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Synchrotron X ray absorption student projects in community college and gateway for chemical engineering related education

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A committed chemist, researcher, educator, and innovator with an unwavering desire for excellence, clar-ity of reflection, multi-disciplinary learning accomplishments, ground-breaking innovations, collaborative studies, entrepreneurship, intellectual and ethical responsibility, and service to the scientific, national, and international communities.

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Abstract:
A Synchrotron radiation student project in our community college consists of data collection, data analysis, and discussion which includes the formulation of a new hypothesis. Although the on-site data collection at National Labs such as NSLS II at BNL, Cornell High Energy Synchrotron Source are limited by the Synchrotron beam time availability students were able to participate on site data analysis from previously collected data. The data analysis component fully engages the students in Extended X ray Absorption Fine Structure(EXAFS), X ray absorption Near Edge Structure (XANES), and X ray absorption pre edge feature analysis. These tools were used to analyze microstructure of iron and zinc compounds in a variety of samples. In EXAFS experiments data consists of absorption coefficient of element under investigation versus X ray energy at the vicinity of an absorption edge and about 200 eV below & 1000 eV above the edge energy. Analysis of EXFS data yields the amount of the element under investigation and structural parameters such as oxidation state, near neighbor bond length, number of near neighbor atoms and disorder. The advantage of this method is minimal sample preparation and no chemical treatments to samples. The pedagogy encourages mindful reading of the latest Synchrotron based research articles with faculty guidance to build a relationship to a chemical engineering related education. The pedagogy of using the Synchrotron radiation student projects in community college has been found to broaden the prospect and build connections to chemical engineering related education in the senior college setting. The data analysis steps of several different material and structure interpretations will be presented.

Introduction:

X ray absorption spectroscopy, including Extended X ray Absorption Fine Structure (EXAFS), X ray Absorption Near edge Structure(XANES) and Pre-edge feature analysis, is a valuable tool in structure determination of unknown materials. X ray absorption in a sample occurs when incoming X rays have sufficient energy to remove a core electron of absorbing atom. Core shell binding energy is unique to type of absorbing atom. Therefore, by tuning incoming X ray energy structure of different type of atoms can be studied. Analysis of X ray absorption spectra will yield oxidation state, type and bond length of near neighbor atoms. But to extract this information high resolution absorption spectrum is required. Therefore, it is almost impossible to use regular x rays from x ray tubes for these experiments. Synchrotron X rays provide better alternative to tube x rays. Because of extremely high intensity high resolution x ray spectrum can be collected within short time using synchrotron x rays. At Queensborough Community College, several pre- engineering and REU students conduct research projects based on synchrotron X rays. We are fortunate to have two synchrotron facilities, NSLS II at Brookhaven and Cornell high energy synchrotron source, in New York. But because of high demand, getting experimental beam time is highly competitive. Therefore, whenever we receive experimental beam time at one of these facilities we run many samples from different projects. Students spend most of their research time by analyzing previously collected data.

Experimental:

