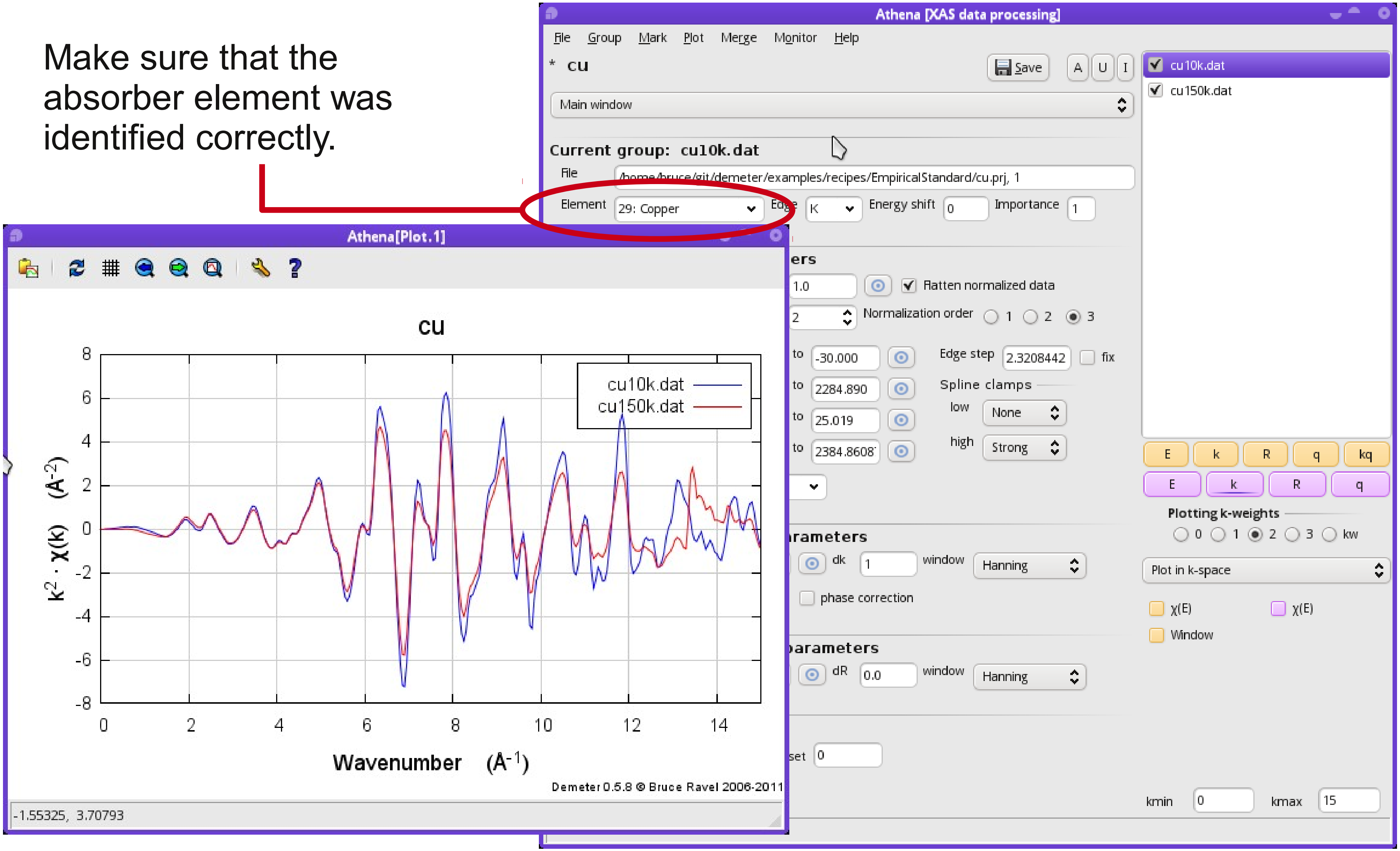
Using Empirical Standards in Demeter

This demonstration uses copper data at 10 K and 150 K. The data is in an Athena project file that comes with the Demeter source code or can be found at github at the URL below.

