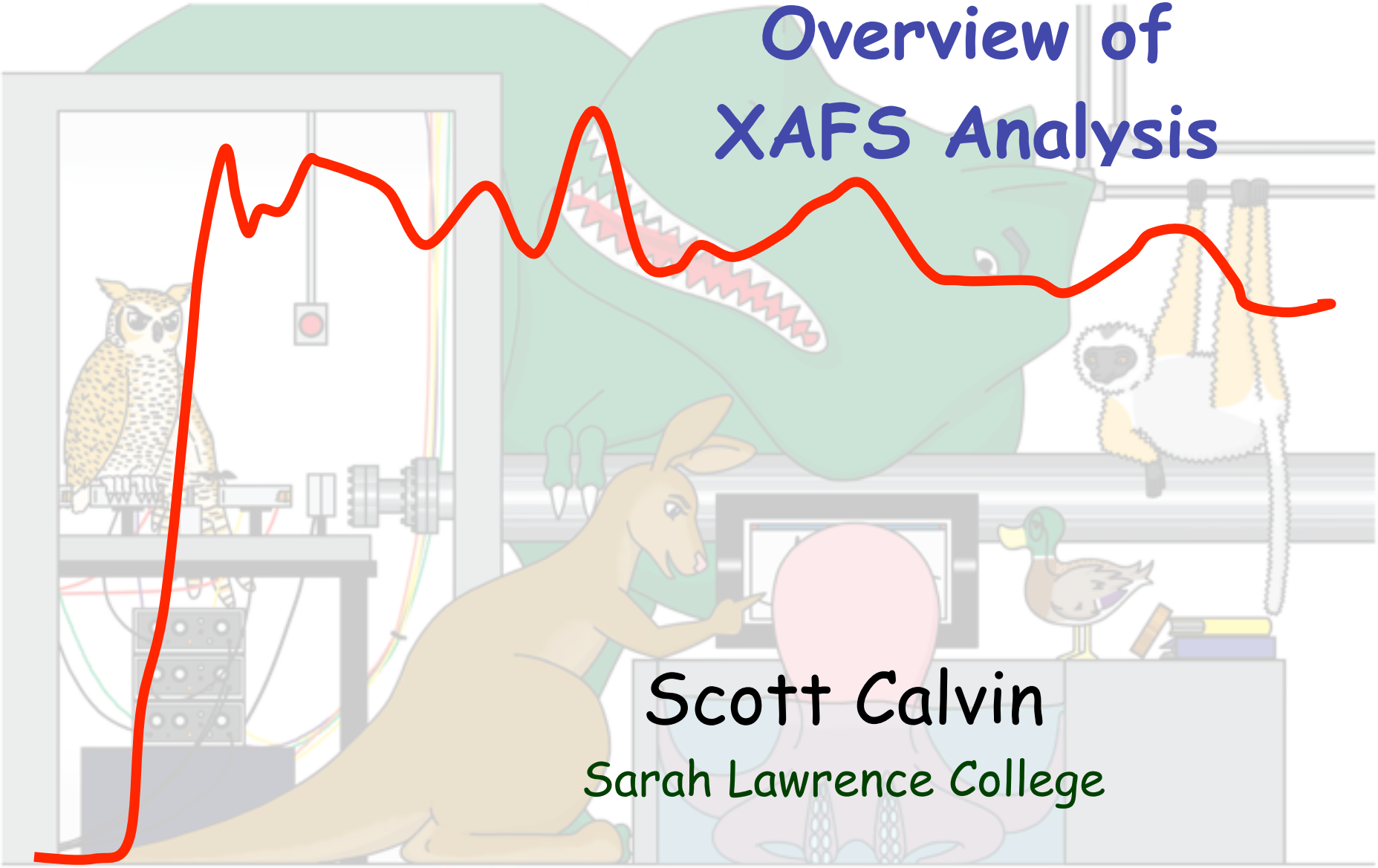


Overview of XAFS Analysis

Scott Calvin

Sarah Lawrence College

Some Typical Questions

Formulating a Problem

NSLS
XAFS Online Orientation

Choose the question you would like to answer about your sample

Questions related to what substances are present in the sample (speciation):

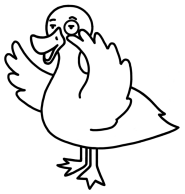
- Is it pure X?
- Is X present?
- How much of X is present?
- Which of several possible substances are present?
- Which of several possible substances are present, and in what proportions?
- How do qualitative features of the structure change with conditions?

Questions related to characteristics of the substances in the sample (characterization):

- I have a modified version of X. How does it differ structurally from pure X?
- How is the local structure different from the known average structure?
- What is the immediate coordination environment of each element in my strongly disordered or novel substance?
- What is the valence of element Y in my sample?
- My sample contains a small amount of element Y (a dopant or impurity) in a known substance X. In what environments do the atoms of Y reside?
- How do subtle features of the structure change with conditions?

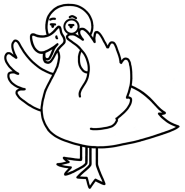
Introduction to XAFS
Overview of an Experiment
Formulating a Problem
Proposal Writing
Sample Preparation
Data Collection
Looking Forward to Analysis

"EXAFS"

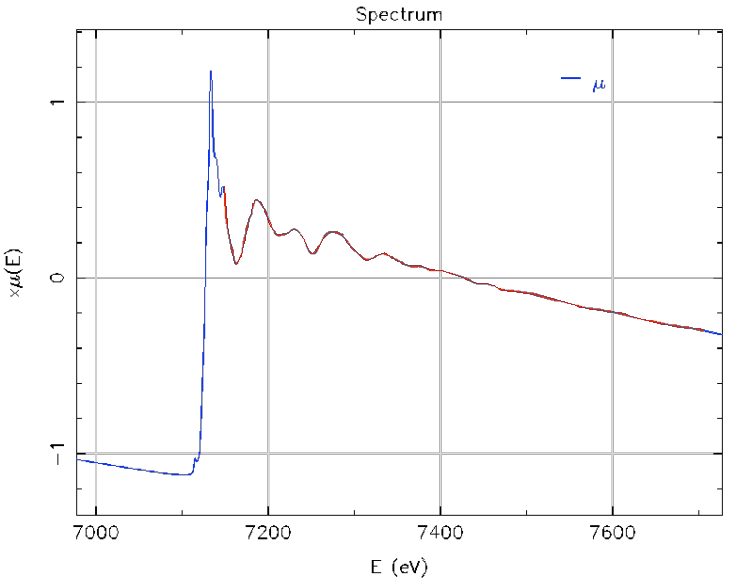


Acronym for extended x-ray absorption fine structure.

