8. XAFS Measurements and Errors
XAFS Measurements

X-ray detectors:
- Ionization chamber detectors
- Solid state detectors
- Electron yield detectors
- Scintillation detectors
Transmission Measurement

Total absorption is given as

\[ I = I_0 e^{-\mu x} \]

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

Important points:
1. Uniform thickness.
2. Absorption edge step size is about 0.3 – 0.9.
3. The sample should fully cover the beam cross section.
4. Particle size should be uniform and less than 2~3 absorption length.
X-ray Absorption Length
XAFS Transmission Measurement

\[ \mu t = \ln\left(\frac{I_0}{I}\right), \mu(E) = \mu_0[1 + \chi(E)] \]

\[ \chi(k) = \frac{\mu(k)}{\mu_0} - 1 \]

EXAFS, \( \chi \), is obtained without depending on the sample thickness.
The x-ray absorption can be controlled by gas in the ionization chamber. In general, He, N₂, Ar or a mixed gas of any two is used.

To avoid statistical error, the total x-ray counts should be more than 100,000. Than the error is less than 0.3 % of the signal.
Gas Absorption Calculation

http://s20.xor.aps.anl.gov/cgi-bin/gasmix_cgi.pl

Gas Absorption Calculations

This form calculates the absorption of a gas over a given path length, or the mixture of two gases required to produce a specified absorption. Absorption data from McMaster et al., 1969, as retold in McBook by Matt Newville.

v2 6/97 DB

X-ray energy (required): 9 keV Path length (required): 20 cm

Absorption: 15 % (Required if 2nd gas is specified, ignored otherwise)

First Gas: Ar  Second Gas (optional): N2

Total pressure (optional): Torr

(The defaults to 760.0)

15.0% absorption isn’t possible with the given combination of gases and pressure. The closest possibility is 10.9% absorption using pure N2.

The required mixture for 15.0% absorption is:
1.88% Ar (13.4 torr)
98.22% N2 (746.6 torr).
Important points:
1. Sample thickness of the region where x-rays hit should be uniform or less than couple of absorption lengths.
2. Take enough fluorescence counts, more than several tens of thousands.
3. Avoid background noisy as much as possible.
Principle of Fluorescence

\[ \Pr \text{sample} \]

\[ \theta_i, \theta_f \]

\[ t, z, dz \]

\[ I_0, E, E_f, I_r \]

\[ \text{Conduction state} \]

\[ \text{M-edges} \]

\[ 2 \text{P}_{3/2}, 2 \text{P}_{1/2} \]

\[ L_{III}, L_{II}, L_I \]

\[ K\text{-edge} \]

\[ \kappa_{a1}, \kappa_{a2}, \kappa_\beta \]
Theory of Fluorescence XAFS

\[ I_f = \int dI_f (z) = I_0 \varepsilon (E) \mu (E) \int_0^t e^{-\left[ \frac{\mu_T (E)}{\sin \theta_i} + \frac{\mu_T (E_f)}{\sin \theta_f} \right] z} \, dz / \sin \theta_i \]

\[ I_f = \frac{I_0 \varepsilon (E) \mu (E)}{\mu_T (E) + \mu_T (E_f) \sin \theta_i / \sin \theta_f} \left[ 1 - e^{-\left[ \frac{\mu_T (E)}{\sin \theta_i} + \frac{\mu_T (E_f)}{\sin \theta_f} \right] t} \right] \]

\( \mu_T (E) = \mu (E) + \mu_B (E) \), where \( \mu_B (E) \) is the absorption coefficient of the x-rays of which energy is not \( E \). In general, \( \mu (E) \gg \mu_T (E_f) \) and \( \mu (E) \gg \mu_B (E) \).

\[ \frac{I_f}{I_0} = \varepsilon (E) \{ 1 - [ 1 - \frac{\mu (E) t}{\sin \theta_i} ] \} = \varepsilon (E) \frac{\mu (E) t}{\sin \theta_i} \]

For a small \( t / \sin \theta_i \), after normalizing the data, \( \mu (E) = I_f / I_0 \)

Fluorescence and Transmission XAFS

In general transmission XAFS measurements give better information than fluorescence XAFS does. However, sometimes we cannot make transmission XAFS measurements due to the specimens, thin films on TiO$_2$. 