X ray absorption experiments were done in fluorescence mode using ion chambers and Lytle type or semiconductor detectors to measure incident and fluorescence intensities. Dry powder samples with same amount by mass were mounted on identical sample holders with Kapton tapes. For quantification, same area of the samples were exposed to x rays. Absorption coefficients were measured as a function of incident X ray energy. X ray energy is scanned through the binding energy of the atom under investigation from about 200 eV below the absorption edge to 1000 eV above the edge. There is no absorption occurs below the absorption edge but as X ray energy reaches binding energy of core shell, there is sharp increase in the absorption cross-section. This is the so-called absorption edge. This absorption edge energy is sensitive to oxidation state of the atom under investigation[1-3]. The rise or height of the absorption spectrum at the edge energy depends on amount of absorbing atoms in the sample[4]. In the case of iron, small absorption feature appears before the absorption edge. This is called pre-edge feature and is due to forbidden 1s to 3d transition. This transition is forbidden by selection rules but becomes allowed when there is mixing of iron 3d orbital and oxygen 2p orbitals. Therefore, this feature is visible only Fe-O compounds. Furthermore, asymmetry of bonding favors more mixing of orbitals and hence enhance intensity of the pre edge feature[5]. As x ray energy increases beyond the edge, extra energy is taken by ejected core electrons as kinetic energy. These ejected photo electrons were scattered back toward the central atom by neighboring atoms. Therefore, at the vicinity of absorbing atom two types of electron waves exists. Namely, outgoing photo electron wave and backscattered waves by neighboring atoms. These two waves interfere constructively or destructively depending on type and distance of near neighbor atoms. The resulting absorption spectra exhibit fine oscillations above the edge. These oscillations are called EXAFS[6]. Extracting these EXAFS, the near neighbor bond length can be calculated. Some of our research projects include Iron absorption of plants under different pH vales., Distribution of iron in plants at different growth stages, Dependance of iron absorption on soil contamination, Structure of iron nano particles prepared by sol gel method and spin coating.

Data analysis:

As beam of X rays with intensity I_0 travelling through homogeneous medium the beam intensity, I. decreases as path length, x, increases according to $I=I_0 \exp(-\mu x)$ where μ is absorption coefficient. Absorption coefficient μ is a function of incident photon energy. Typical x ray absorption spectrum is the graph of absorption coefficient μ Vs photon energy. X rays are absorbed by matter primarily through photoelectric effect. This occurs when bound core electron is ejected to a continuum state with kinetic energy, $E_k = E - E_0$. Where E is the photon energy and E_0 is the core electron energy. For photon energies less than E_0 absorption is not possible. Sharp rise in absorption occurs as photo energy increases beyond E_0. The ejected photo electrons are nearly free and can be considered as spherical outgoing waves. As these electrons propagate through the solid, they undergo scattering at the neighbor shell of atoms. These outgoing electron waves and back scattered electron waves interfere constructively or destructively depending on the phase difference between them. The phase difference depends on the type of central atom, type of near neighbor atoms, and near neighbor distance. The resulting absorption spectrum looks like figure 2a with some oscillations of absorption coefficient above the edge. In the single scattering approximation, the normalized absorption, $\chi(k) =(\mu(k) -\mu_0)/\mu_0$ is given by[7]

$\chi(k) =\Sigma S_i(k)\, N_iF_i(k)\, \exp(-\sigma_i^2k^2)\exp(2r/\lambda)\mathrm{Sin}(2kr+\phi_i+\phi_j) /kr^2$ where $k=\{2mE_k/\hbar^2\}^{1/2}$, m= mass of an electron, N=number of near neighbor atoms, r=near neighbor atom distance, S is a correction factor, F=back scattered amplitude function that depends on the type of near neighbor atom, λ is the mean free path of photo electrons, σ is the De Bye Waller factor which also includes thermal vibrations of atoms, ϕ_i depends on the absorbing atom and ϕ_j depends on the type of near neighbor atom. Basic steps of EXAFS analysis are shown in Figure 2.

Results and discussion:

X ray absorption spectrum of a typical sample containing iron is shown in the figure 1.

