

Quick Instruction

For EXAFS Data Analysis

Using WinXAS, FEFF 7 and ATOMS Programs

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Last updated: December 2002

Step 1 : Double click on the WinXAS97 icon.

Step 2: Click on File in toolbar, and go to Open.

In Open dialog box, via "Look in", go to the file directory:
C:\WinXAS\data\ and select the file *.dat ; click Open

Step 3: The horizontal axis is energy (eV) and the vertical axis is absorption
($\log I_0/I_1$ or I_f/I_0).

Click on Edit in toolbar, and go to Modify Abscissa...

In the "multiply with factor" box, write "0.001" while in the
"Sort- and exchange modulus" section, "with Y axis" is pointed.

Click on Apply and then, OK. The photon energy unit is changed to KeV now.

Step 4: Click on XAFS in toolbar and go to Background correction, followed by
Polynomial Fit. In the "degree" box, write "1".

Now you have to choose two points in the pre-edge region (not too close to
the edge) by clicking on them. The position of these two points are appeared
in the "left border" and "right border" boxes.

Click on Fit. The blue line shows the background absorption in the pre-edge
region. Click OK. The background is subtracted from the whole of spectrum,
and you can see a smooth line in pre-edge area at $\mu=0$. Also, the Y-axis unit
is absorption unit [a.u.] now. Here, you can estimate the edge jump.

For comparison, just Click on the window. Two windows will appear which
show the sequence of the treatment. Click and Drag the right window over the
left and look at the difference before and after background correction. Continue
the following steps on the corrected spectrum (window No. 2).

Step 5: Click on XAFS in toolbar and go to Normalization...

In this step, we are going to normalize the spectrum and eliminate the effect of
sample thickness, concentration or other variable parameters in the absorption.
Try to choose two points in EXAFS region, where it seems as a smooth line.

Click on Fit. The horizontal blue line corresponds to the unit "1" in the
normalized spectrum. Click OK.

The Y-axis unit has changed to "normalized absorption [a.u.]".

For comparison, Click on current window (No.3). Three windows will
appear. Click and Drag window No. 3 over No. 2 and see the difference.

1	2
3	4

Step 6: Click on XAFS in toolbar and go to Set E_0 ... and then, select "Set E_0 ".

E_0 or "edge energy" corresponds to the threshold energy of absorbant atom.
Ask the E_0 value; remember that the energy unit must be in KeV.

Click OK.

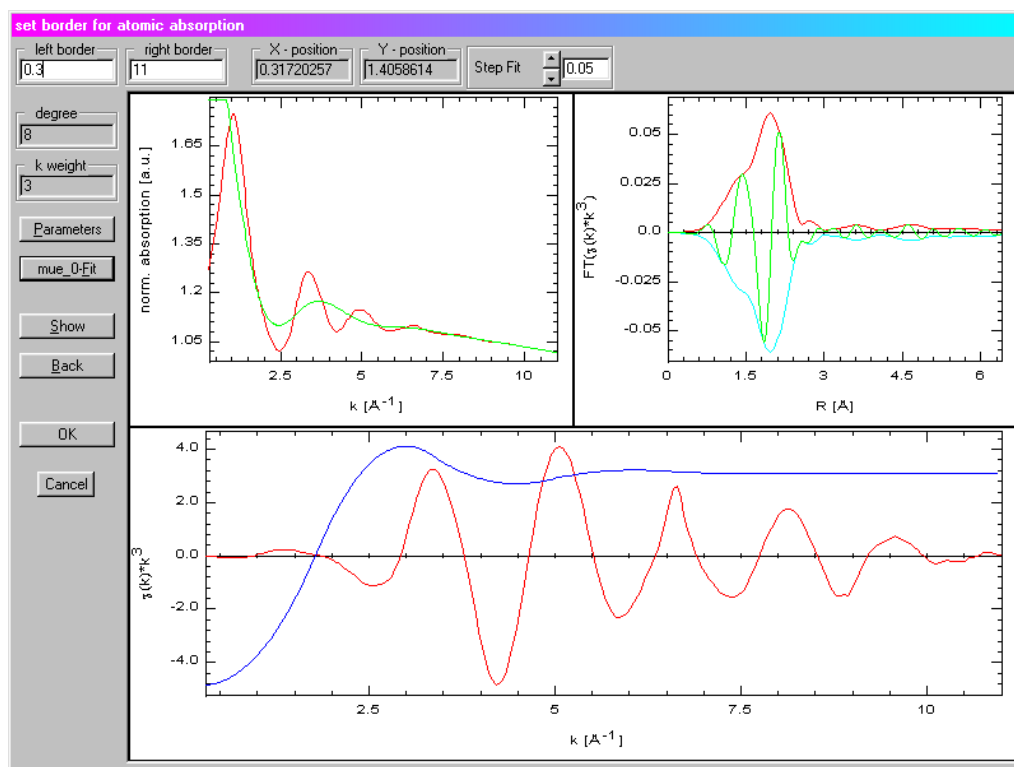
- Step 7: Click on XAFS in toolbar and go to Conversion.
A dialog box will appear to reconfirm the threshold energy value. Click OK.
Now X-axis represents the photoelectron kinetic energy, k (\AA^{-1}).
Remember that at $k=0$, the energy of the incident photon E , is equal to threshold energy of absorbant atom, E_0 .

