambda_0$ is proportional to a certain incident angle $\theta$. 
X-ray Diffractometer

At what angle $\theta$ must diffractometer be positioned to measure x-rays with a wavelength of $\lambda_0=0.1\text{nm}$ incident on a crystal with spacing $d=0.252\text{nm}$?

$$2 \cdot d \cdot \sin \theta = \lambda_0$$

$$\theta = \sin^{-1} \frac{\lambda_0}{2 \cdot d} = \sin^{-1} \frac{0.1}{2 \cdot 0.252}$$

$$\theta = 23.4^0$$
Applications for XRF techniques

Non-destructive applications
Analysis of small amounts <100 µg of material
Determination of chemical content and structure

• ancient coin material - metal composition
• ancient oil and varnish material
• pigment in ancient paint
• medieval scripts and miniatures
The secret of the varnish of the violins made around 1660 by Andrea Guarneri in Cremona has been solved by XRF analysis of the varnish contents - oil, resin, wax. Additional inorganic substances influence color, hardness etc. The varnishing technique of the Cremona violin builders has been lost! The detailed XRF analysis of all the contents:

- Provides the recipe for the varnish.
- Detects forgery.
What kind of varnish does he use?
Total x-Ray Fluorescence

20 different elements detected:
Fe, As, Pb, pigments in varnish
Zn, Cu, Pb drying substrate in oil
Characteristic X-ray energies for varnish element K-transitions

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

for S: \( Z = 16 \); \( E_x = (15)^2 \cdot 13.6 [eV] \cdot \left(1 - \frac{1}{2^2}\right) = 2.29 \ \text{keV} \)

for Ca: \( Z = 20 \); \( E_x = (19)^2 \cdot 13.6 [eV] \cdot \left(1 - \frac{1}{2^2}\right) = 3.68 \ \text{keV} \)

for Ti: \( Z = 22 \); \( E_x = (21)^2 \cdot 13.6 [eV] \cdot \left(1 - \frac{1}{2^2}\right) = 4.50 \ \text{keV} \)

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: \( Z = 30 \); \( E_x = (29)^2 \cdot 13.6 [eV] \cdot \left(1 - \frac{1}{2^2}\right) = 8.58 \ \text{keV} \)
Hemoglobin:
$\text{C}_{3032}\text{H}_{4816}\text{O}_{872}\text{N}_{780}\text{S}_{8}\text{Fe}_{4}$
Comparison between Violins Recipes
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>Other pigments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony white</td>
<td>Basic copper sulfate</td>
</tr>
<tr>
<td>Lithopone</td>
<td>Chromium oxide</td>
</tr>
<tr>
<td>Permanent white</td>
<td>Chrome yellow</td>
</tr>
<tr>
<td>Titanum white</td>
<td>Cobalt green</td>
</tr>
<tr>
<td>White lead</td>
<td>Emerald green</td>
</tr>
<tr>
<td>Zinc white</td>
<td>Malachite</td>
</tr>
<tr>
<td>Zirconium oxide</td>
<td>Verdigris</td>
</tr>
<tr>
<td>Chalk</td>
<td>Yelow pigments</td>
</tr>
<tr>
<td>Gypsum</td>
<td>Arsenic red</td>
</tr>
</tbody>
</table>

Yellow pigments:
- Auripigmentum
- Cadmium yellow
- Chrome yellow
- Cobalt yellow
- Lead-tin eye yellow
- Madder
- Naples yellow
- Strontium yellow
- Titanum yellow
- Yellow ochre
- Zinc yellow

Red pigments:
- Cadmium red
- Cadmium vermilion
- Chrome red
- Molybdenum red
- Realgar
- Red lead
- Red ochre
- Vermilion

Bluish pigments:
- Antimony black
- Black iron oxide
- Carbon or charcoal black
- Encaustic black
- Iron blue
- Manganese oxide

Blue pigments:
- Azure
- Cerulean blue
- Cobalt blue
- Cobalt violet
- Egyptian blue
- Manganese blue
- Prussian blue
- Ultramarine

Other pigments:
- CaSO₄·2H₂O
- Cu₂O
- CuSO₄·5H₂O
- Cu₃(AsO₄)₂
- Cu₂O₃·H₂O
- CuO
- CuO·H₂O
- Cu₂O·CuO·H₂O
- Cu₃(AsO₄)₂·2H₂O
- Cu₃(AsO₄)₂·3H₂O
- Cu₃(AsO₄)₂·3H₂O
Breviariuim King Manuel of Portugal, 1510

Two X-ray spectra taken of red area (a) and yellow area (b):

Red color is a mix of white lead paint $2\text{PbCO}_3$ & red lead $\text{Pb}_3\text{O}_4$ (minium).

Yellow-brown color is a mixture of Au and $\text{Fe}_2\text{O}_3$ (rust).

$^{26}\text{Fe}, ^{29}\text{Cu}$: K-transitions
$^{79}\text{Au}, ^{82}\text{Pb}$: L-transitions
The characteristic transition energies

Calculate the characteristic X-ray transitions for gold and compare it with the Au transitions shown in the X-ray spectrum at 9.6, 11.5 and 13.5 keV of the King Manuel I Breviary.

Data for Au; $Z = 79$
atomic weight = 197.200;
density = 19.3700

$K$-edge: 80.7230 keV
$L$-edges: 14.3530, 13.7330, 11.9180 keV
$M$-edge: 3.42500 keV

$K\alpha_1,K\beta_1$: 68.7790 77.9680 keV
$L\alpha_1,L\beta_1$: 9.71100 11.4390 keV
The Annunciation

X-ray spectrum of red dress shows Pb and Hg, indicating a mix of white lead $2\text{PbCO}_3$ and Vermilion $\text{HgS}$

The folds of the blue coat had changed to green with time! X-ray fluorescence showed from intensity analysis; blue was expensive ultramarine with Fe and Ca, in the dark areas was Smalt added, a cheap alternative, containing CoAsS and CoAs$_2$ that in time turned greenish.
Fake or Forgery?

X-ray spectrum indicated the use of cerulean blue $\text{CoO} \cdot n \cdot \text{SnO}_2$ 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.
The content of ink

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

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

15th century manuscript by Raphael de Mercatellis (1437-1508)
Discovery & Analysis of Medieval Scriptures
Raphael de Mercatellis

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 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
- \( K\alpha_1, K\beta_1: 6.40300 \) \( 7.05700 \) keV

**Data for Zn; Z = 30**

- **K-edge at:** 9.65900 keV
- **L-edges at:** 1.19600, 1.04400, 1.02100 keV
- \( K\alpha_1, K\beta_1: 8.63800 \) \( 9.57100 \) keV

\[
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\]

for Fe: \( Z = 26 \)

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E_x = (25)^2 \cdot 13.6 [eV] \cdot \left(1 - \frac{1}{2^2}\right) = 6.37 [\text{keV}]
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for Zn: \( Z = 30 \)

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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
Cellini’s Perseus

Bronze Alloy Composition

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

Absorption in Patina
Details in alloy composition

Cu-Au composition

Bronze
Cu-Sn composition
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.