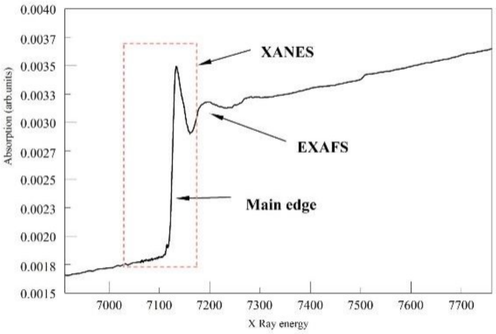
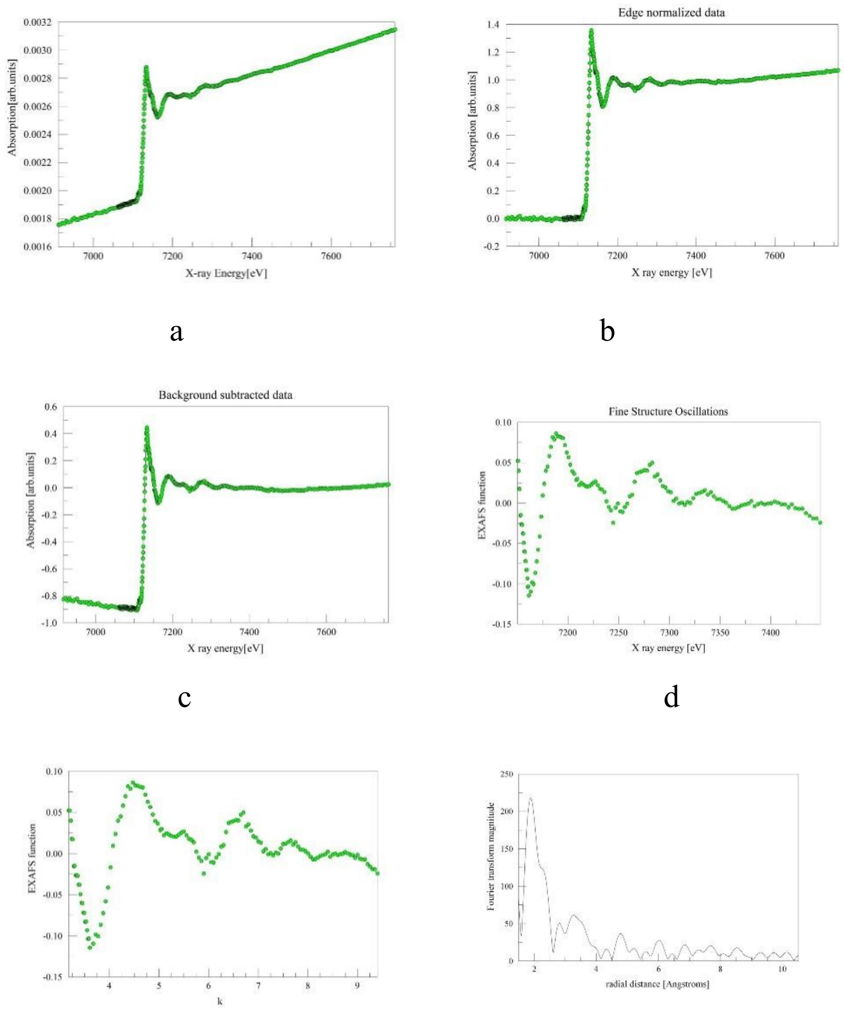


Figure 1: X ray absorption spectrum of typical sample containing iron

Since iron K edge energy is 7111 eV, during the experiment incoming x ray energy scanned through 6900 eV to 8000 eV. As expected no absorption occurs before the edge energy except small pre-edge feature. Small oscillations appear after the main edge is the so called EXAFS. Analysis of EXAFS involves several steps.



a b

c d

e f

Figure 2: Extended X ray Absorption Fine Structure (EXAFS) data analysis steps.

a. Raw data b. Edge normalized data c. Back ground subtracted data

d. Extracted EXAFS data e. Exafs data transformed to K space

f. Fourier transformed data

First step is the edge normalization. That is subtraction of part of the absorption spectrum due to other atoms of the sample and other electron shells of the absorbing atom. This is accomplished by fitting a function to the pre edge region and extrapolating the fit over the entire EXAFS region, and subtracting it from the data. After the edge normalization background subtraction were done by fitting smooth spline function through data above the edge to find absorption coefficient per atom. Background subtracted spectrum is shown in figure 2(c). Then as shown in figure 2 (d) only region with EXAFS was selected. After that energy in the X axis changed to wave number k as shown in 2(e). Then Fourier transformation of the data result in radial distribution function as shown in the figure 2(f). Peaks in the figure 2(f) represent shells of atoms around central iron atom. For quantitative analysis of number of near neighbor atoms and type of near neighbor atoms each peak shown in radial distribution function, figure 2(f), can be back transformed to k space and fitted to EXAFS function. This curve fitting part is not shown here.