$$k = \{2m_e(E-E_0)/\hbar\}^{1/2} = [0.262 (E-E_0)]^{1/2}$$

- Step 8: Click on File and Save File as “*_co.dat “ in the directory:
C:\WinXAS\data\

- Step 9: Click on XAFS and go to μ_0 -Fit; then choose cubic spline-fit ...
At this very critical stage, we are going to define the absorption of isolated absorbant atom, μ_0 , as a smooth line. This stage is usually called *Splining*.
Remember that when this μ_0 is subtracted from the total absorption, μ , the residual part is EXAFS oscillation.
The smooth line or *spline* is defined with a few points.
Start with “No. of spline points” = 7 or 8, and “k weight” = 2 or 3; Click OK.
Then you have to define two borders for spline; the program will put those spline points in this area.

Try the left border with $k=$ “1.00” (it should never be a negative value) and right border at the highest k that the data are collected. Click on “ μ_0 -Fit”.



The upper-left window shows the zero-weighted absorption curve (red) and spline or atomic absorption (μ_0 , green). The lower window shows the extracted EXAFS wave [$k^3 \cdot \chi(k)$, red], when the spline is subtracted from the total absorption. The blue curve is the 1st derivative of spline function.

The spline (blue curve) should be as smooth as possible, and should not introduce any extra feature in the EXAFS oscillation.

The upper-right window shows the preliminary Fourier-transform of the EXAFS wave.

Try different splines by changing the borders and/or parameters.

When you found the best $\mu(0)$ -fit, Click OK.

Step 10: Now the EXAFS wave is extracted and it's better to save this data.

Click on XAFS in toolbar and go to k-Weighting.

Adjust the k-weight to zero; Click OK.

This curve is zero-weighted EXAFS oscillation; $\chi(k)$.

Click on File and Save File as “*_chi.dat”.

The following steps are performed on this file.

Close all open windows.

* Go to FEFF calculation section, and after that continue with the following steps.

Step 11: Open the “*_chi.dat” file.

Click on XAFS in toolbar and go to k-Weighting.

We usually work on k^2 - or k^3 -weighted EXAFS. (Compare the difference!)

So write 2 or 3 in the dialog box; Click OK.

Step 12: Fourier-Transformation;

EXAFS oscillation can be represented as the sum of sine waves:

$$k^n \cdot \chi(k) = k^{n-1} \sum A_i(k) \sin [2kR_i + \varphi_i(k)]$$

in which $\chi(k)$ is zero-weighted EXAFS oscillation.