The EXAFS region starts around 30 eV above the edge.



EXAFS properly refers to the oscillations and other features visible within that region.



The EXAFS Equation

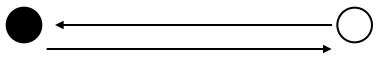
$$\chi(k) = \sum_j \frac{S_0^2 N_j f_j(k) e^{-2R_j/\lambda(k)} e^{-2k^2\sigma_j^2}}{k R_j^2} \sin[2kR_j + \delta_j(k)]$$

In the EXAFS region, the oscillations can be thought of as a sum of individual scattering paths *j*.

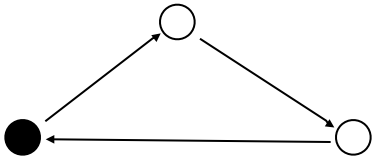
- R_j : the absorber-scatterer distance
- σ^2_j : the variance in the absorber-scatterer distance for path j
- N_j : the coordination number for path j
- S_o^2 : the "amplitude reduction factor"
- f_j, δ_j: scattering parameters based on identity of scattering atom(s)
- λ: mean-free path of the photoelectron

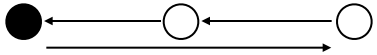
For multiple-scattering paths, the parameters are defined in analogous fashion; i.e. R_j is half of the total path length)

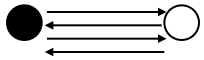
Single-scattering:



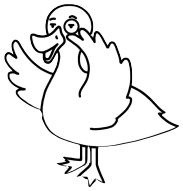
Multiple scattering:





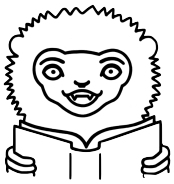


"XANES"



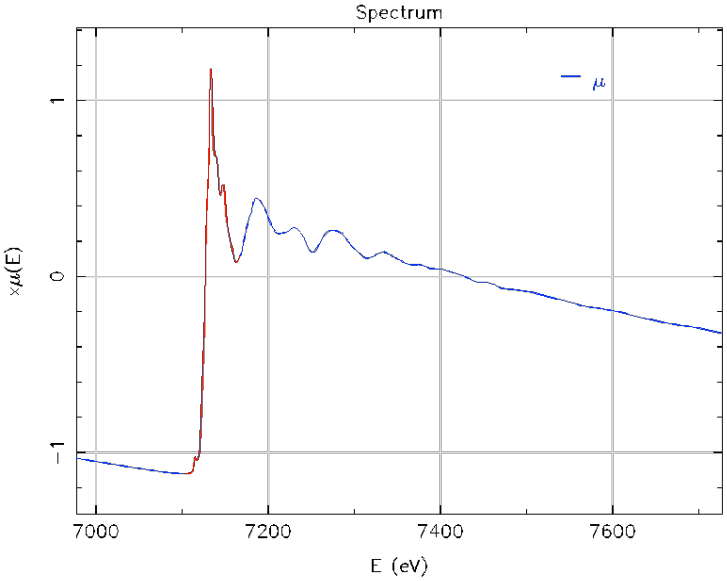
Acronym for x-ray absorption near edge fine structure.

The part of the spectrum from the edge to 30 eV or so above the edge.



While progress is being made in calculating XANES spectra theoretically, these calculations are not yet generally as accurate as they are for the EXAFS part of the spectrum.

NEXAFS (near-edge x-ray absorption fine structure) is a synonym for XANES, although NEXAFS tends to be used at edge energies below 1000 eV and XANES at higher energies.



Comparison to other Characterization Techniques

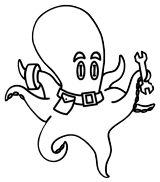
	DLS	ICP	TEM	XANES	EXAFS	XRD	IR	NMR
Stoichio-metry								
Phases Present								
Lattice Constants								
Bond Lengths								
Particle Size								
Defect Structure								

Supporting Information

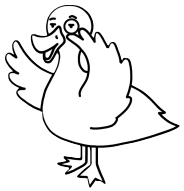
Partial Information

Preferred Technique

"E_o"

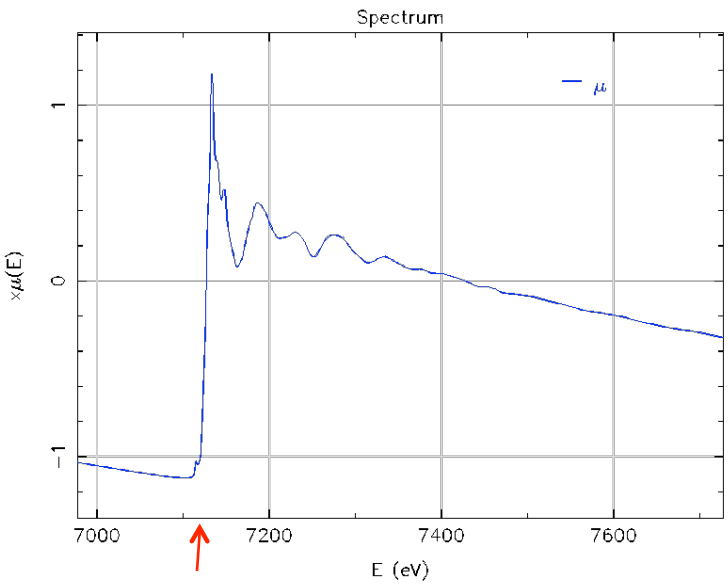


E_o is supposed to be the "energy origin" for the electron released when the sample absorbs an x-ray, but there is not a single precise way to define this quantity!

