Introduction to x-ray absorption spectroscopy

Giuliana Aquilanti
Elettra – Sincrotrone Trieste
Outline

• X-ray absorption
• X-ray absorption fine structure
• XANES
• Some examples of EXAFS and XANES studies for cultural heritage
Outline

• X-ray absorption
• X-ray absorption fine structure
• XANES
• Some examples of EXAFS and XANES studies for cultural heritage
Spectroscopic methods

- They measure the response of a system as a function of energy.
- The energy that is scanned can be that of the incident beam or the energy of the outgoing particles (photons in x-ray fluorescence, electrons in photoelectron spectroscopy).
- In all cases, the incident radiation is synchrotron light, which is absorbed, resulting in an ejection of an electron (photoelectric effect).

Photoelectric absorption
An x-ray is absorbed by an atom, and the excess energy is transferred to an electron, which is expelled from the atom, leaving it ionized.
The absorption coefficient - 1

- Quantitatively, the absorption is given by the **linear absorption coefficient** $\mu$.
- $\mu dz$ : **attenuation** of the beam through an infinitesimal thickness $dz$ at a depth $z$ from the surface.
The intensity $I(z)$ through the sample fulfills the condition
\[-dI = I(z)\mu dz\]
which leads to the differential equation
\[\frac{dI}{I(z)} = -\mu dz\]
If $I(z=0) = I_\downarrow 0$, ($I_\downarrow 0$ : incident beam intensity at $z=0$) then

\[I(z) = I_\downarrow 0 e^{\uparrow -\mu z}\]
\[ I(z) = I_0 e^{-\mu z} \Rightarrow \ln I_0 / I = \mu z \]

Experimentally, \( \mu \) can be determined as the ratio of the beam intensities with and without the samples (or beam intensity before and after the sample).
Transmission
The absorption is measured directly by measuring what is transmitted through the sample

Fluorescence
The re-filling the deep core hole is detected. Typically the fluorescent X-ray is measured
XAFS at Elettra
Atomic cross section

\[ \mu = \rho_{\text{at}} \sigma_{\text{a}} = \left( \rho_{\text{m}} N_{\text{A}} / A \right) \sigma_{\text{a}} \]

\[ \sigma_{\text{a}} \text{ [cm}^2\text{]} \]

\[ \sigma_{\text{a}} \text{ [barn]} \quad 1 \text{ barn} = 10^{-28} \text{ m}^2 \]

\[ \sigma_{\text{a}} \text{ [cm}^2\text{/g]} = N_{\text{A}} / A \quad \sigma_{\text{a}} \text{ [cm}^2\text{]} = \mu / \rho_{\text{m}} \]
μ vs E and μ vs Z

μ depends strongly on:

• x-ray energy E
• atomic number Z
• density ρ
• atomic mass A

In addition, μ has sharp *absorption edges* corresponding to the characteristic core-level energy of the atom which originate when the photon energy becomes high enough to extract an electron from a deeper level.
Absorption edges and nomenclature

Table 2.1  Correspondence between x-ray absorption edges and their electronic configurations.

<table>
<thead>
<tr>
<th>Edge</th>
<th>Configuration</th>
<th>Edge</th>
<th>Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>1s</td>
<td>N₁</td>
<td>4s</td>
</tr>
<tr>
<td>L₁</td>
<td>2s</td>
<td>N₂</td>
<td>4p₁/₂</td>
</tr>
<tr>
<td>L₂</td>
<td>2p₁/₂</td>
<td>N₃</td>
<td>4p₃/₂</td>
</tr>
<tr>
<td>L₃</td>
<td>2p₃/₂</td>
<td>N₄</td>
<td>4d₃/₂</td>
</tr>
<tr>
<td>M₁</td>
<td>3s</td>
<td>N₅</td>
<td>4d₅/₂</td>
</tr>
<tr>
<td>M₂</td>
<td>3p₁/₂</td>
<td>N₆</td>
<td>4f₅/₂</td>
</tr>
<tr>
<td>M₃</td>
<td>3p₃/₂</td>
<td>N₇</td>
<td>4f₇/₂</td>
</tr>
<tr>
<td>M₄</td>
<td>3d₃/₂</td>
<td>O₁</td>
<td>5s</td>
</tr>
<tr>
<td>M₅</td>
<td>3d₅/₂</td>
<td>O₂</td>
<td>5p₁/₂</td>
</tr>
</tbody>
</table>

(b) Continuum

Intro to XAS – smr2738

giuliana.aquilanti@elettra.eu
Absorption edge energies

The energies of the $K$ absorption edges go roughly as $E_K \sim Z^2$

All elements with $Z > 16$ have either a $K$-, or $L$- edge between 2 and 35 keV, which can be accessed at many synchrotron sources.
De-excitation process

