

4.7: Experimental modes and Data Analysis

Designing the experiment requires an understanding of the four primary detection methods in X-ray Absorption Spectroscopies (XAS): (1) Transmission, (2) Fluorescence, (3) "Auger" Electron yield and (4) Total Electron Yield.

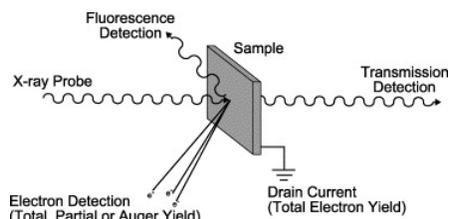


Figure 4.7.1: Schematic of the possible measurement techniques for XAS. The absorption process depicted in Fig. cannot be detected directly and so the signal must be detected through either the absence of the absorbed photons in the transmitted X-rays (transmission detection) or through the particles ejected during the relaxation process that follows (fluorescence detection or electron detection). Energy discrimination allows the electron detection technique to be broken down into total (TEY), partial (PEY) and Auger (AEY) electron yield detection schemes. (all rights reserved)

Transmission Mode

Absorption Length = distance over which x-ray intensity sets the fundamental length scale for choosing sample thickness, particle size, and sample homogeneity. This is often about 10 microns but varies depending on density and element that is probed. Sample cannot be significantly larger or it absorbs all the x-ray light.

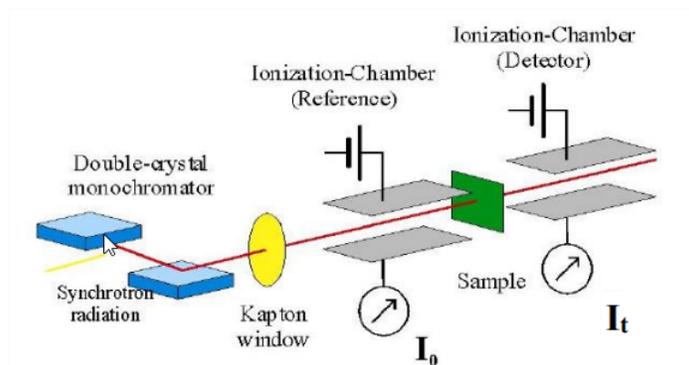


Figure 4.7.2: Experimental XAS setup transmission mode. (Copyright; author via source)

The XAS technique is *insensitive* and higher concentrations of metal will provide higher quality data (up to around 5 mM or so). Sample cuvettes are commonly made out of machined polycarbonate or Lucite with one X-ray transparent (e.g., Mylar) window. Minimum volumes useful on current generation beamlines are dictated by the cross section of the beam and usually one needs at least 50 microliters. One major limitation to the use of this technique is its inability to distinguish multiple site structures within a given sample. If the sample has heterogeneous metal environments, the resulting XAS-derived structure would simply be the weighted sum of all the structures contained in the sample. Thus, many EXAFS reports describe an "average" structure. It is usually helpful to have some independent measurement that suggests that all of the metal being probed exists in a homogeneous type of site.

This schematic of an X-ray absorption spectrometer shows that the essential components are analogous to those required for any spectroscopic technique. However, operating in the X-ray region of the electromagnetic spectrum requires that each component be designed differently than their analogs in the UV, visible, or IR regions.

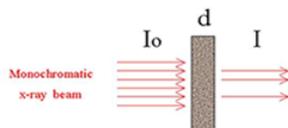


Figure 4.7.2B: A schematic representation of x-ray absorption spectroscopic measurements in transmission mode.

X-ray detectors are either gas ionization chambers (X-rays ionize an inert gas and charged plates collect and record the microcurrent generated) or fluorescence photon-counting detectors (scintillation counters, solid-state detectors). X-ray

monochromators are two parallel single crystals of silicon (usually) that take advantage of Bragg diffraction to monochromate the X-rays. Tuning occurs by simply rotating the crystals to different incident angles. A light bulb is *not* a good source of X-rays, so instead all biological XAS is performed using synchrotron radiation generated by a storage ring.

You measure absorption just like in UV-VIS and IR (dispersive):

$$\frac{I}{I_0} = e^{-\mu(E)x}$$

which can be converted to

$$\mu(x)x = \ln\left(\frac{I_0}{I}\right)$$

Fluorescence Mode

X-ray fluorescence or XRF is the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by bombarding with high-energy X-rays. X-ray fluorescence. If the electron has enough energy it can knock an orbital electron out of the inner shell of a metal atom, and as a result electrons from higher energy levels then fill up the vacancy and X-ray photons are emitted. This process produces a discrete spectrum of X-ray frequencies, called spectral lines. The spectral lines generated depends on the target (anode) element used and thus are called characteristic lines. Usually these are transitions from upper shells into K shell (called K lines), into L shell (called L lines) and so on.