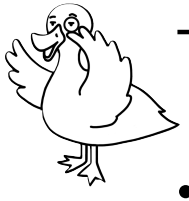


In practice, therefore, E_o may be defined in any one of a number of reproducible, but fundamentally arbitrary, ways:

- At the first peak of the first derivative
- At the largest peak of the first derivative
- Half way up the steep rise
- In such a way as to agree with theoretical models of EXAFS
- From a table of elemental absorptions

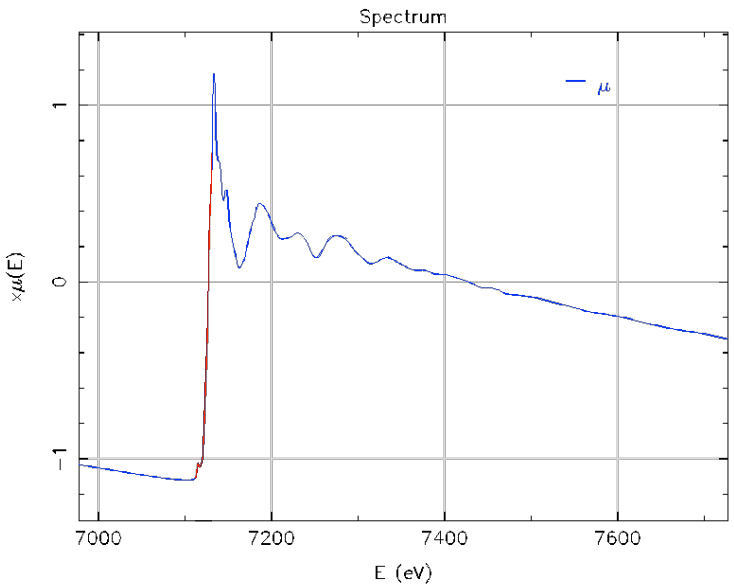


"Edge"

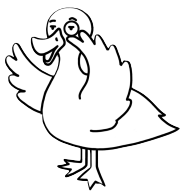


The term "Edge" is used in several different ways:

- It is often used to identify the orbital of the absorbing electron: "the spectrum at right is of the iron K edge."
- It is sometimes used as a synonym for E_o: "the edge is at 7112 eV."
- It is often used to represent the sharply rising part of the spectrum, although perhaps stopping before the white line: "I managed to collect data over the edge, but then I lost beam."

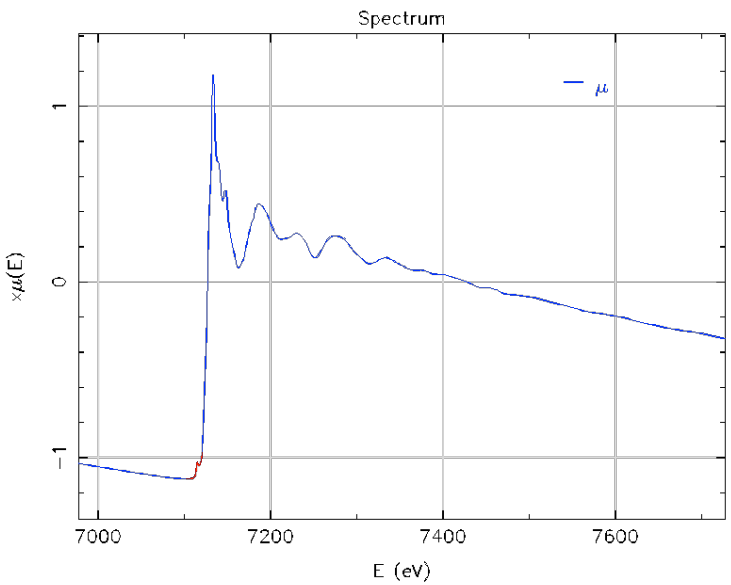


"Pre-Edge"



This term is used in at least two ways:

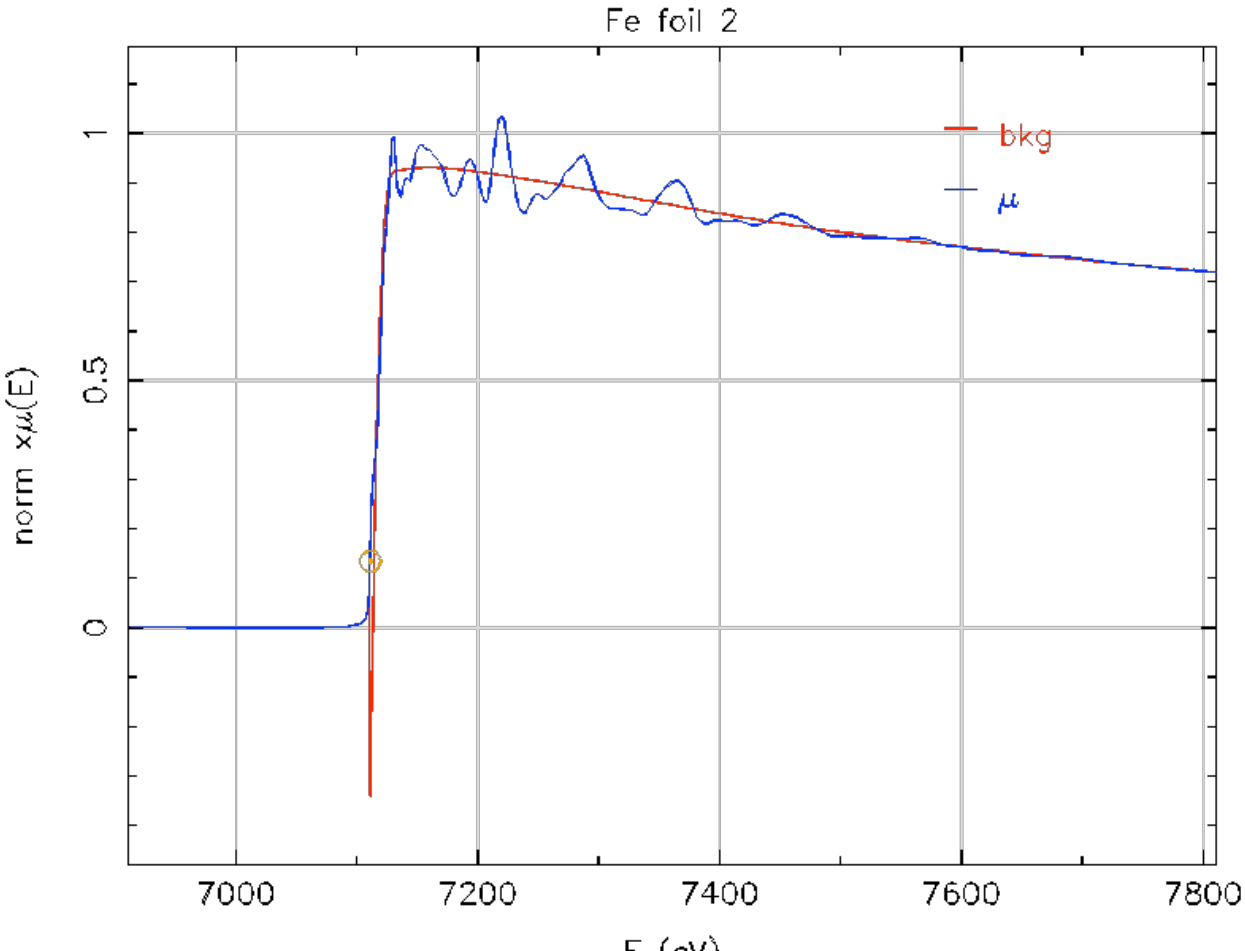
- To identify the fairly featureless part of the spectrum before the sharp rise associated with the edge.
- To identify small features on the rising portion of the spectrum, such as the small bump highlighted to the right. For this purpose, it is often used as an adjective: "pre-edge feature."