Absorption → Excited state → Decay to the ground state

Core hole + photoelectron

X-ray Fluorescence
An x-ray with energy equal to the difference of the core-levels is emitted

Auger Effect
An electron is promoted to the continuum from another core-level

X-ray fluorescence and Auger emission occur at discrete energies characteristic of the absorbing atom, and can be used to identify the absorbing atom.
Core-hole lifetime ($\tau_h \sim 10^{-15} – 10^{-16}$ s)

Total de-excitation probability per unit time

The deeper the core hole and the larger the atomic number $Z$

\[ \downarrow \]

The larger the number of upper levels from which an electron can drop to fill the hole

\[ \downarrow \]

The shorter the core hole lifetime

$\tau_h$ is un upper limit to the time allowed to the photoelectron for probing the local structure surrounding the absorbing atom.

From the time-energy uncertainty relation: $\Gamma_h \simeq \hbar / \tau_h$ the core hole lifetime is associated to the energy width of the excited state $\Gamma_h$ (core hole broadening) which contributes to the resolution of the x-ray absorption experimental spectra.
K-edge core hole broadening
• X-ray absorption
• X-ray absorption fine structure
• XANES
• Some examples of EXAFS and XANES studies for cultural heritage
**X-ray Absorption Fine Structure**

**What?** Oscillatory behaviour of the x-ray absorption as a function of photon energy beyond an absorption edge

**When?** Non isolated atoms

**Why?** Proximity of neighboring atoms strongly modulates the absorption coefficient
A little history

1895  Discovery of x-rays (Röntgen) (high penetration depth)
1912  First x-ray diffraction experiments (Laue, Bragg)
1913  Bohr’s atom electron energy levels
1920  First experimental observation of fine structure
1931  First attempt to explain XAFS in condensed matter (Krönig)

1970  Availability of synchrotron radiation sources for XAFS
1971  XAFS becomes a quantitative tool for structure determination
**XANES and EXAFS - 1**

- **X-ray Absorption Near Edge Structure (XANES)**
- UP TO ~ 60 eV ABOVE THE EDGE

- **Extended X-ray Absorption Fine Structure (EXAFS)**
- FROM ~ 60 eV TO 1200 eV ABOVE THE EDGE
XANES and EXAFS - 2

XANES  ⇔  same physical origin  ➔  EXAFS

transitions to
unfilled bound states, nearly bound states, continuum

• Oxidation state
• Coordination chemistry (tetrahedral, octahedral) of the absorbing atom
• Orbital occupancy

transitions to
the continuum

• Radial distribution of atoms around the photoabsorber (bond distance, number and type of neighbours)
EXAFS qualitatively – isolated atom

- X-ray photon with enough energy ejects one core (photo)electron (photoelectric effect)

\[ E_k = E_{h\nu} - E_0 = \frac{p^2}{2m} = \frac{(\hbar k)^2}{2m} \]  
    \text{Kinetic energy of the p.e.}

\[ k = \sqrt{\frac{2m(E_{h\nu} - E_0)}{\hbar^2}} \]  
    \text{wavevector of the p.e.}

\[ \lambda = \frac{2\pi}{k} \]  
    \text{wavelength of the p.e.}

- The photoelectron can be described by a wave function approximated by a spherical wave

\[ E \]
EXAFS qualitatively – condensed matter

- The photoelectron can scatter from a neighbouring atom giving rise to an incoming spherical wave coming back to the absorbing atom.

- The outgoing and ingoing waves may interfere.

\[ \Delta E \propto \frac{1}{2} - \frac{2\Delta E_0}{\hbar} \]
The interference between the outgoing and the scattering part of the photoelectron at the absorbing atom changes the probability for an absorption of x-rays i.e. alters the absorption coefficient $\mu(E)$ that is no longer smooth as in isolated atoms, but oscillates.

In the extreme of destructive interference, when the outgoing and the backscattered waves are completely out of phase, they will cancel each other, which means that no free unoccupied state exists in which the core-electron could be excited to.

Thus absorption is unlikely to occur and the EXAFS oscillations will have a minimum.

The phase relationship between outgoing and incoming waves depends on photoelectron wavelength (and so on the energy of x-rays) and interatomic distance $R$.

