S K-edge XAS: Theory and Data Collection
(Scope, Advantages and Pitfalls)

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An XAS edge discontinuity results when a core electron absorbs energy equal to or greater than its binding energy.

Edges are labeled according to the shell the core electron originates from.

X-ray Absorption Edge

- K-edge
- L-edge
- L₂,₃-edges
- Continuum

S K-edge ~2400 eV
S L-edges ~160-230 eV
Cu K-edge ~9000 eV
Cu L-edges ~930 eV
Cu M-edges ~70-120 eV
Fe K-edge ~7000 eV
Fe L-edges ~720 eV
Fe M-edges ~50-100 eV

XAS is an element specific technique

Regions of the XAS Spectra

- rising-edge
- EXAFS
- pre-edge

- Geometric, Electronic Structure
- 1. electronic structure
- 2. spin state
- 3. deviation from centrosymmetry

Normalized Absorption

Energy (eV)
1. Pre-edge feature is dipole-forbidden: 1s to 3d transition
2. At higher energy the peaks are broader, e.g. at 9000 eV (Cu), the natural width is 1.55 eV

The result is an inherently sharper, feature-rich S K-edge spectrum

S in Open Shell Environments

In molecules where the S 3p orbital(s) gains “hole” character, a low-energy pre-edge transition may be observed.
Pre-edge Analysis

The Pre-edge energy position and intensity can be used to determine:

1. Covalency &/or Bond Strength
2. Ligand Field
3. Effective Charge on S

In this Example:

Red is 3 times more intense than Black: Red probably has a stronger Metal-S overlap.

Red pre-edge is higher in energy: Red probably has a stronger ligand field.

Applications of pre-edge:

a) Covalency determination in Electron Transfer Proteins.
b) Ligand-Metal Overlap estimation in systems with non-innocent ligands.
c) Determination of oxidation state of the metal site (Indirect)
d) Determination of oxidation state of S

Effect of Oxidation State

Large energy shifts associated with oxidation state changes

Excellent for fingerprinting & speciation analysis in a sample containing a mixture of S containing species
Differences in Spectral Shape

- Spectral difference are due to 0.02 Å difference in the single bond S-O distances: 1.70 in ECS vs 1.72 in DMS
- Small changes in bonding can lead to large shifts in valence MO energy levels and hence strikingly different spectral shapes.

Complications with Unknowns

- Need some chemical information to perform speciation analysis.
- Or have an extensive database of standards to choose from.
The Facility

Stanford Synchrotron Radiation Lightsource

SSRL Beamline Map

Enter through the back door!

20 pole 2T Wiggler Beamline 4-3

The Experimental Setup

High Energy (>5000 eV)

Tender Energy (2-5 KeV)
The Experimental Setup

Tender Energy (2-5 KeV)

Calibrant paddle

He flight path

Sample

The sample box has a separate He purge source

The Calibration Issue

- No I1 or I2 = No Internal Calibration
- Calibration is achieved by measuring the standard before and after the sample.
- For S, the typically used calibrant is NaSO3 (lowest energy peak at 2472.02 eV)
- Higher error in estimating true energy position

If the goal is to know small energy shift between spectra very accurately- the following method should be used:

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<th>time</th>
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<tr>
<td>LCYST_054.001</td>
<td>12:36:11</td>
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<td>LCYST_054.002</td>
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<td>LCYST_054.003</td>
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<td>LCYST_054.004</td>
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<td>SCALIB_053.001</td>
<td>14:28:10</td>
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</table>

Energy of the peak in your data: 2472.522 eV
The Calibration Issue

Other calibration methods commonly used and associated errors

<table>
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<td>2472.000</td>
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<table>
<thead>
<tr>
<th>Method</th>
<th>Error</th>
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</thead>
<tbody>
<tr>
<td>Interpolation of energy shift between the 2 calibrants and applying a</td>
<td>Artificial broadening of the average spectrum</td>
</tr>
<tr>
<td>linear shift per scan.</td>
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</tr>
<tr>
<td>Using only 1 before-calibration scan and applying the energy shift to</td>
<td>Error in energy position.</td>
</tr>
<tr>
<td>the first scan of data.</td>
<td></td>
</tr>
<tr>
<td>Using an average of the before and after calibrant and applying it to</td>
<td>Error in energy position if large variations in mono energy.</td>
</tr>
<tr>
<td>each spectrum.</td>
<td></td>
</tr>
</tbody>
</table>

Sample Considerations

- Amorphous solid samples ground to a very small particle size.  
  Conc > 100 ppm.