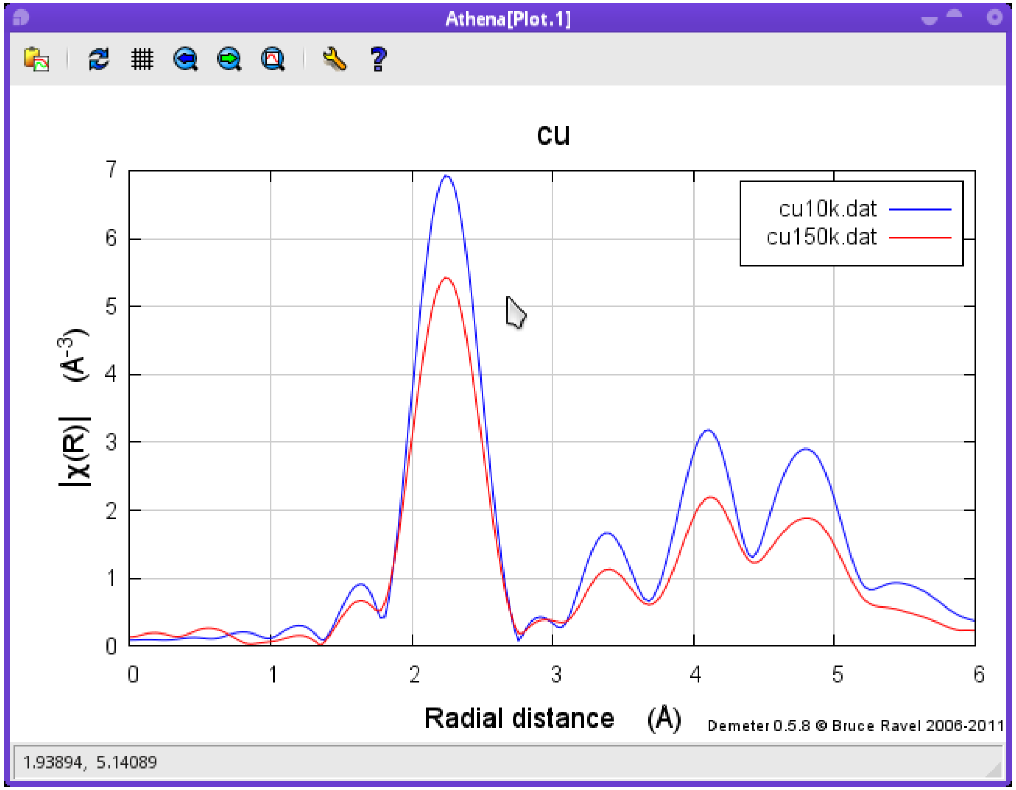
https://github.com/bruceravel/demeter/tree/master/examples/recipes/EmpiricalStandard/cu.prj