Yeah, it's weird that all the different ways in which the terms "edge" and "pre-edge" are used can lead to a "pre-edge" feature occurring after the "edge." In practice, however, you'll figure it out by context.

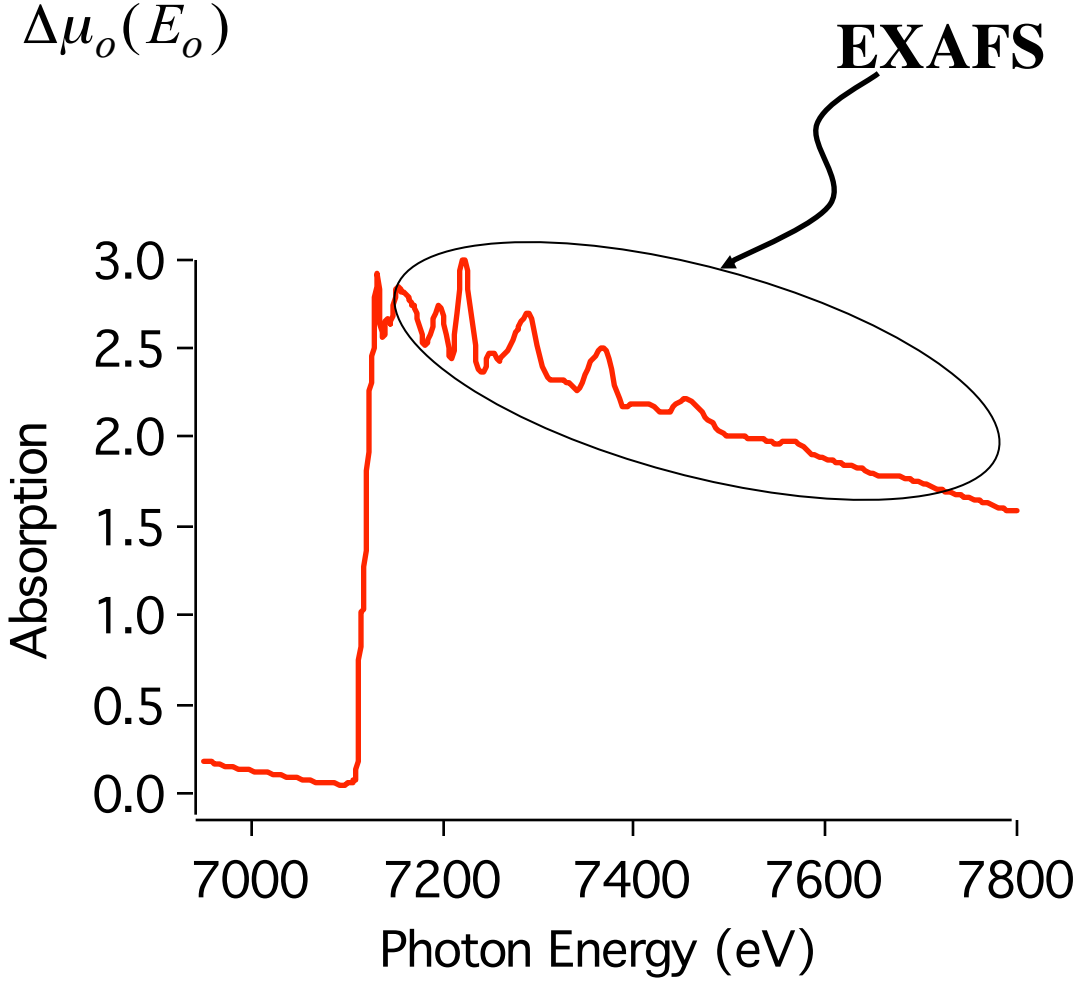
EXAFS Data Reduction

- Normalize so edge step is 1
- Estimate what the spectrum would look like if the atom were isolated; this is called the background function, symbolized by $\mu_o(E)$