- Homogeneous solution samples.  
  Conc > 5mM in S, 200 uL

- Whole samples, e.g: Leaves, wood, soil, etc. Specific sections of the sample can be targeted to see differences in speciation.

- Solid samples with high S concentrations should be applied as a thin layer.

- Solution samples have to be placed within thin x-ray transparent windows-  
  (4-5um polypropylene or other S-free film)

- For quantitative analysis : Homogenous S site structure

- For speciation analysis : The sample and the standards should be measured  
  under the same experimental condition.
Data Processing

Fluorescence data from beamline 4-3. Red line mimics the background. Post edge should pass through 1.00. Pre-edge should pass through 0.00.

Our favourite softwares are often slightly off with normalization. Recheck manually in excel or other graphing software.

Self Absorption

Self Absorption is observed in a spectrum of too concentrated a sample due to variations in penetration depth that affects the fluorescence yield. Concentrated samples can only be measured reliably with fluorescence where the sample thickness is comparable to or smaller than 1/e absorption depth.
Data Analysis

- Linear Combination Analysis (DATFIT)
- Peak Deconvolution Analysis (EDG_FIT, PEAKFIT)
- EXAFS Analysis
- Structure Determination using Near-edge Analysis (MXAN)
- DFT calculation of electronic structure and simulation of spectra (STOBE)
- DFT and TD-DFT methods to simulate XAS spectra (ORCA, Gaussian)

Linear Combination Analysis

- Program: DATFIT (Part of EXAFSPAK) or other peak fitting software
- Data: 2 Column data file. (Energy and background subtracted normalized data)
- Standards: A complete set of standard data on species expected to be similar to those in the unknown mixture

Range of oxidation states?
Are data self absorbed?
Are so many peaks expected?
**Linear Combination Analysis**

- Perform several fits by sequentially increasing number of standards.
- A best fit:
  - has least number of standards
  - fit over the entire energy range
  - makes chemical sense
- E.S.D: 3 times the value printed in DATFIT (if fit is very good).

**DATFIT Interface**

- $R^2 = 0.99 \times 10^{-1}$
- $R^2 = 2.4 \times 10^{-2}$
- $R^2 = 3.9 \times 10^{-3}$
- $R^2 = 1.1 \times 10^{-5}$

**Considerations**

- Data and standards should be free of self absorption.
- Data and standards should be normalized to 1.00.
- Data and standards should have very near flat pre-edges and post-edges.
- Always have your chemists hat on when using linear combination analysis.
**Peak Deconvolution Analysis**

- **Program:** Edg_Fit (Part of EXAFSPAK) or other peak fitting software
- **Data:** 2 Column data file. (Energy and background subtracted normalized data)
- **Information:** Some idea about the origin of the different spectral features

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1 or 2 pre-edge features?  

Edge features/contaminant?

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**Peak Deconvolution Analysis**

- **Edg_Fit Interface**

- Perform several fits by varying:
  a) # of peaks  
  b) energy range  
  c) weight of second derivative
- **A best fit:**
  a) has least number of unjustified peaks  
  b) fit over a reasonable eV range  
  c) a good fit to the second derivative.
- **Error bar:**
  Is obtained by estimating standard deviation among chosen best fits.
Considerations

- Data with strange backgrounds require special manipulation to obtain flat pre-edges & post-edges. Errors in normalization which can affect peak area.

- Using black box normalization methods. Differences in normalization in different data sets.

- Use 2nd derivative fitting method to separate overlaying peaks.

Acknowledgements

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Thank You

Please direct additional questions to: ritis@slac.stanford.edu