The amplitude is determined by the number and type of neighbours since they determine how strongly the photoelectron will be scattered.
Which information

Frequency of the oscillations

Distance from neighbours

Amplitude of the oscillations

Number and type of neighbours
Some spectra

**Kr gas**

**Rh metal**
Fermi’s Golden rule

According to the time dependent perturbation theory, the Fermi’s Golden rule gives the transition rate (probability of transition per unit time) per unit volume between an initial and a final eigenstate due to a perturbation

\[ w_{fi} = \frac{2\pi}{\hbar} |\langle \Psi_f | H_{\text{int}} | \Psi_i \rangle|^{2} \rho(E_f) \]

\[ \mu = -\frac{1}{2} \frac{dl}{dz} = \sum f \frac{\pi c}{\omega} A_0 \langle \rho(E_f) \rangle \]

- Sum over all final states
- Number of microscopic absorbing element per unit volume
Absorption process

\[ \mu \propto \sum f \uparrow (\psi \downarrow f | e \cdot r | \psi \downarrow i ) \uparrow \rho(E \downarrow f) \]

- \(*\) : initial state of energy \( E_i \)
  - core electron (\( e.g. \) 1s electron wave function)
  - very localized
  - NOT altered by the presence of the neighboring atoms

- \(|f\rangle\) : final state of energy \( E_f = E_i + \hbar \omega \)
  - core hole + photoelectron
  - multibody process
  - altered by neighbouring atoms

photon polarization

Electron position
Initial and final states

Wavefunction of the initial state:

\[ |i> = Y_{l_0,m_0} (\hat{r}) R_{l_0}^0 (r) \]

Where \( l_0 \) angular momentum of the electron spherical harmonic functions

\[ \gamma_{l_0,m_0} \]

(solution of the angular part of the Schrödinger equation)

For the final state a potential must take into account that the electron moves in the condensed matter

Muffin Tin Potential

Spherical regions centered on each atom in which the potential has a spherical symmetry. Wavefunctions described by a radial + angular part

Interstitial region with a constant potential. Wavefunctions described by plane waves
The dipolar selection rules determine the transition from the initial to the final state

\[ \Delta \ell = \pm 1 \]
\[ \Delta s = 0 \]
\[ \Delta j = \pm 1, 0 \]
\[ \Delta m = 0 \]

<table>
<thead>
<tr>
<th>EDGE</th>
<th>INITIAL STATE</th>
<th>FINAL STATE</th>
</tr>
</thead>
<tbody>
<tr>
<td>K, L_1</td>
<td>s (\ell=0)</td>
<td>p (\ell=1)</td>
</tr>
<tr>
<td>L_2, L_3</td>
<td>p (\ell=1)</td>
<td>s (\ell=0), d (\ell=2)</td>
</tr>
</tbody>
</table>
The EXAFS signal $\chi(k)$ - 1

- The EXAFS signal is generally expressed as a function of the wavevector of the photoelectron $k = \sqrt{2m(E \downarrow \hbar \nu - E \downarrow 0)/\hbar \uparrow 2}$.
- The oscillatory part of the spectrum contains the structural information.
- We define the EXAFS function as $\chi(k) = \mu - \mu \downarrow 0 / \Delta \mu \downarrow 0$.

![Graph of EXAFS signal](image)

- $\mu_0(E)$ Smooth function representing the bare atomic background.
- $\Delta \mu_0$ Edge step at the absorption edge normalized to one absorption event.
The EXAFS signal $\chi(k)$ - 2

XAFS originates from an *interference effect*, and depends on the wave-nature of the photoelectron.

$\chi(k)$ is often shown weighted by $k^2$ or $k^3$ to amplify the oscillations at high-$k$.
\( \chi(k) \): sum of damped waves

\( \chi(k) \) is the sum of contributions \( \chi_j(k) \) from backscattered wavelets:

\[
\chi(k) = \sum_j = \chi_j(k)
\]

Each \( \chi_j(k) \) can be approximated by a damped sine wave of the type:

\[
\chi(k) = (A_j(k) \sin(\varphi_j(k))
\]

The larger the number of neighbours, the larger the signal

The stronger the scattering amplitude, the larger the signal

Damping of the amplitude at large \( k \), due to static and thermal disorder

Each shell contributes a sinusoidal signal which oscillates more rapidly the larger the distance

The larger the number of neighbours, the larger the signal

The stronger the scattering amplitude, the larger the signal

Damping of the amplitude at large \( k \), due to static and thermal disorder

Each shell contributes a sinusoidal signal which oscillates more rapidly the larger the distance
EXAFS formula

\[ \chi(k) = \sum_j N_j S_j^2 f_j(k) e^{-2R_j/\lambda(k)} e^{-2k^2\sigma_j^2} \frac{\sin[2kR_j + \delta_j(k)]}{kR_j^2} \]

- \( f(k) \) scattering amplitude
- \( \delta_j(k) \) phase-shift
- \( R \) Distance to the neighbouring atom
- \( N \) Coordination number of the neighbouring atom
- \( \sigma^2 \) Disorder in the neighbouring distance

scattering properties of the atoms neighbouring the photoabsorber (depend on the atomic number)
The shape of the envelope of each wave is indicative of the nature of backscatterer atom.