Fourier-transform helps to separate the frequencies.

Click on XAFS in toolbar and go to Fourier transformation

Select “Bessel” as window function.

To define the window border, Click on G (graphic).

Then Click on two points of oscillation curve.

Try to choose the left border between $2 < k < 3 \text{ \AA}^{-1}$, depend on the amount of multiple scattering.

Click on E (show window). The blue line is window function, and the green curve shows the effect of the window function on the experimental EXAFS oscillation (red); it reduces truncations effects in Fourier-transform.

Click EXIT.

Click on K (show k * FT). Here, you see the effect of different k-weighting on the resulting FT. (Window No. 4 shows their comparison.) Click Return.

Click OK.

The resulting peaks in FT are related to the distances between absorber and backscatterers. However, these peaks are not corrected for phase shift (φ_i) and therefore, do not show the real distances. The Fourier-transform here, is *not* a true “Radial Distribution Function” (RDF).

The pre-peaks at low R-values ($< \sim 1.2 \text{ \AA}$) are artifacts due to problems like choosing a bad spline; they should not be considered as real peaks.

Step 13: * Skip this step for k-space fitting.

For R-space-fitting, Click on Edit and go to Show FT Magnitude.

Then continue the fitting as Step 15.

Step 14: Fourier-Filtering;

If you are interested in a limited range of absorber-scatterer distances, and if you do not want to include high order multiple scattering paths, you can filter out the major FT peaks for k-space fitting.

For Fourier back-transformation, Click on XAFS and go to Fourier-transform. Click on G to define the filtering region.

Select the left and right borders. Click OK.

Click OK. The result is a zero-weighted oscillation.

Click on XAFS and go to k-Weighting.

Weigh the oscillation with a factor of 2 or 3. Click OK.

Step 15: Fitting the data;

Now it is the time to extract the information such as distance (R), coordination number (N), temperature factor (σ^2) and also, type of coordinating atom from the EXAFS.

For this purpose, we can simulate a theoretical EXAFS for an assumed structural model compound, which contains similar absorber and back-scatterer atoms. Then we can compare the experimental EXAFS with the theoretical one. FEFF program is extremely useful for such theoretical calculations.

* After doing the FEFF calculations, return to this section and continue.

Click on XAFS and go to EXAFS-Fit ...

On the right side of dialog box, Click on FEFF-Fit to select scattering paths.

In "Look in" section, go to the directory: C:\Feff\data\ ; then Click on your compound and select the "files.dat" file. Click Open.

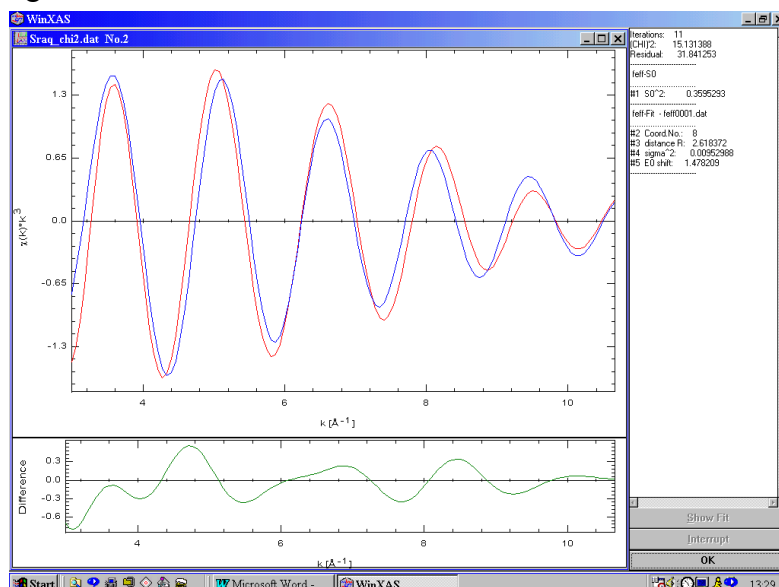
At the beginning, choose one or two of the most probable scattering paths (considering their ratio) by clicking on them. Click OK.

