Study of microstructure of iron species in plants using X-ray absorption spectroscopy

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Abstract—The X-ray absorption spectroscopy including Extended X ray Absorption Fine Structure (EXAFS) , X ray Absorption Near Edge Structure (XANES) and X-ray absorption near edge and pre edge feature is used to analyze the nature and concentration of iron in plants, spinach and parsley. Primary data was collected at Cornell High Energy Synchrotron Source. Data analyses were done by community college students. EXAFS data analysis process include edge normalization, back ground subtraction, transformation to k space from energy, Fourier transformation, back transform of selected peaks, and curve fitting to identify type and number of near neighbor atoms. X ray absorption pre=edge feature, which appears as very small absorption peak before the main peak, is used to study iron-oxygen bonding and asymmetry of iron compounds. Pre edge data analysis include extraction of the pre-edge from main absorption spectrum, normalization to main edge height, and Lorentzian fit to back ground subtracted data. X-ray absorption data from spinach and parsley, as well as several iron supplements and the soil of which plants were grown was analyzed. The preliminary data analysis pre edge feature yields two forms of iron in both plants. One form has oxygen as near neighbor atoms and the other without oxygen

Keywords—X ray; XANES; pre-edge; iron;

I. INTRODUCTION

Iron is vital to all life, for transporting oxygen and production of energy. For plants, Iron is an essential micronutrient. By understanding its distribution in plants, it is crucial for understanding nutrition, agriculture, environmental monitoring, food safety and human health. Humans attempt to get the necessary levels of iron in their diet through vegetables and meat. Although vegetables contain iron, it is non-heme form as opposed to the heme iron found in meat. Non-heme iron is more difficult to absorb compared to heme iron[1]. Iron absorption mechanism by human body is unclear[2]. Study by Lynch SR, and Cook JD indicates Vitamin C enhances the absorption of non-heme iron due to its iron-chelating and reducing abilities, converting ferric iron to ferrous iron, which is more soluble[3]. Therefore ferrous form is the preferred form for easy absorption. Additionally, compounds containing iron-oxygen bonds are also difficult to absorb by the body. Thus, it is important to know the type and amount of iron found in common plants. This study focus on common plants of Spinacia oleracea (spinach) and Petroselinum crispum(parsley). In order to find the chemical and elemental properties of iron found in plants, a technique known as X ray absorption spectroscopy was applied. This is a type of inner-shell spectroscopy where X ray interacts with core electrons rather than valence electrons. By comparing the X ray absorption spectra valuable information such as charge or valence state and amount of iron present can be found. In addition to two plants, iron in soil in which plants were grown are also studied for comparison.

II. EXPERIMENTAL

All x-ray absorption data were collected at beam line F_3 at Cornell High Energy Synchrotron Source (CHESS). This beam line uses a monochromator with Si (111) crystal to select X-rays of required energy from the white x-ray beam. Intensities of incident and transmitted x-rays were measured using ionization chambers filled with N_2 and fluorescence intensity was measured with solid state detectors. All plant leave samples were dried at 200^0F and grounded to fine powder form. Then equal quantities by mass from each sample mounted in between Kapton tapes with identical sample holders exposing equal areas to incoming x-rays. During the X-ray absorption experiment, the absorption coefficient of all samples was measured as a function of the incoming x-ray energy at the vicinity of the iron absorption edge of 7112 eV.

III. DATA ANALYSIS

Typical X ray absorption spectra consist of absorption coefficient as a function of X ray energy. X ray energies are chosen in range of about 200 eV below the K edge to about