AgF (rocksalt structure)
The **frequency** of the single wave, for the same atomic pair, is indicative of the distance of the backscatterer atom (the lower the frequency the closer the neighbour).

**AgF** (rocksalt structure)
The scattering amplitude $F(k)$ and phase shift $\delta(k)$ depend on the atomic number. 

The scattering amplitude $F(k)$ peaks at different $k$ values and extends to higher $k$ for heavier elements. For very heavy elements, there is structure in $F(k)$. 

These scattering functions can be accurately calculated and used in the EXAFS modeling. 

$Z$ can usually be determined to within 5 or so. Fe and O can be distinguished, but Fe and Mn cannot.
Multiple scattering events may occur

The photoelectron scatter from more than one atom before returning to the central atom

- **SS** $\rightarrow g_2(r)$
  - $f = 2R_1$

- **MS** $\rightarrow g_2(r)$
  - $f = 4R_1$

- **MS** $\rightarrow g_3(r)$
  - $f = R_1 + R_2 + R_3$

- **MS** $\rightarrow g_3(r)$
  - $f = 2R_1 + 2R_3$

Through multiple scattering EXAFS can give information on the n-body distribution functions $g_n(r)$.
The frequencies contained in the EXAFS signal depend on the distance between the absorbing atom and the neighbouring atoms (i.e. the length of the scattering path).

A Fourier Transform of the EXAFS signal provides a photoelectron scattering profile as a function of the radial distance from the absorber.
Quantitative structural determination

Structural determinations depend on the feasibility of resolving the data into individual waves corresponding to the different types of neighbours (SS) and bonding configurations (MS) around the absorbing atom.
Diffraction Methods (x-rays, Neutrons)

- Crystalline materials with long-range ordering -> 3D picture of atomic coordinates
- Materials with only short-range order (amorphous solid, liquid, or solution) -> 1D RDF containing interatomic distances due to all atomic pairs in the sample

XAFS

- 1D radial distribution function (centered at the absorber)
- Element selectivity
- Higher sensitivity to local distortions (i.e. within the unit cell)
- Charge state sensitivity (XANES)
- Structural information on the environment of each type of atom:
  - distance, number, kind, static and thermal disorder
  - 3-body correlations
EXAFS: typical applications

Element selectivity
Local structure sensitivity

- Local structure in non-crystalline matter
- Local environment of an atomic impurity in a matrix of different atomic species
- Study of systems whose local properties differ from the average properties
- Detection of very small distortions of local structure
Outline

• X-ray absorption
• X-ray absorption fine structure
• XANES
• Some examples of EXAFS and XANES studies for cultural heritage
**XANES**

XANES is the region of the absorption spectrum within ~ 60 eV of the absorption edge.

X-ray Absorption Near Edge Structure (XANES) includes also the "pre-edge features" if any.
Mn: [Ar] 3d⁵ 4s²

Ground state

Excited state

Mn³⁺

\( \epsilon_p \)

4p

3d

1s

\( \epsilon_p \)

4p

3d

1s

\( \epsilon_p \)

4p

3d

1s

\( \epsilon_p \)

4p

3d

1s

\( \mu f(E) \) (arb. units.)

Energy (keV)

pre-edge

main edge

continuum

Intro to XAS – smr2738
Chemical shift

Mn: [Ar] 3d⁵ 4s²

Ground state

Excited state

Mn³⁺

Mn⁴⁺

Intro to XAS – smr2738

giuliana.aquilanti@elettra.eu
The edges of many elements show significant edge shifts (binding energy shifts) with oxidation state.

**Mn oxides**

- Mn
- MnO
- MnO$_2$
- Mn$_2$O$_3$
- Mn$_3$O$_4$
The heights and positions of pre-edge peaks can also be reliably used to determine Fe$^{3+}$/Fe$^{2+}$ ratios (and similar ratios for many cations).
XANES can be used simply as a fingerprint of phases and oxidation state.