Again, Click OK to close the EXAFS-Fit window.

In order to limit the number of parameters, which have to be refined, it is better to fix or correlate a few of them. For example, if you know the coordination number, write it in "Coord. No." box and then, Click on "Fixed" in Flags section.

It is better to start the refinement process with reasonable values rather than 0. Therefore, for example, start the σ^2 with 0.005 and E0 shift = 3 or 4. Click OK.

After the first refinement, you can approximately guess which values to put for σ^2 and E0 shift for next time.



The red curve is the experimental $\chi(k)$ and the blue curve is the theoretical $\chi(k)$. The green curve is the residual. Click OK. The fit results can be seen in the RESULTS window.

(If you have done number of fittings and you want to have all results, Click the right mouse button in the Result window and select HISTORY).

Fit results: Residuals and χ^2 are calculated from

$$(\text{CHI})^2 \text{ (minimized parameter in fit)} : \chi^2 = \frac{1}{\sigma^2} \cdot \sum_{i=1}^N [y_{\text{exp}}(i) - y_{\text{theo}}(i)]^2$$

$$\text{Residual [\%]} = \frac{\sum_{i=1}^N [y_{\text{exp}}(i) - y_{\text{theo}}(i)]}{\sum_{i=1}^N [y_{\text{exp}}(i)]}$$

in which y_{exp} and y_{theo} are the experimental and theoretical data points, N the number of data points and σ is an estimate for the experimental error.