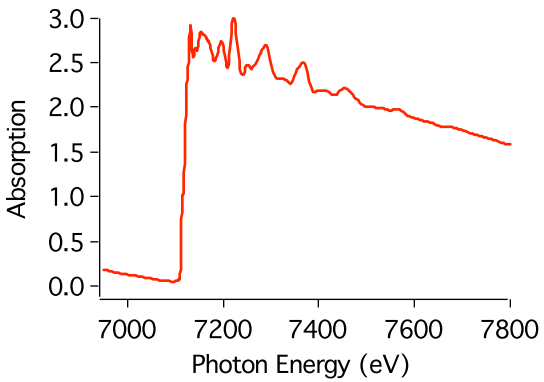


EXAFS Data Reduction

$$\chi(E) = \frac{\mu(E) - \mu_o(E)}{\Delta\mu_o(E_o)}$$

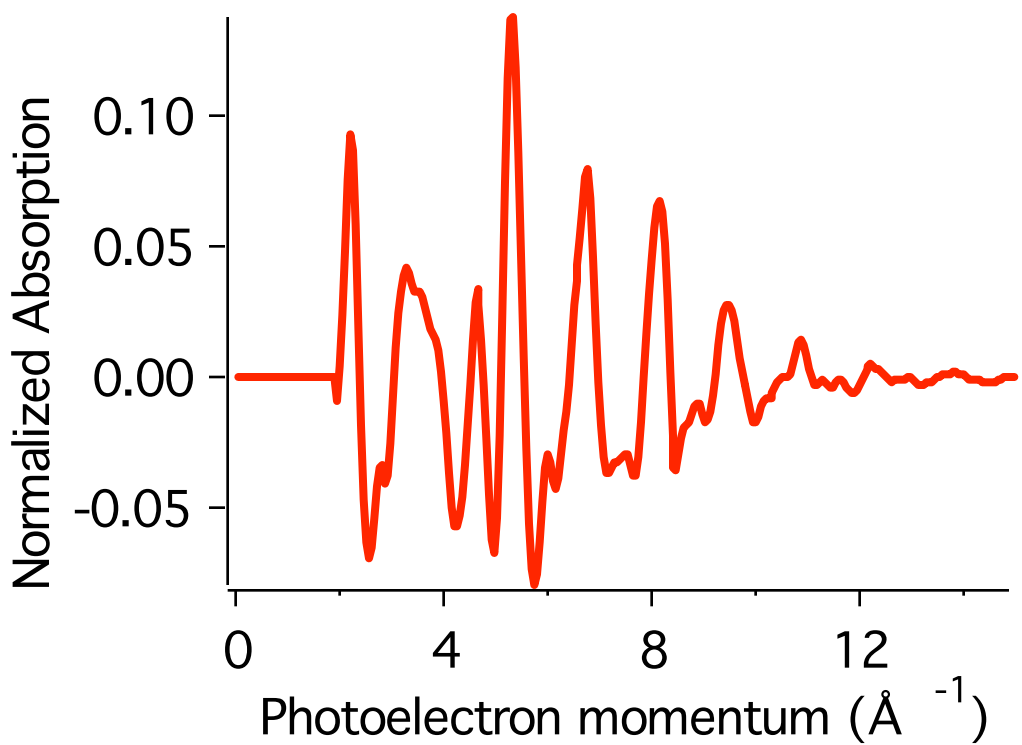


EXAFS Data Reduction

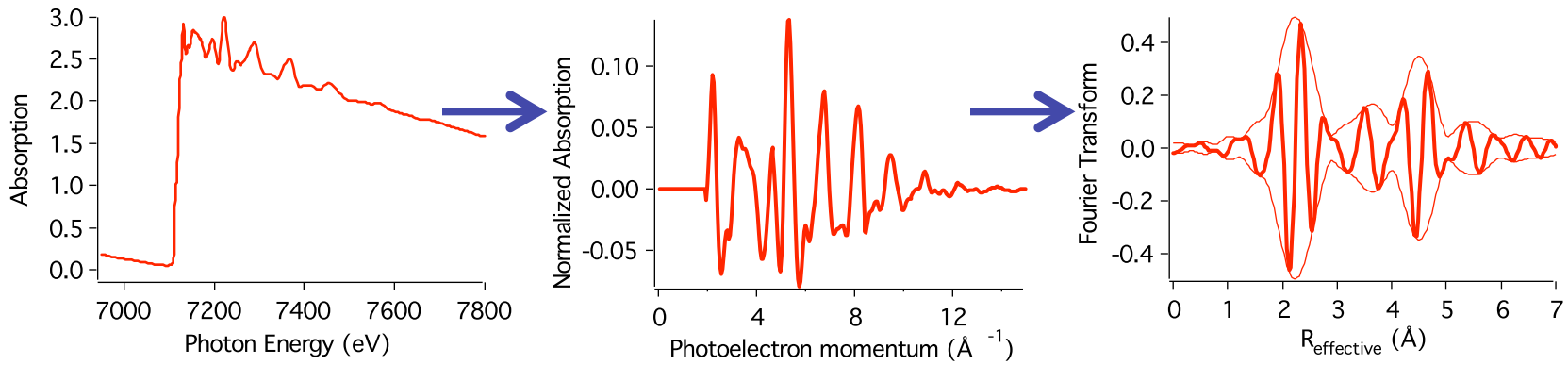


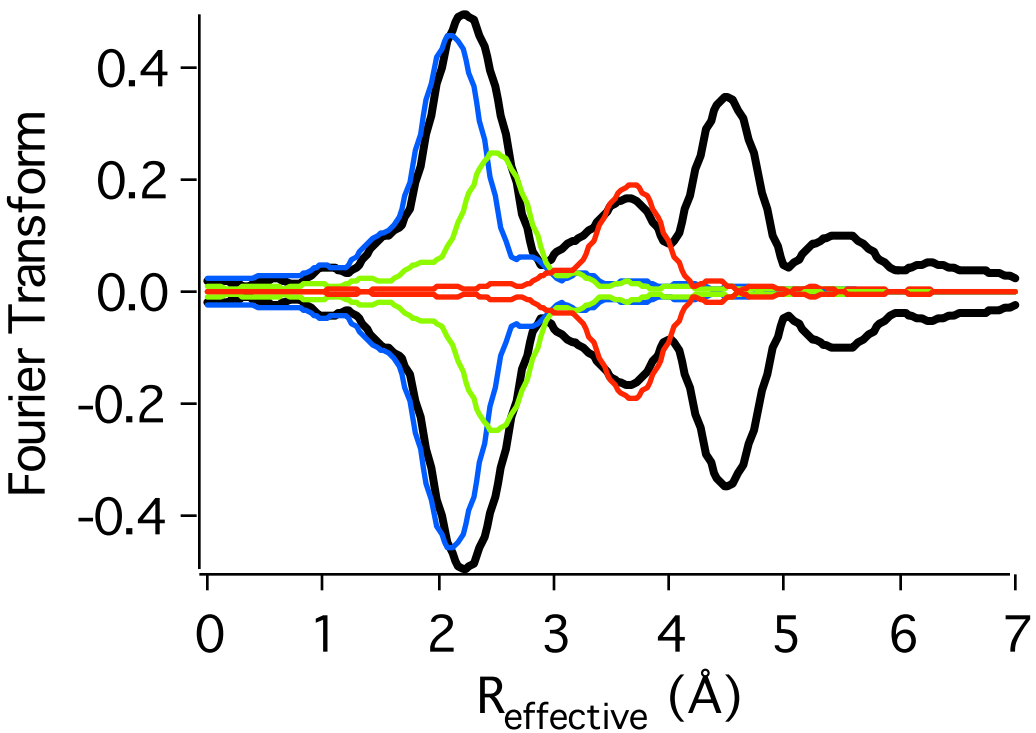
$$k = \frac{1}{\hbar}\sqrt{2m_e(E - E_o)}$$