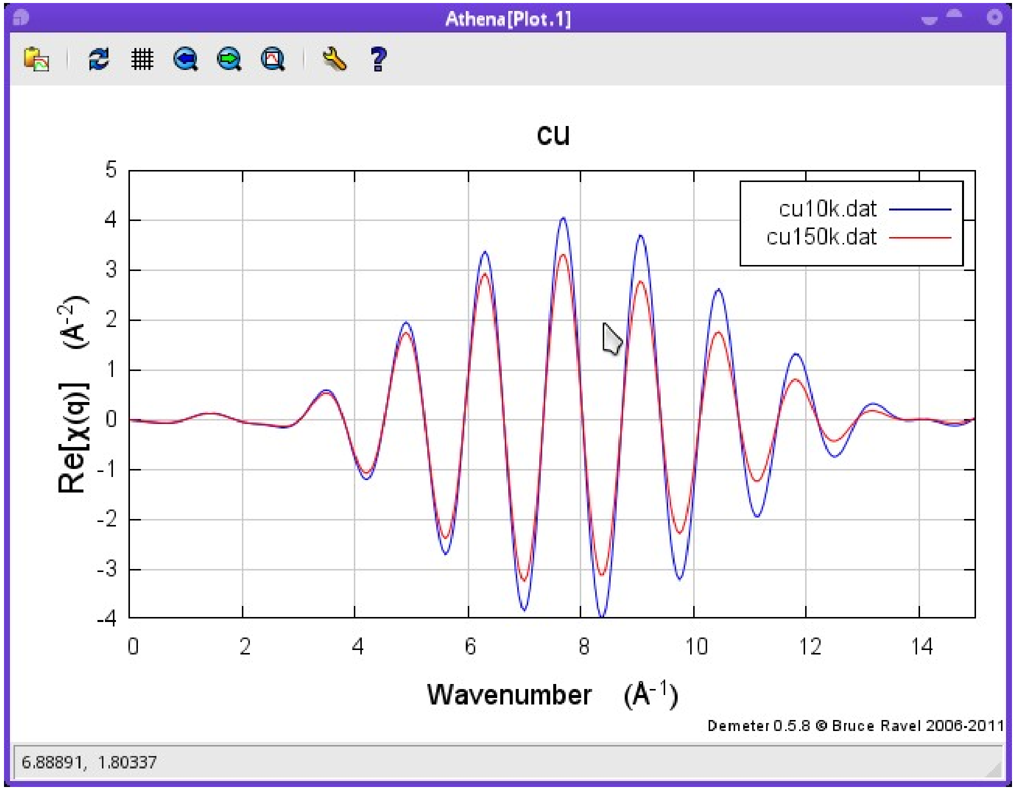
Here is the copper data imported into Athena. Because the 150K data has that wonky bit at 13 A^{-1}, I have made the forward transform range [3:12]. The back transform range is [1.7:2.8], i.e. around the first peak in R. Take care to align your data and to make each data group's E_0 the same.

Make sure that the absorber element was identified correctly.



Here are the data plotted in R and q.