XANES analysis can be as simple as making linear combinations of "known" spectra to get compositional fraction of these components.
Dipole selection rules apply:

\[ \Delta \ell = \pm 1 \]
\[ \Delta s = 0 \]
\[ \Delta j = \pm 1, 0 \]
\[ \Delta m = 0 \]

<table>
<thead>
<tr>
<th>EDGE</th>
<th>INITIAL STATE</th>
<th>FINAL STATE</th>
</tr>
</thead>
<tbody>
<tr>
<td>K, L_1</td>
<td>s (\ell=0)</td>
<td>p (\ell=1)</td>
</tr>
<tr>
<td>L_2, L_3</td>
<td>p (\ell=1)</td>
<td>s (\ell=0), d (\ell=2)</td>
</tr>
</tbody>
</table>

The final state is usually not atomic-like and may have mixing (hybridization) with other orbitals.

This is often the interesting part of the XANES
Transition from 1s to 4p states

Pure octahedron
- Centro-symmetry: no p-d mixing allowed
- Only (weak) quadrupolar transitions
- No, or very low intensity prepeak

Distorted octahedron
- Centro-symmetry broken: p-d mixing allowed
- Dipole transition in the edge
- Moderate intensity prepeak

Tetrahedron
- No centro-symmetry: p-d mixing allowed
- Dipole transition in the edge
- High intensity prepeak
Prepeak: local coordination environment

Ti K-edge XANES shows dramatic dependence on the local coordination chemistry
The XANES of $\text{Cr}^{3+}$ and $\text{Cr}^{6+}$ shows a dramatic dependence on oxidation state and coordination chemistry.
White line intensity of L$_3$-edge of XANES of 4d metals

Transition from 2p$_{3/2}$ to 4d states

Linear correlation between white line area and number of 4d-holes for Mo to Ag

Increasing d states occupancy
White line intensity: oxidation state

Re $L_3$-edge: transition from $2p_{3/2}$ to $5d$ states

Re metal ($\text{Re}^0$) – $5d^5$

ReO$_2$ ($\text{Re}^{4+}$) – $5d^1$

NH$_4$ReO$_4$ ($\text{Re}^{7+}$) $5d^0$
The EXAFS equation breaks down at low-k, and the mean-free-path goes up.

This complicates XANES interpretation:

A simple equation for XANES does not exist

XANES can be described *qualitatively* (and nearly *quantitatively*) in terms of:

- **Coordination chemistry**: regular, distorted octahedral, tetrahedral, . . .
- **Molecular orbitals**: p-d orbital hybridization, crystal-field theory, . . .
- **Band-structure**: the density of available electronic states
- **Multiple-scattering**: multiple bounces of the photoelectron
XANES: conclusions

XANES is a much larger signal than EXAFS
• XANES can be done at lower concentrations, and less-than-perfect sample conditions

XANES is easier to crudely interpret than EXAFS
• For many systems, the XANES analysis based on linear combination of known spectra form “model compounds” is sufficient

XANES is harder to fully interpret than EXAFS
• The exact physical and chemical interpretation of all spectral features is still difficult to do accurately, precisely, and reliably.
Outline

- X-ray absorption
- X-ray absorption fine structure
- XANES
- Some examples of EXAFS and XANES studies for cultural heritage
XAFS spectroscopy is a potentially very useful technique to be applied in Cultural Heritage studies

- It is a non-destructive method which can be applied in air
- It virtually does not require any restriction on the type and size of the sample (metal, ceramic, glass, cloth, paper, etc.)
- It is applicable to most of the elements of interest, even in very low concentration

All these characteristics are particularly important in archaeological applications, in which samples are precious cultural heritage made of very different materials.
Chromophores and pigments

• The chromatic response of a pigment is linked to the symmetry, valence state and local geometry of the chromophore (usually a 3d metal)
• The color is also influenced by the oxidation state of the metal cation
• In general metals were added to production or painting materials with the aim of giving a particular hue to the manufacture but they are present in limited amount, typically below 1 at% (fluorescence mode detection)
Fe and Mn K-edge XANES study of ancient Roman glasses

- Study of ancient glasses from Patti Roman Villa (Messina, Sicily)
- From the chemical point of view, the samples are 'low-magnesia' glasses, with a composition typical of the Roman period
- Glasses of different colors from light green to pale brown
- Fe and Mn K-edge XANES

Aim of the work
- To test the influence of iron oxidation state on the color of the studied samples
- To identify the possible decolorant role of manganese oxide in the almost uncolored samples

Fe and Mn K-edge XANES study of ancient Roman glasses

Fragments of perfume bottles (2nd century AD)

Fe and Mn K-edge XANES study of ancient Roman glasses

Glass A: pale green
Glass B: uncolored
Glass C: pale brown

- B and C similar to each other: both in the general Shape and in the energy position of the different features
- Features (b) and (d) fall at high energy characteristic of Fe$^{3+}$