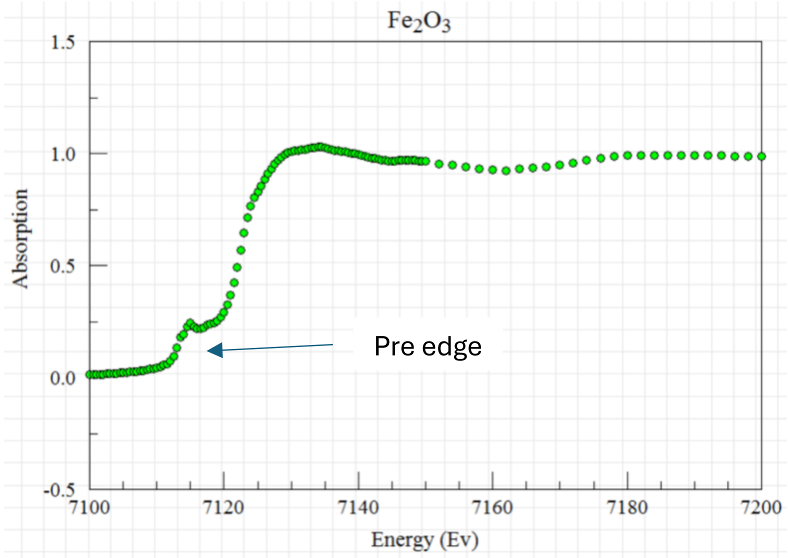


Figure 3: X ray absorption near edge spectrum of standard iron oxide-Fe_2O_3.

X ray absorption near edge region (XANES) of iron oxide standard is shown here. Analysis of pre edge feature shown here get an idea about Fe-O bonding of the sample[7]. Expanded pre-edge data is shown in the figure 4(a). To isolate pre-edge from the main edge, a function is fitted to main absorption edge and subtracted from the original data. After that Gaussian function is fitted to subtracted data as shown in the figure 4(b). This procedure was done for all samples. In this case we studied iron in a carrot plant. Several regions of a carrot plant, leaves, stem and the root, were selected. Dried powder samples were used in the experiment.