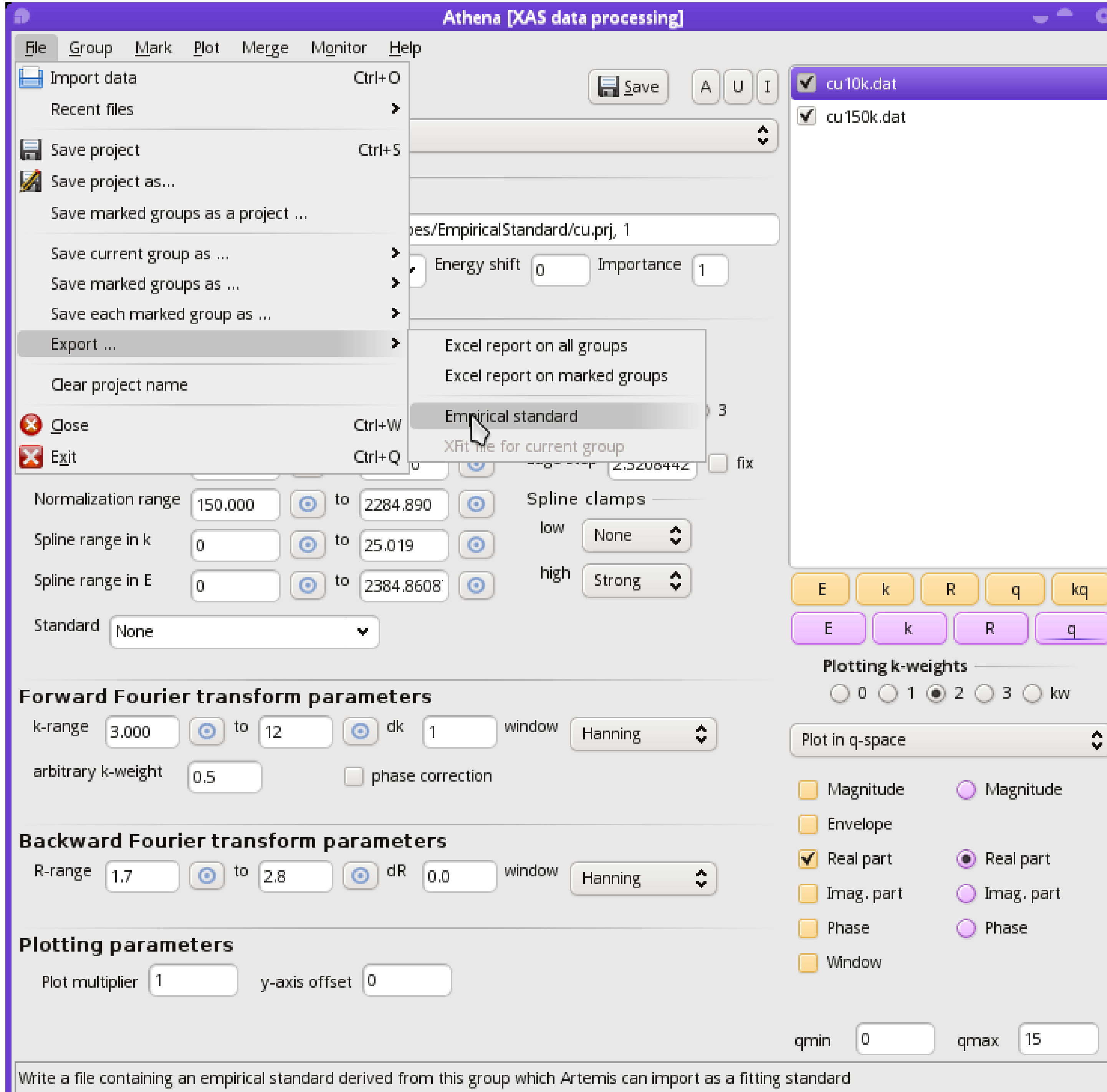


Select the “standard” (in this case, the lower temperature data) in the group list.

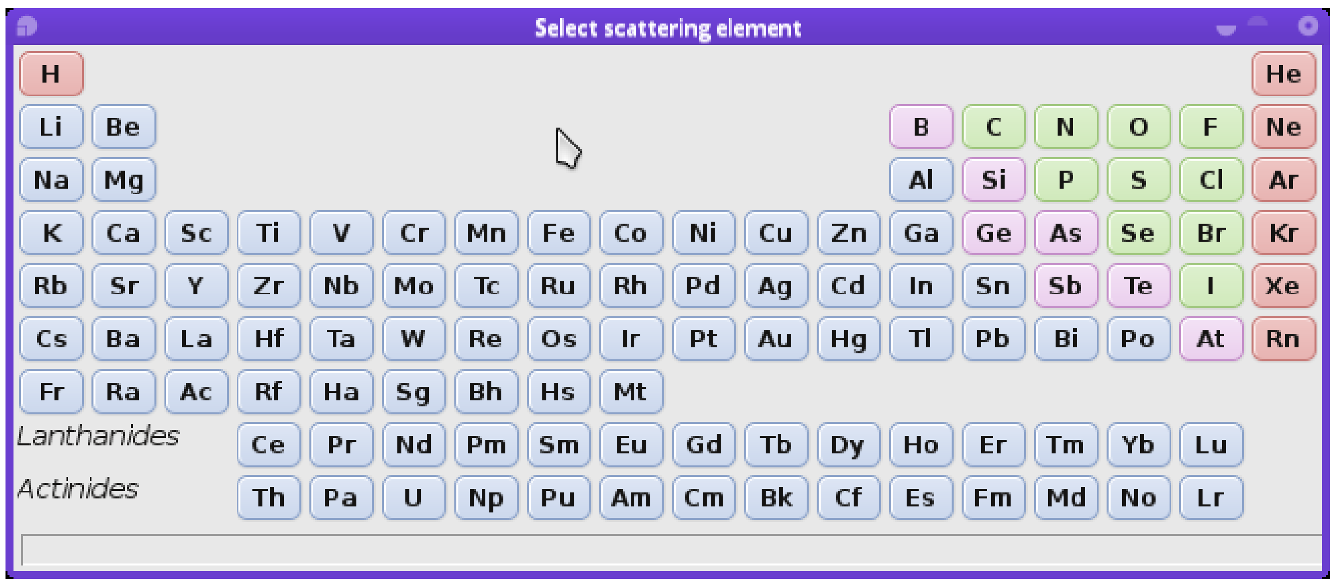
Export an empirical standard by digging down through the “File” menu.