![Graph showing Fluorescence and Transmission XAFS](image)
Fluorescence XAFS (SABCOR)

If $t / \sin \theta_i$ is larger than $2 \sim 3$ absorption length ($1/\mu=1$ absorption length), self absorption may distort the $\chi$ and $\mu(E) = I_f / I_0$ is no longer good. Therefore, the $\chi$ and $\mu(E)$ should be properly corrected.

EXAFS self-absorption correction software was developed by Corwin Booth. [http://lise.lbl.gov/RSXAP/index.html](http://lise.lbl.gov/RSXAP/index.html)

Fluorescence XAFS (FLUO)

Self-absorption correction software of XANES fluorescence was developed by Daniel Haskel.

X-ray Self-absorption Corrections in Athena
XANES Self-Absorption Correction (FLUO)

Algorithm:
- XANES (Flux)
- EXAFS (Gooth)
- EXAFS (Troger)
- EXAFS (Atoms)

Group: pnc_06.03.0047
Element: Cu
Edge: K
Formula: Cu
Angle in: 45°
Angle out: 45°
Thickness: 3 μm

Feedback:
Edge energy = 8966.02214301
The dominant fluorescence line is Kalpha1 (K-L3)
Fluorescence energy = 8046.30

element  number
----------  ----------
Cu  1.000

Document section: self absorption corrections

Return to the main window

Doing Flu correction... done!
EXAFS Self-Absorption Correction (SABCOR)

**Algorithm**
- XANES (Fluo)
- EXAFS (Booth)
- EXAFS (Trogi)
- EXAFS (Atoms)

**Group**
- pnc_06_03.0047

**Element**
- Cu

**Edge**
- K

**Formula**
- Cu

**Angle in**
- 45° ± 1°

**Angle out**
- 45° ± 1°

**Thicknss**
- 3 μm

**Feedback**

Edge energy = 8985.02214381

The dominant fluorescence line is Kalphal (K-L3) fluorescence energy = 6046.30

**Element**

<table>
<thead>
<tr>
<th>Element</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>1000</td>
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</tbody>
</table>

You are in the thin sample regime.
Using the nearly exact expression.

**Graphs**

- pnc_06_03.0047
- x(k)
- SA corrected

**Plot data and correction**

- Plot information depth

**Make corrected data group**

**Document section: self absorption corrections**

**Return to the main window**

**Doing Booth/Bridges correction (thin sample regime) ... done!**
Errors in XAFS

1. **Statistical error:** Counting x-rays by a detector can be treated as a Poisson distribution. For the Poisson distribution, the uncertainty is $\sqrt{N}$. Therefore, the portion of the error in a signal is $1/\sqrt{N}$.

To reduce the statistical error, one should take the counts as much as possible. In general $I_0$ is larger than $10^6$ (the incident x-rays of a synchrotron source are $10^{12} \sim 10^{14}$ photons/sec.), and $I_t$ or $I_f$ is more than $10^5$ photons/sec.

Since EXAFS data are analyzed in $r$-space after the absorption data are taken as a function of the incident x-ray energy, the statistical error cannot be counted in the analysis. The Fourier transformed data with the error will be further distorted.

2. **Systematic error:** this error is occurring from equipments and/or other environments. Systematic error can be a background noisy in EXAFS signal in $r$-space. However, it is still difficult to eliminate this error.

3. **Random error:** unexpected circumstance curses the random noisy. To reduce the random noisy, do not change experimental setting during a scan. Take several sans and compared them if there is any difference among scans.
Remind Points

1. Sample thickness should be uniform (less than 1 absorption length)
2. Take enough counts (more than 100,000 counts). If count is low, take many scans and average over $\chi$ (EXAFS) values in k-space.
3. Measure a standard sample as a counterpart.
4. Try to avoid any error during measurements as much as possible because the error cannot be distinguished from signals in $r$-space (scan more than three times).
5. In XAFS measurement set up, the x-ray should be hit the region with a uniform thickness, not with a maximum intensity.
6. Very carefully analyze the XAFS data.
Find further information of XAFS at

Korean XAFS Society homepage: http://www.xafs.or.kr

The next XAFS School may be held in January, 2015.

In order to obtain the information of the next XAFS School, check the Korean XAFS homepage in Dec. 2014.