Standard Deviation and Goodness of Fit

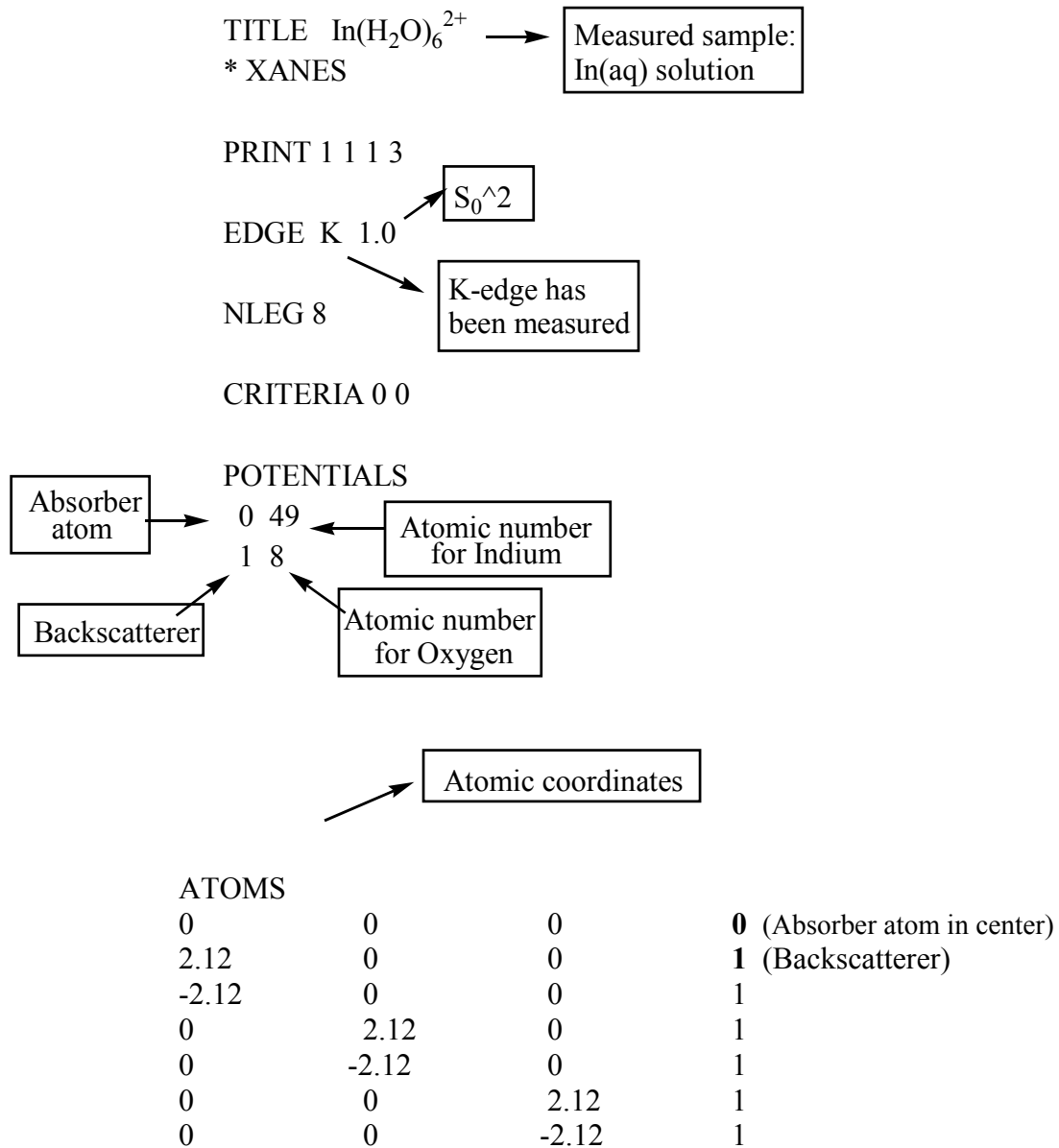
According to T. Ressler, “The fit errors in WinXAS program are calculated from the covariance matrix of the Levenberg-Marquard least-squares algorithm. To calculate this matrix and, hence, meaningful errors in the XAFS parameters, an *experimental error* is needed that reflects the overall error in the XAFS data. However, this *experimental error* is sort of fuzzy (in WinXAS an error estimate can be entered in the ‘Enter Parameters’ dialog box). In this program, the *experimental error* is estimated from the noise in the data file. For XAFS fits in k-space it is estimated from the noise at high k of the zero-weighted $\chi(k)$, and for XAFS fits in R-space it is estimated from the corresponding $\chi(k)$.

However, the *experimental error* is more than just data noise; it also includes systematic errors of the experiment, data reduction, extraction of phases and amplitudes or theoretical calculations. The later is much harder to estimate. So far there are no consistent recommendation on how to extract a meaningful experimental error from the data.

As for ‘goodness of fit’ values, the R value (Res.) in WinXAS does not depend on the *experimental error* but only reflects the deviation of the theoretical XAFS curve from the experimental one. The χ^2 on the other hand, is calculated from the squared difference between theory and experiment divided by the *experimental error*.

To summarize, the errors obtained in the program is estimated from the noise in the data. Glitches at high k -values could increase the apparent estimated error. However, several sources of systematic errors are also present. It is useful to estimate the influence of such errors from the variation of the parameter values from refinement at different conditions.

An Example for FEFF input File (Feff.inp)



Note: Remember to save the feff input file as “Text Only”; like Inaq.txt.
It must be saved in same directory as Feff7.exe file.
Then change its name and extension as: “**feff.inp**”
and run the Feff7.exe, just by double-clicking on its icon.

Feff program will produce number of files:

chi.dat crit.dat files.dat list.dat log.dat misc.dat paths.dat potph.dat
feff0001.dat (feff0002.dat; etc)

files.dat and list.dat contain a list of possible scatterings paths with *amplitude ratio* (the possibility with which that scattering path happens) higher than 4%.
paths.dat shows that between which atoms these scatterings happen.