800 eV above the edge. As shown in the Fig. 1, full absorption spectrum can be divided into 3 main regions namely pre-edge feature, X ray absorption near edge structure (XANES) and extended X ray Absorption Fine Structure (EXAFS).During this study pre edge feature and XANES were used to explore iron present in samples. Pre edge feature is the small absorption feature that appears before the main edge. This absorption feature appears when there is a transition of electrons from 1s to 3d orbitals[4]. This transition is forbidden by selection rules but becomes allowed when there is a mixing of iron 3d orbitals and oxygen 2p orbitals. Therefore, this feature appears only in Fe-O compounds. The intensity of the pre-edge feature depends on the symmetry of Fe-O bonds. As seen in Fig.2, the pre-edge feature is very close to the main absorption edge. The analysis of pre-edge requires removal of overlapping part of main absorption edge. In order to isolate the pre-edge for analysis, a function was fitted to the main absorption edge, and it was subtracted from the original data. After the removal of background pre-edge features can be isolated. background By doing so, this background edge was subtracted from the original pre-edge, leaving only the isolated pre-edge. Then intensity of pre-edge
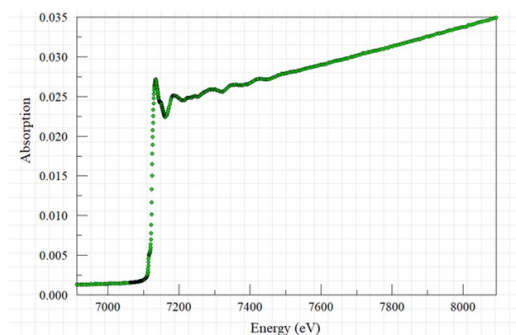
is normalized to the main absorption edge height which depends on the total amount of iron present on the sample. The last step of analysis is to fit isolated pre-edge data to a Gaussian function. Normalized intensity of pre-edge features of plants and soil compared with that of Fe_2O_3. Iron atoms in Fe_2O_3 Octahedrally coordinated with 6 oxygen atoms. Therefore, that is the most symmetrical form of iron-oxygen bonds. As shown in Fig 4, normalized pre-edge intensities of soil and plants are much less than that of iron oxide. From this we can conclude that only some of the iron bonded to oxygen in soil and both plants. Area of these curves proportional to the number of iron atoms bonded to oxygen. In case of iron oxide all of the iron atoms bonded to oxygen. Percentages of iron in different samples bonded to oxygen are shown in table 1.

Fig 3: Pre-edge background removal. A- Original data, B- Fitted function to main absorption edge.

Fig 1: Typical X ray absorption spectrum of iron containing sample.

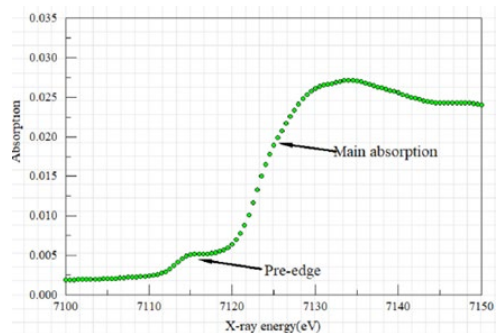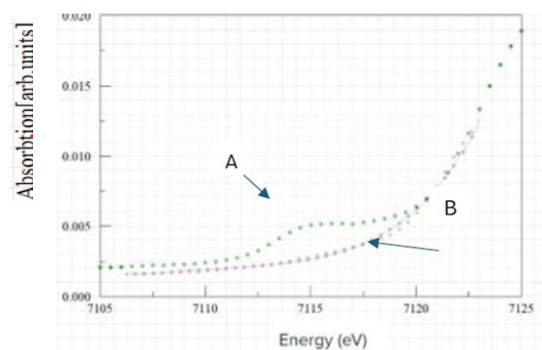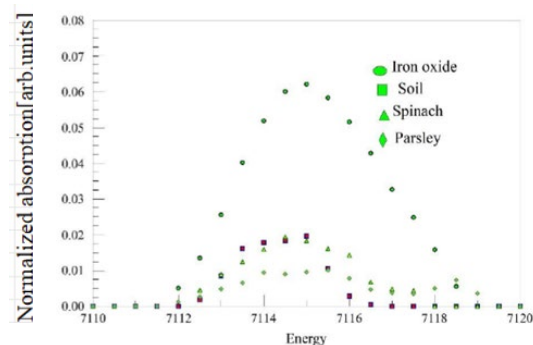Fig.4: Background subtracted and normalized pre-edge features of iron oxide, soil, spinach and parsley.

Fig. 2: X-ray absorption near edge of Fe-O compound showing pre-edge feature and main absorption edge.

Sample	Normalized pre-edge	% of iron bonded to oxygen
Fe_2O_3	0.22	100
Spinach	0.06	27
Soil	0.05	23
Parsley	0.04	20

Table 1: Normalized pre-edge intensities and percentage of iron bonded to oxygen.

IV CONCLUSION

Iron (III) Oxide adopts an octahedral geometry (a symmetrical molecular geometry). Based on the normalized pre-edge intensities of the five samples, conclusions about iron bonded to oxygen in the samples can be made. Since the pre-edge intensities of the plant samples and soil were lower than Iron (III) Oxide's, the compounds in these samples contain fewer iron in form of Iron-Oxygen bonds. Hence, most of the iron in parsley is bound to other elements such as nitrogen and therefore slightly easier to absorb than spinach. Therefore, we can conclude that all leave samples contain two forms of iron, some bonded to oxygen and rest bonded to other elements. The main edge height of spectra depends on the total amount of iron present in samples. From the baseline level proportional to the amount of iron present. Therefore, the Parsley contains a greater amount of iron compared to spinach. . The peak energy (eV) for all five samples are within a similar range. Therefore, the most dominant type of iron found in these samples is Fe3+.

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