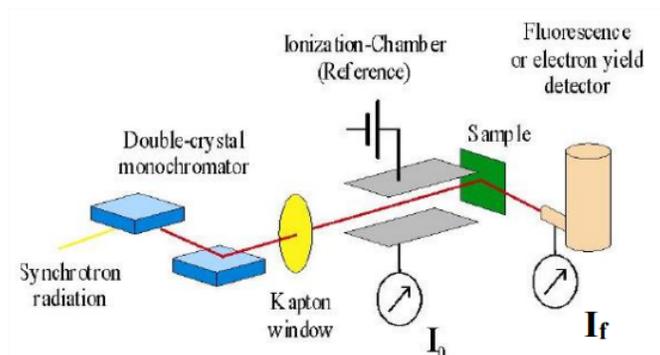
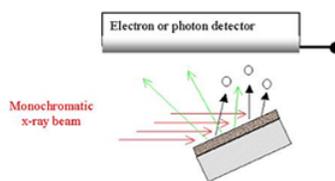


Figure 4.7.3: Experimental XAS setup fluorescence mode. (Copyright; author via source)

"Auger" Electrons

When an electron is removed from a core level of an atom, leaving a vacancy, an electron from a higher energy level may fall into the vacancy, resulting in a release of energy. Although sometimes this energy is released in the form of an emitted photon (XRF), the energy can also be transferred to another electron, which is ejected from the atom. This second ejected electron is called an **Auger electron**.



$$I \propto I_0 \epsilon \omega \Omega x \mu$$

with

- μ -absorption coefficient
- x -layer thickness
- ω -radiative or nonradiative yield
- Ω -solid angle of collection
- ϵ -detection efficiency

Upon ejection the kinetic energy of the Auger electron corresponds to the difference between the energy of the initial electronic transition and the ionization energy for the electron shell from which the Auger electron was ejected. These energy levels depend on the type of atom and the chemical environment in which the atom was located.

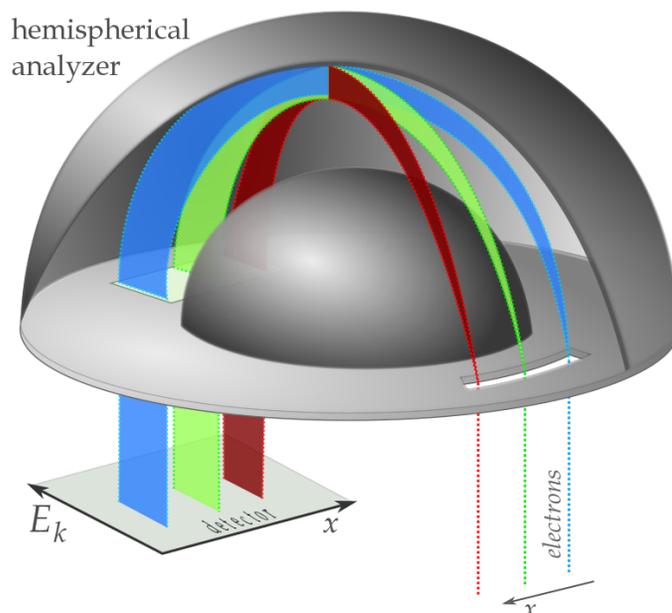


Figure 4.7.4: Hemispherical electron energy analyzer. Electron of different energies are dispersed to different channels of the detector in the direction perpendicular to the entrance slit.. (CC BY-SA 4.0; Ponor via Wikipedia)

Total Electron yield

In the total electron yield detection mode, a solid is illuminated with a monochromatic beam of x-rays. Core electrons are excited into the conduction band of the solid, and the resulting current measured in the variant known as **total electron yield**. The intensity of the emitted primary Auger electrons is a direct measure of the x-ray absorption process are highly surface sensitive, similar to XPS. As they leave the sample, the primary Auger electrons create scattered secondary electrons (Figure 4.7.4) which dominate the total electron yield (TEY) intensity. The TEY cascade involves several scattering events and originates from an average depth, the electron sampling depth L .

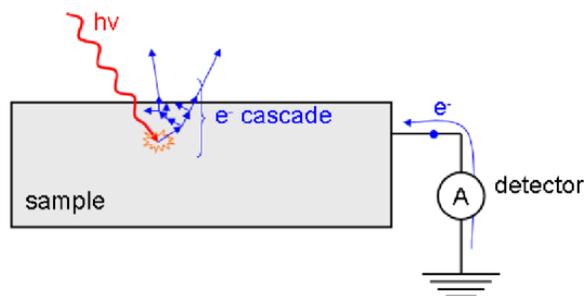


Figure 4.7.5: Principle of total electron yield XAS measurement. (all rights reserved)

This detection scheme has significantly limitations for non-conducting samples.

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