For least-square curve-fitting procedure using WinXAS program, we can select different scattering paths (feff000*.dat files) and combine their amplitude functions and phase shifts, in order to find the best fit. Better to choose those with higher *amplitude ratio* first!

Example for ATOMS input File (ATOMS.inp)

Title $[\text{Sr}(\text{H}_2\text{O})_8]^{2+}$ solid \longrightarrow solid sample with known crystalline structure
 space P 4/N C C \longrightarrow space group
 ! Tetragonal \longrightarrow crystal system
 core Sr \longrightarrow Absorber
 r_{max} 3.0 \longrightarrow In resulting feff.inp file, ATOMS will define the coordinates of all atoms in unit cell, with maximum distance from the core (Sr) equal to 3 Å.
 a=9.0168 }
 b=9.0168 } unit cell parameters
 c=11.6090 }
 alpha=90 }
 beta=90 }
 gamma=90 }
 atom

! At.type	x	y	z	tag
Sr	0.75	0.25	0.25	Sr
O	0.75	0.75	0.0942	O1
O	0.75	0.75	0.3409	O2
O	0.6566	0.0273	0.1257	O3
O	0.5289	0.3462	0.1233	O4

 Atomic coordinates, available from the crystallography data

Note: Similar to feff.inp file, save the ATOMS input file as “Text only”, **.txt**.
 Save it in same directory as ATOMS.exe file.
 Then change its name and extension as: “**ATOMS.inp**”. Run ATOMS program, just by double-clicking on its icon.

ATOMS program will make a **feff.inp** file.
 Transfer this *feff.inp* file to the same directory as Feff7.exe.

Note: Before running the Feff program, Open the feff.inp by double-clicking on it.
 In the “PRINT” section, we have: 1 1 1 0
 Change it to: 1 1 1 3
 And then save the file.
 Now run the Feff program.

The feff.inp file produced by ATOMS program for solid $[\text{Sr}(\text{OH}_2)_8]^{2+}$:

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* This feff.inp file generated by ATOMS, version 2.46b
* ATOMS written by Bruce Ravel and copyright of The Univ. of
Washington, 1994

* Space group p 4/n c c is commonly referenced with alternative
origins.
* If you are displeased with the resulting atom list, shift all
atomic
* coordinates in atom.inp by (-.25,.25,0) and run atoms again.

* -- * -- * -- * -- * -- * -- * -- * -- * -- * -- * -- * -- * -- * -- * --
- *
*          total mu =          67.5 cm^-1, delta mu =          55.7 cm^-1
*          specific gravity = 1.743, cluster contains          9 atoms.
* -- * -- * -- * -- * -- * -- * -- * -- * -- * -- * -- * -- * -- * -- * --
- *
*          mcmaster corrections:  .00028 ang^2 and  .163E-06 ang^4
* -- * -- * -- * -- * -- * -- * -- * -- * -- * -- * -- * -- * -- * -- * --
- *

TITLE    [Sr(H2O)8]2+ crystal

HOLE 1    1.0      Sr K edge  ( 16.105 keV), s0^2=1.0

*          mphase,mpath,mfeff,mchi
CONTROL   1      1      1      1
PRINT     1      1      1      0 →(Change it to 3)

RMAX      2.62496

*CRITERIA    curved    plane
*DEBYE       temp     debye-temp
*NLEG        8

POTENTIALS
*   ipot    z    label
*       0    38    Sr
*       1     8     O

ATOMS
.00000      .00000      .00000      0    Sr          .00000
.84217      2.00804     -1.44300     1    O3          2.61223
-2.00804     -.84217      1.44300     1    O3          2.61223
-.84217     -2.00804     -1.44300     1    O3          2.61223
2.00804      .84217      1.44300     1    O3          2.61223
-1.99361     .86742      -1.47086     1    O4          2.62495
.86742     -1.99361     1.47086     1    O4          2.62495
-.86742     1.99361     1.47086     1    O4          2.62495
1.99361     -.86742     -1.47086     1    O4          2.62495

END

```