Fe and Mn K-edge XANES study of ancient Roman glasses

Fe and Mn K-edge XANES study of ancient Roman glasses

Glass A: pale green
Glass B: uncolored
Glass C: pale brown

- In sample A the features (b) and (d) are at much lower energy, nearer to those present in the olivine spectrum characteristic of Fe$^{2+}$

Fe and Mn K-edge XANES study of ancient Roman glasses

Fe and Mn K-edge XANES study of ancient Roman glasses

Glass A: pale green
Glass B: uncolored
Glass C: pale brown

• In glass C and in glass B, Fe is predominantly in 3+ oxidation state
• In glass A there is a high percentage of Fe$^{2+}$

Fe and Mn K-edge XANES study of ancient Roman glasses

- Mn is in reduced form
- Strong similarity between the two Mn$^{2+}$-silicatic reference compounds
Glass A: pale green
Glass B: uncolored
Glass C: pale brown

Conclusion

• In sample B and C, Mn$^{4+}$ has oxidised Fe$^{2+}$ to Fe$^{3+}$ and therefore is present in the reduced form
• It is confirmed the hypothesis of a redox interaction between manganese and iron as a results of a deliberate addition of pyrolusite (mineral containing MnO$_2$) – reported in literature as the main decolorant in the Roman period – during the melting procedure of the uncolored glass

By the 13th century traders were importing majolica into Italy through the Isle of Majorca. Therefore the Italian called this new type of ceramic Maiolica, regardless of its place of origin.

The creation of Maiolica is a complex “Five-Step” process

-First firing (about 1000 °C )

-Glazing (inmersion on a mix of sand, potassium carbonate, salts and oxides, such as lead and tin oxides, with water)

-Painting the glazed surface

-Second firing at 900 °C

If lustre: extra step needed to achieve the reflections and iridescences on majolica. A third firing in very complex conditions was the key of the process.

The local artisans became keepers of refined and secret recipes and techniques for decorating ceramic objects.

Italian potters began to create their own maiolica, firstly by coping the Spanish and Islamic designs, then mixing and adding their very own.
A bit of history

Italian potters began to create their own maiolica, firstly by coping the Spanish and Islamic designs, then mixing and adding their very own.

Indeed, a new style was developed, called istoriato, with lustre decoration, and representing the most beautiful Renaissance productions.

**During the late 15th and early 16th centuries: peak of artistic quality**
XAS studies of Italian and Hispano-Moorish Majolicas

Aim of this work

To investigate the chemical state and the local environment of metal atoms in the glaze, lustre and blue pigment, to understand the technological processes and materials in different production

Experiments: X-Ray absorption Spectroscopy

XAS measurements were performed on XAFS beamline, at Elettra Sincrotrone Trieste. A Si (111) double-crystal monochromator was used. The beam size was set at 1x1 mm2 and the photon flux was about 1010 photons/s. All spectra were collected at Fluorescence mode.

XAS studies of Italian and Hispano-Moorish Majolicas

Studied Maiolicas

Hispano-Moorish (LIM1) (s.XIII)

Blue decorated and lustred ceramic

L19 (s.XV)
Italian renaissance production

Blue decorated and lustred majolica

XAS studies of Italian and Hispano-Moorish Majolicas

Analysis of the Lustre

Lustre: Thin metallic film containing silver, copper and other substances, like iron oxide and cinnabar, applied in a reducing atmosphere on a previously glazed ceramic.

\[ \text{Cu K-edge} \]

XANES

\[ L19 \rightarrow \text{Cu}^{1+} \]

\[ \text{LIM1} \rightarrow \text{Cu}^{2+} \text{ indicating lower reduction state} \]

Analysis of the Lustre

Lustre: Thin metallic film containing silver, copper and other substances, like iron oxide and cinnabar, applied in a reducing atmosphere on a previously glazed ceramic.

EXAFS

Just the contribution of the first Cu-O shell (amorphous)

Cu-O interatomic distance: at L19 are those of Cu_2O, at LIM1 those of CuO

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shell</th>
<th>N</th>
<th>r (Å)</th>
<th>σ^2 (Å^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO</td>
<td>Cu-O</td>
<td>4</td>
<td>1.95</td>
<td></td>
</tr>
<tr>
<td>Cu_2O</td>
<td>Cu-O</td>
<td>2</td>
<td>1.84</td>
<td></td>
</tr>
<tr>
<td>LIM1</td>
<td>Cu-O</td>
<td>3.5 ± 0.4</td>
<td>1.92 ± 0.01</td>
<td>0.006 ± 0.002</td>
</tr>
<tr>
<td>L19</td>
<td>Cu-O</td>
<td>3.2 ± 0.1</td>
<td>1.84 ± 0.01</td>
<td>0.005 ± 0.003</td>
</tr>
</tbody>
</table>