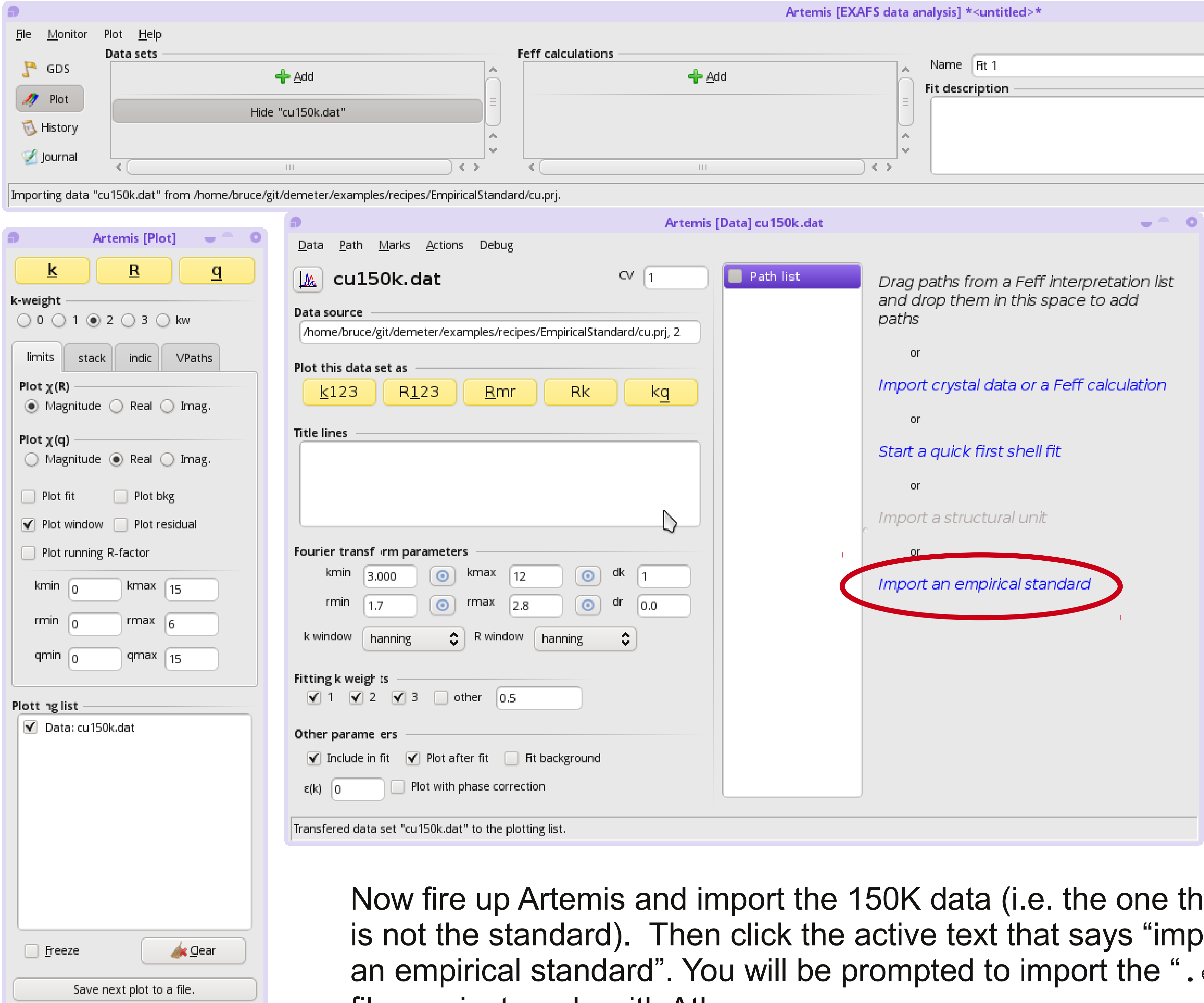
This will prompt you for a file name. The default file is the name of the data group with “`.es`” as the extension.