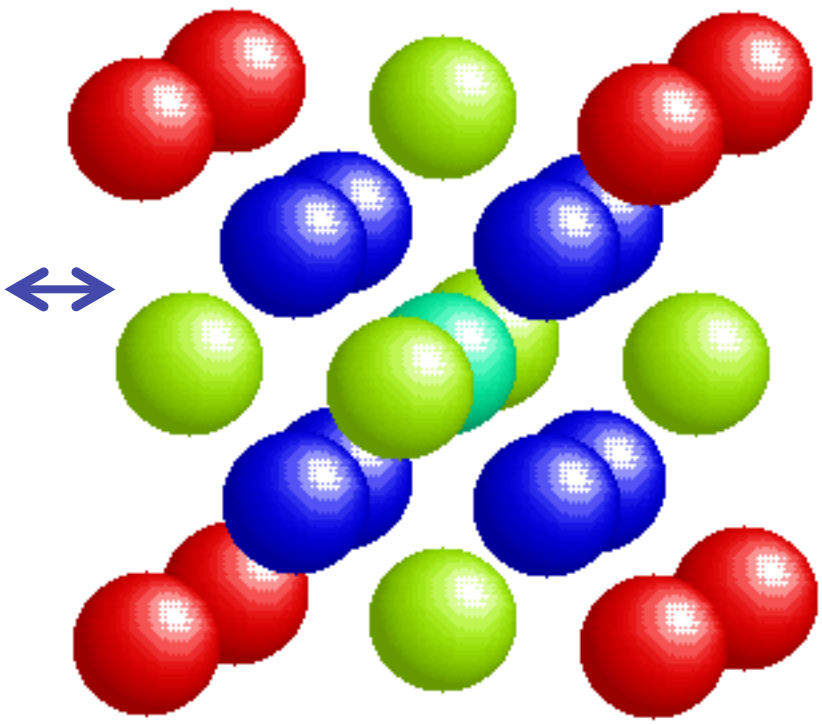
$$\chi(E) \rightarrow \chi(k)$$



EXAFS Data Reduction







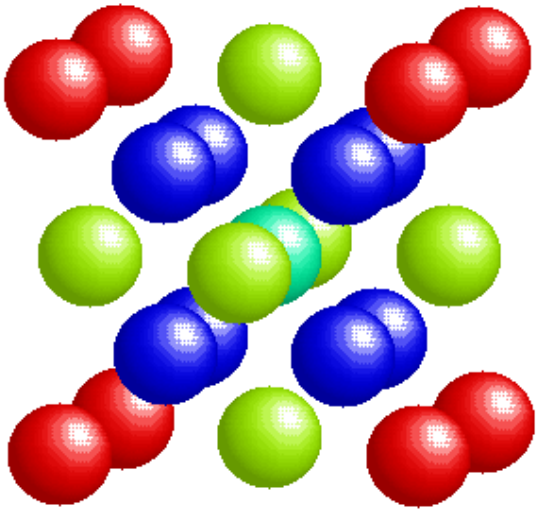
Why XAFS is not a Black Box

Data →

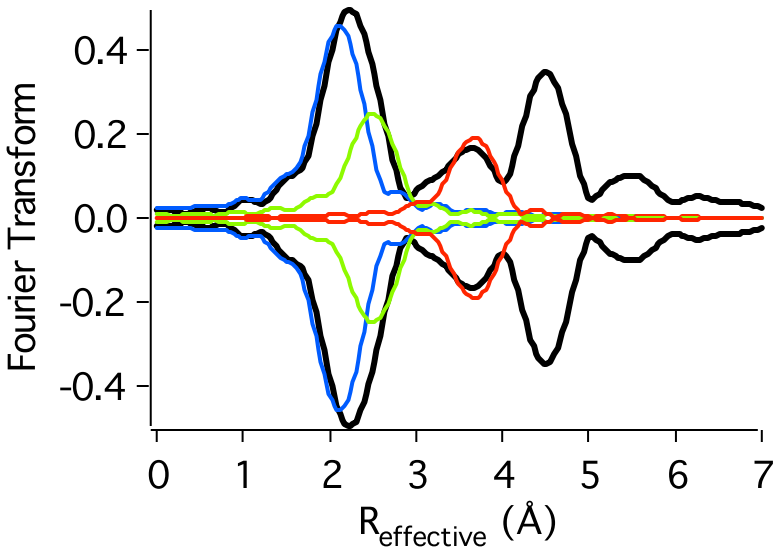
→ Structure

The Inverse Problem

This is "easy":