Preservation of the XVII-century Warship VASA - 1

- It sunk to a depth of 30 m in Stockholm harbour in 1628
- The salty and anaerobic conditions of the harbours water prevented wood-consuming plants, fauna or bacteria, from attacking the ship, thereby preserving the VASA in excellent conditions.
- It was raised in 1961 and after 30 years of preservation treatment was put on display in Stockholm in 1990.
- First problems detected in 2000
  - Crusty patches of salt in the surface
  - Softening of the woods
- XRD indicated the presence of sulphates (SO$_4^{2-}$) and sulphur (S$_8$). It appeared that these materials were leaching out of solution from the bulk of the wood.

• XANES had to be used instead of XRD because of the poor crystallinity of the sample and because of the spurious signals originating from the wood.

• The XANES spectra shows also intermediate oxidation state of sulphur, corresponding to the overall oxidation state reaction to sulphuric acid.

\[
S(s) + \frac{3}{2}O_2 + H_2O \rightarrow 2H^+ (aq) + SO_4^{2-}
\]
• Iron gall inks is one of the most important inks in the history of the western civilization, of a widespread use from the middle ages until the 20\textsuperscript{th} century
• These inks induce degradation of paper
• The two main reasons for iron gall ink corrosion are:
  • Acid hydrolysis
  • Oxidation (catalyzed by ferrous ions)
• Determination of the concentration of Fe\textsuperscript{2+} in inks in historic documents is therefore relevant in assessing the potential risk of further oxidation of cellulose and in devising an effective stabilization treatment

XANES analysis of Fe valence in iron gall inks

- XANES has been used to determine Fe$^{2+}$/Fe$^{3+}$
- Model compounds of iron gall ink have been prepared with different amounts of Fe$^{2+}$/Fe$^{3+}$
- Standard compounds with well-established Fe valence and local symmetry were also measured

XANES analysis of Fe valence in iron gall inks

Outline

- X-ray absorption
- X-ray absorption fine structure
- XANES
- Some examples of EXAFS and XANES studies for cultural heritage
- EXAFS data analysis
Step for reducing measured data to $\mu(E)$ and then to $\chi(k)$:

1. convert measured intensities to $\mu(E)$
2. subtract a smooth pre-edge function, to get rid of any instrumental background, and absorption from other edges.
3. normalize $\mu(E)$ to go from 0 to 1, so that it represents 1 absorption event
4. remove a smooth post-edge background function to approximate $\mu_0(E)$ to isolate the XAFS $\chi$.
5. identify the threshold energy $E_0$, and convert from $E$ to $k$ space: $k = \frac{\sqrt{2m(E-E_0)}}{\hbar}$
6. weight the XAFS $\chi(k)$ and Fourier transform from $k$ to $R$ space.
7. isolate the $\chi(k)$ for an individual “shell” by Fourier filtering.
Converting raw data to $\mu(E)$

For transmission XAFS:

$I = I_0 \exp[-\mu(E) t]$

$\mu(E) t = \ln \left[ \frac{I_0}{I} \right]$
Transmission
The absorption is measured directly by measuring what is transmitted through the sample

Fluorescence
The re-filling the deep core hole is detected. Typically the fluorescent X-ray is measured
Pre-edge subtraction and normalization

**Pre-edge subtraction**

We subtract away the background that fits the *pre edge* region. This gets rid of the absorption due to other edges (say, the Fe L_{III} edge).

**Normalization**

We estimate the *edge step*, $\mu_0(E_0)$ by extrapolating a simple fit to the above $\mu(E)$ to the edge.
Determination of $E_0$

Derivative and $E_0$

We can select $E_0$ roughly as the energy with the maximum derivative. This is somewhat arbitrary, so we will keep in mind that we may need to refine this value later on.
Post-edge background subtraction

Post-edge background

• We do not have a measurement of $\mu_0(E)$ (the absorption coefficient without neighboring atoms).
• We approximate $\mu_0(E)$ by an adjustable, smooth function: a spline.
• A flexible enough spline should not match the $\mu(E)$ and remove all the EXAFS. We want a spline that will match the low frequency components of $\mu_0(E)$. 
$\chi(k)$
The raw EXAFS $\chi(k)$ usually decays quickly with $k$, and difficult to assess or interpret by itself. It is customary to weight the higher $k$ portion of the spectra by multiplying by $k^2$ or $k^3$.