You will then be prompted....



… for the species of the scattering element. Athena has no way of knowing this, so you have to provide this information. In this case, you would click on Cu since this is copper metal.





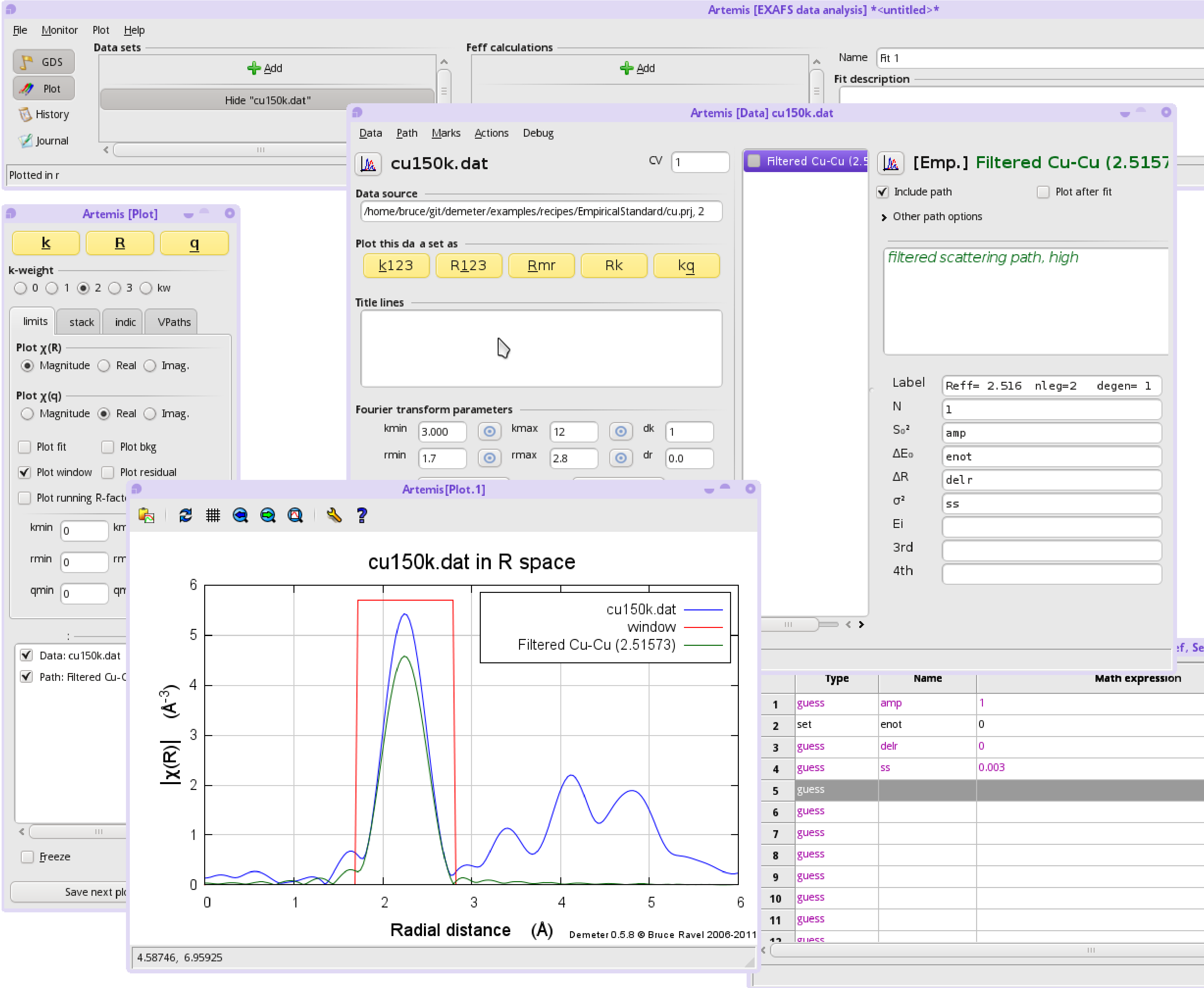
Now fire up Artemis and import the 150K data (i.e. the one that is not the standard). Then click the active text that says “import an empirical standard”. You will be prompted to import the “`.es`” file you just made with Athena.