Structure

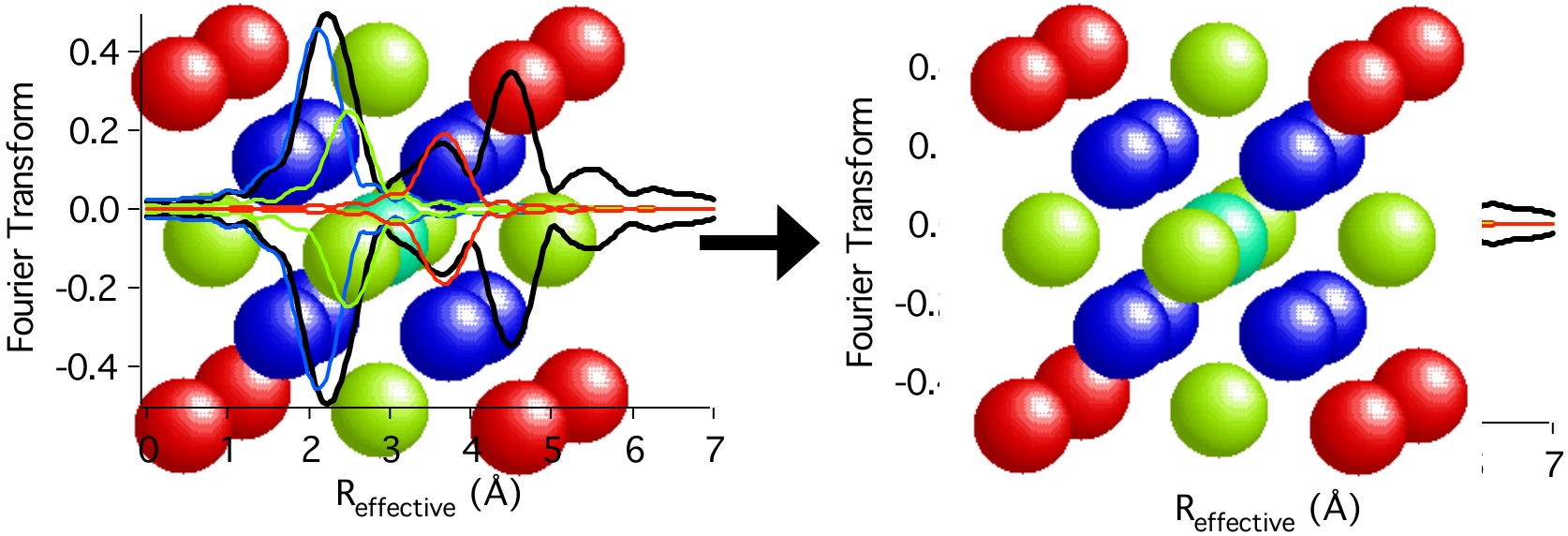


Fourier Transform of EXAFS

There is software that does this

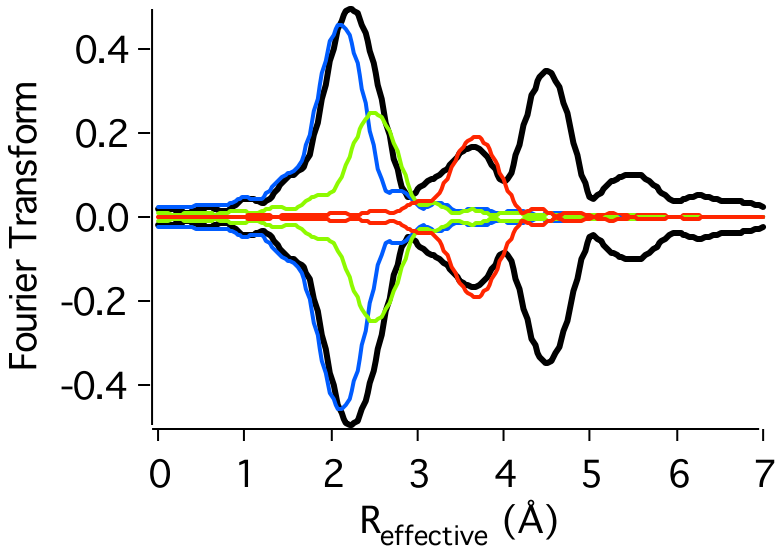
The Inverse Problem

This is "hard":



What Makes it Hard?

The Fourier Transform peaks are shifted down from the actual absorber-scatterer distances, usually by about 0.3 to 0.5 angstroms.



Multiple-scattering may be significant

More than one structure may correspond to the same spectrum!

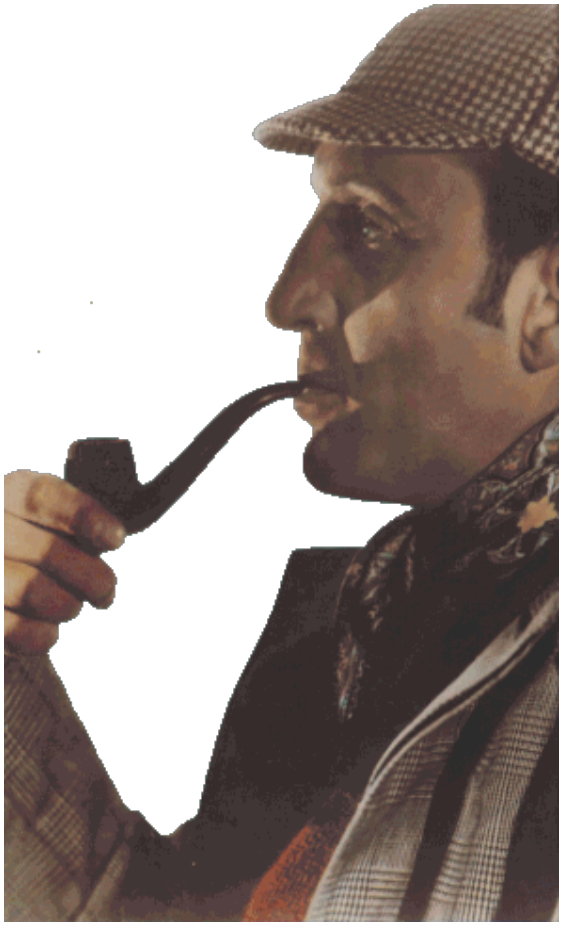
In a sense, the task is not just hard, it is impossible!

Detective Work

While XAFS cannot yield a structure absent other information, it can rule out structures, so:

Make an **educated guess** as to possible structures, then use XAFS to eliminate those that are incorrect.

"When you have eliminated all which is impossible, then whatever remains, however improbable, must be the truth."--Sherlock Holmes

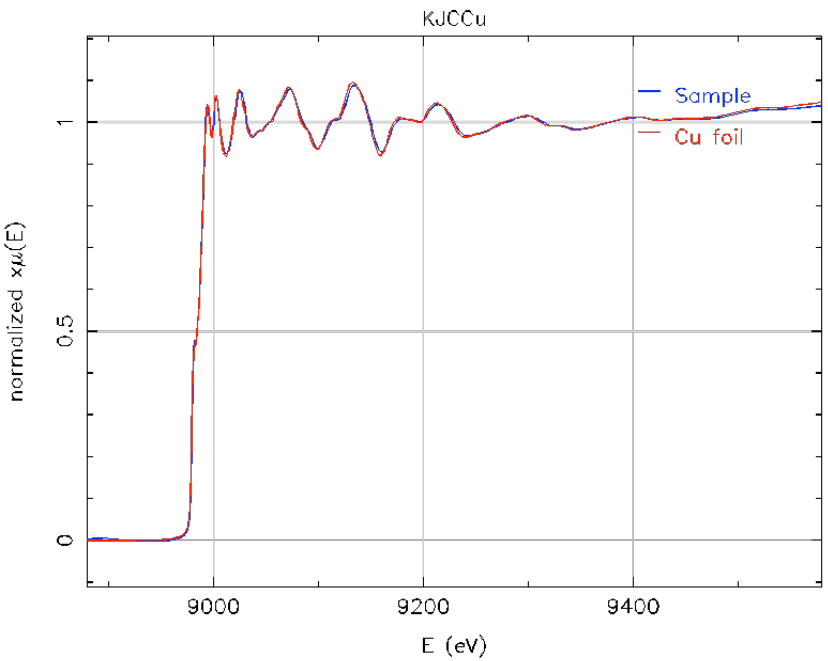


XAFS Analysis Techniques

There are four common techniques for analyzing XAFS data. All rely, in one way or another, on making educated guesses as to what is in the material:

- Fingerprinting
- Linear combination analysis
- Principle component analysis
- Modeling ("Curve fitting to a theoretical standard")

Analysis Technique: Fingerprinting



In this technique, the spectrum of a sample is visually compared to the spectrum of a standard to see if they match.