$k$-weighted $\chi(k): k^2\chi(k)$
$\chi(k)$ is composed of sine waves, so we’ll Fourier Transform from $k$ to R-space. To avoid “ringing”, we’ll multiply by a window function.
Fourier Transform: $\chi(R)$

$\chi(R)$

The Fourier Transform of $k^2(k)$ has 2 main peaks, for the first 2 coordination shells: Fe-O and Fe-Fe. The Fe-O distance in FeO is 2.14Å, but the first peak is at 1.66Å. This shift in the first peak is due to the phase-shift, $\delta(k)$: \[ \sin[2kR + \delta(k)] \].

A shift of -0.5 Å is typical.

$\chi(R)$ is complex:
The FT makes $c(R)$ complex. Usually only the amplitude is shown, but there are really oscillations in $c(R)$. Both real and imaginary components are used in modeling.
Fourier filtering

$\chi(R)$ often has well separated peaks for different “shells”.

This shell can be isolated by a Filtered Back-Fourier Transform, using the window shown for the first shell of FeO.

This results in the filtered $\chi(k)$ for the selected shell. Many analysis programs use such filtering to remove shells at higher R.

Beyond the first shell, isolating a shell in this way can be difficult.
The information content of EXAFS

• The number of parameters we can reliably measure from our data is limited:

\[ N \approx \frac{2 \Delta k \Delta R}{\pi} \]

where \( \Delta k \) and \( \Delta R \) are the \( k \)- and \( R \)-ranges of the usable data.

• For the typical ranges like \( k = [3.0, 12.0] \text{ Å}^{-1} \) and \( R = [1.0, 3.0] \text{ Å} \), there are \( \sim 11 \) parameters that can be determined from EXAFS.

• The “Goodness of Fit” statistics, and confidence in the measured parameters need to reflect this limited amount of data.

• It is often important to constrain parameters \( R \), \( N \), \( \sigma^2 \) for different paths or even different data sets (different edge elements, temperatures, etc).

• Chemical Plausibility can also be incorporated, either to weed out obviously bad results or to use other knowledge of local coordination, such as the Bond Valence Model (relating valence, distance, and coordination number).

• Use as much other information about the system as possible!
FeO has a rock-salt structure.
To model the FeO EXAFS, we calculate the scattering amplitude $f(k)$ and phase-shift $\delta(k)$, based on a guess of the structure, with Fe-O distance $R = 2.14 \, \text{Å}$ (a regular octahedral coordination). We will use these functions to *refine* the values $R$, $N$, $\sigma^2$, and $E_0$ so our model EXAFS function matches our data.

Fit results

- $N = 5.8 \pm 1.8$
- $R = 2.10 \pm 0.02 \, \text{Å}$
- $E_0 = -3.1 \pm 2.5 \, \text{eV}$
- $\sigma^2 = 0.015 \pm 0.005 \, \text{Å}^2$.

$|\chi(R)|$ for FeO (blue), and a 1st shell fit (red).
Modeling the first shell of FeO - 2

1st shell fit in k space

The 1st shell fit to FeO in k space. There is clearly another component in the XAFS

1st shell fit in R space

|χ(R)| and Re[χ(R)] for FeO (blue), and a 1st shell fit (red).
Modeling the second shell of FeO - 1

To add the second shell Fe to the model, we use calculation for f(k) and δ(k) based on a guess of the Fe-Fe distance, and refine the values R,N, $\sigma^2$.

Such a fit gives a result like this:

$|\chi(R)|$ data for FeO (blue), and fit of 1\textsuperscript{st} and 2\textsuperscript{nd} shells (red).

The results are fairly consistent with the known values for crystalline FeO:

6 O at 2.13Å, 12 Fe at 3.02Å.

Fit results (uncertainties in parentheses):

<table>
<thead>
<tr>
<th>Shell</th>
<th>N</th>
<th>R (Å)</th>
<th>$\sigma^2$ (Å$^2$)</th>
<th>$\Delta E_0$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-O</td>
<td>6.0(1.0)</td>
<td>2.10(.02)</td>
<td>0.015(.003)</td>
<td>-2.1(0.8)</td>
</tr>
<tr>
<td>Fe-Fe</td>
<td>11.7(1.3)</td>
<td>3.05(.02)</td>
<td>0.014(.002)</td>
<td>-2.1(0.8)</td>
</tr>
</tbody>
</table>
Modeling the second shell of FeO - 2

Other views of the data and two-shell fit:

The Fe-Fe EXAFS extends to higher-k than the Fe-O EXAFS. Even in this simple system, there is some *overlap* of shells in R-space. The agreement in Re[χ(R)] look especially good – this is how the fits are done. The modeling can get more complicated than this.