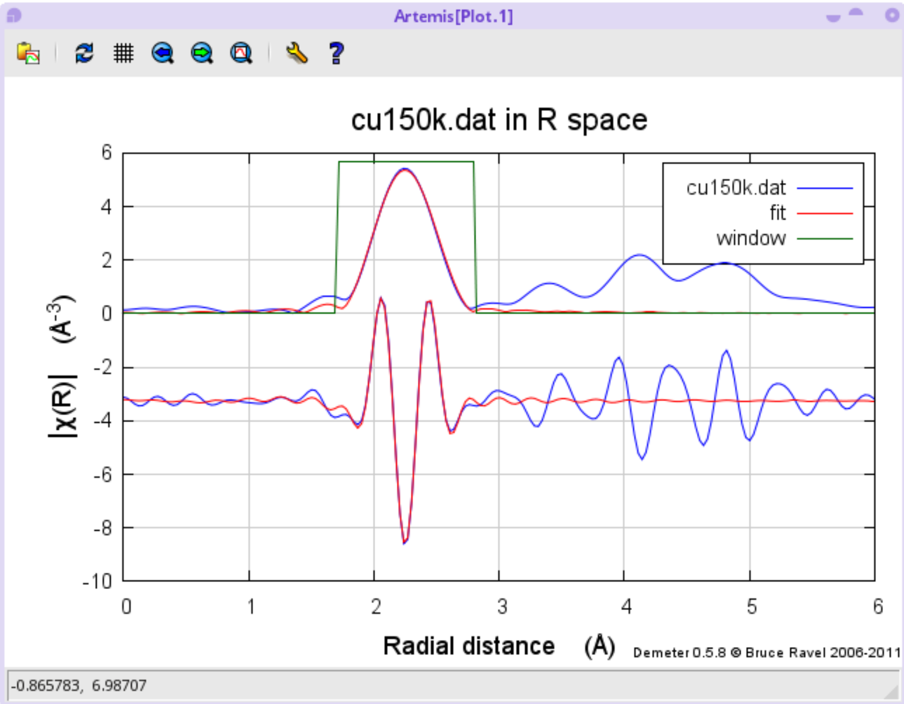
Once the empirical standard is imported, it will be displayed just like any path. You can tell it is an empirical standard because its label contains the token “[Emp.]”.

Here I have set up a 4-parameter fit typical for a first shell fit, except that I have set the E_0 parameter to 0. The amplitude, σ^2, and Δr are guess parameters.

In the plot, I show the 150K data in R along with the empirical standard taken from the 10K data. The initial guess of σ^2=0.003 is clearly a bit too large.

I am now ready to hit the Fit button.