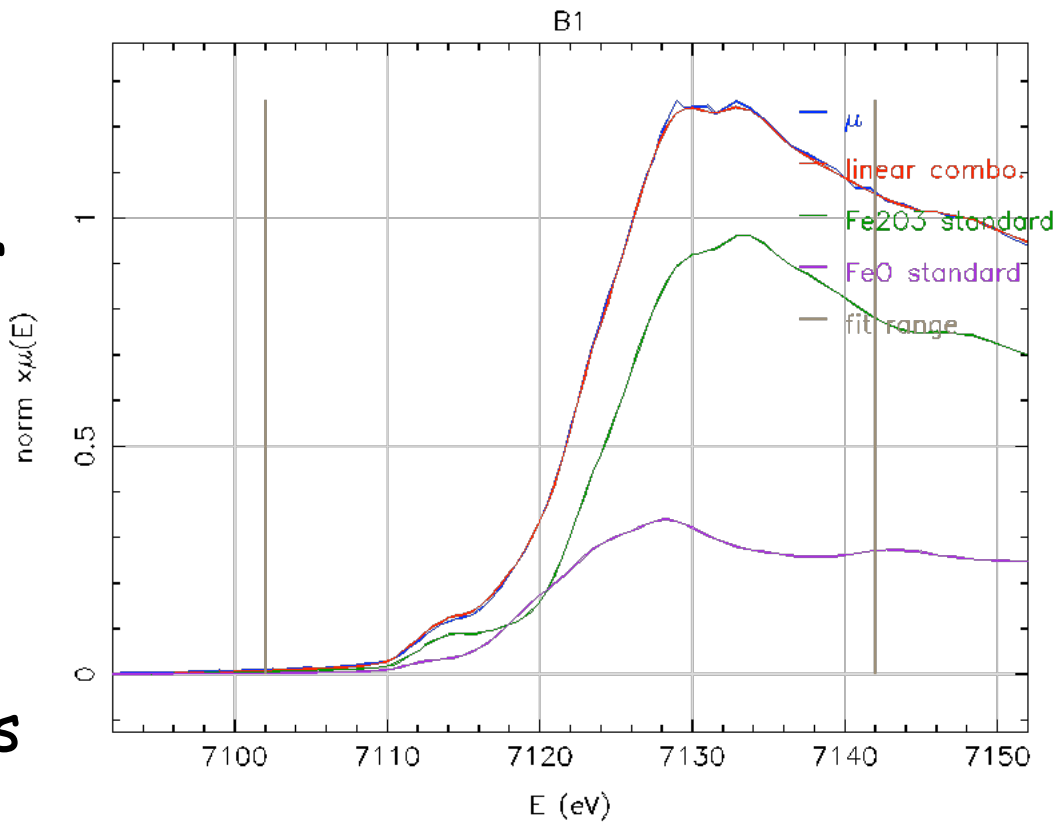
This technique requires very little training, but doesn't work unless the sample is predominantly the same composition as a standard.

Useful for answering the question "is this really X?"

Analysis Technique: Linear Combination Analysis (LCA)

In this technique, a computer attempts to match the spectrum of a sample by adding together fractions of the spectra of standards.

This technique is easy to learn, but won't work unless there are standards for all constituents.



Particularly useful in environmental science.

Analysis Technique: Principal Component Analysis (PCA)

In this technique, a computer takes linear combinations of a set of spectra in such a way as to create a set of "components" that can account for the spectra, in decreasing order of importance.

This technique is best used when there are multiple related spectra, such as a series of samples or a single sample measured under a variety of conditions.

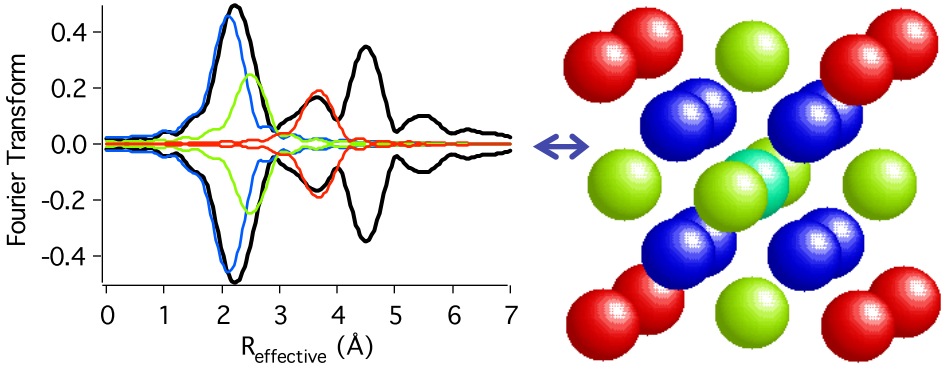
This technique can provide information about how many different constituents are present, and whether individual constituents are present.

PCA is thus useful when you have limited knowledge about your samples, but plenty of data.

Often useful for analyzing changes based on conditions such as temperature, voltage, or pressure. Also useful when looking for a "smoking gun" constituent.

Analysis Technique: Modeling (Curve Fitting to a Theoretical Standard)

In this technique, a computer calculates a theoretical spectrum based on a guess as to the structure of the material, and then adjusts the guessed structure so as to match the measured spectrum.



This is the only technique which can provide information about structures for which there are no good standards, and is the only way of reliably measuring quantitative information such as bond lengths.

This is also the most difficult technique to learn and apply.

Useful for novel materials, particularly modifications or variants of well-known structures