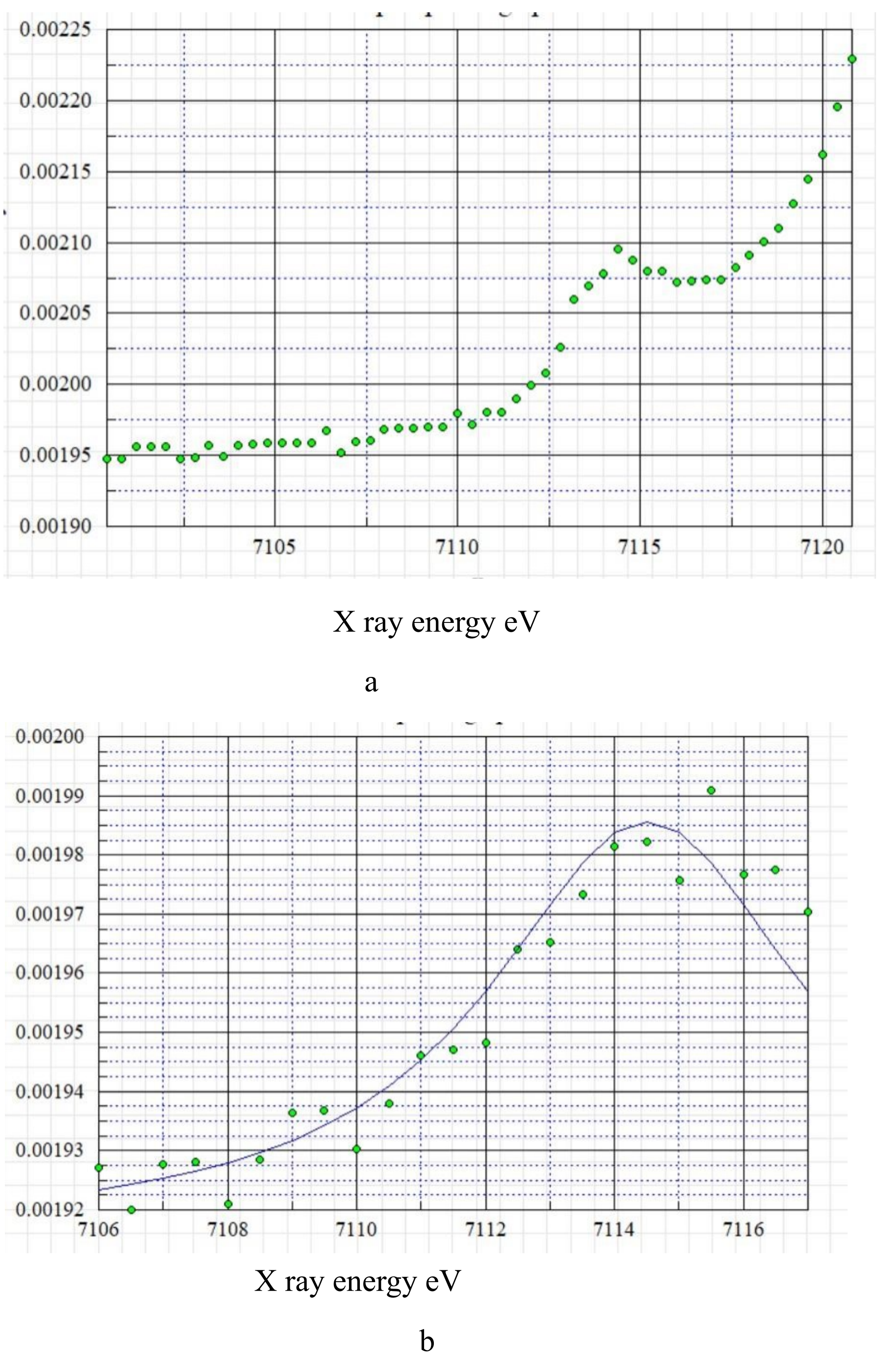


Figure 4:

a. Isolated pre-edge data b. pre edge data and Gaussian fit

Sample	Main edge Intensity	Pre-edge intensity	Normalized pre-edge intensity	% of iron bonded to oxygen
Fe_2O_3	92	24	0.2609	100
Leaves	1.5	0.049	0.0327	12.5
Stem	1.69	0.069	0.0408	15.6
Root	1.79	0.062	0.0346	13.3

Table 1: Pre edge feature analysis results of different regions of a carrot plant

The results of pre-edge feature analysis is shown in the Table 1. Main edge intensity is proportional to the amount of iron in samples and pre edge intensity is proportional to the amount of iron with oxygen as a near neighbor. Once pre-edge intensity is normalized to main edge intensity we can get an idea about Fe-O bonding of samples. In case of Fe_2O_3 all iron atoms octahedrally surrounded by six oxygen atoms. This is most symmetric case which results in least pre edge intensity. But normalized pre-edge intensity of all samples show much smaller values than iron oxide. This indicates out of all iron atoms in samples only small percentage is surrounded by oxygen atoms. Last column of Table 1 shows the amount of iron surrounded by oxygen in different regions of a carrot plant.

Conclusion:

Analysis of X ray absorption data, including EXAFS and pre-edge regions, is a tedious task. But our community college research students were able to perform analysis task systematically and extract valuable information. For them it is a rewarding experience and carry it through their future. In this case analysis of pre-edge region of X ray absorption spectrum of different regions of a carrot plant yield information of Fe-O bonding. According to results leaves have least amount of iron with oxygen as a near neighbor. Rest of the iron not directly bonded to oxygen.

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