Artemis [EXAFS data analysis] *<untitled>*
File Monitor Plot Help
GDS
Plot
History
Journal
Data sets
Add
Hide "cu150k.dat"
Feff calculations
Add
Name Fit 1
Fit description
Plotted in r
Artemis [Plot]
k R q
k-weight
0 1 2 3 kw
limits stack indic VPaths
Plot χ(R)
Magnitude Real Imag.
Plot χ(q)
Magnitude Real Imag.
Plot fit Plot bkg
Plot window Plot residual
Plot running R-fact
kmin 0
rmin 0
qmin 0
Data: cu150k.dat
Path: Filtered Cu-C
Freeze
Save next pl
Artemis [Data] cu150k.dat
Data Path Marks Actions Debug
cu150k.dat
CV 1
Data source
/home/bruce/git/demeter/examples/recipes/EmpiricalStandard/cu.prj, 2
Plot this da a set as
k123 R123 Rmr Rk kq
Title lines
Fourier transform parameters
kmin 3.000 kmax 12 dk 1
rmin 1.7 rmax 2.8 dr 0.0
Filtered Cu-Cu (2.5
[Emp.] Filtered Cu-Cu (2.5157
Include path
Plot after fit
Other path options
filtered scattering path, high
Label Reff= 2.516 nleg=2 degen= 1
N 1
S₀² amp
ΔE₀ enot
ΔR delr
σ² ss
Ei
3rd
4th
Artemis[Plot.1]
cu150k.dat in R space
cu150k.dat
window
Filtered Cu-Cu (2.51573)
|χ(R)| (Å⁻³)
Radial distance (Å)
Demeter 0.5.8 © Bruce Ravel 2006-2011
4.58746, 6.95925
Type Name Math expression
1 guess amp 1
2 set enot 0
3 guess delr 0
4 guess ss 0.003
5 guess
6 guess
7 guess
8 guess
9 guess
10 guess
11 guess

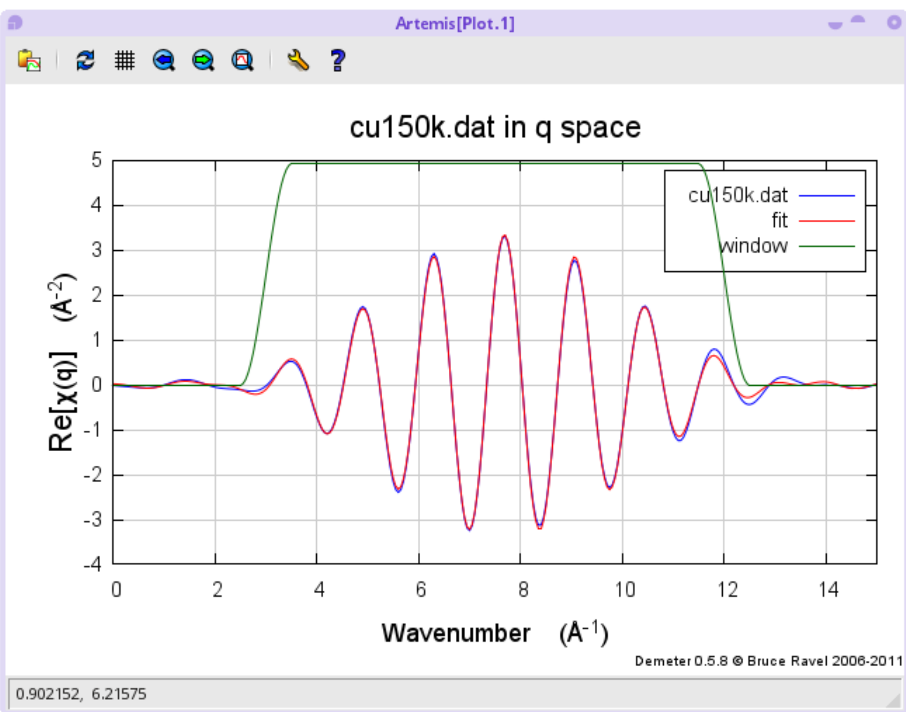


Here is the fit performed in R and plotted in R

Artemis [GDS] Guess, Def, Set parameters

	Type	Name	Math expression	Evaluated
1	guess	amp	1	0.97056 +/- 0.06922
2	set	enot	0	
3	guess	delr	0	0.00111 +/- 0.00193
4	guess	ss	0.003	0.00148 +/- 0.00055
5	guess			
6	guess			
7	guess			
8	guess			
9	guess			
10	guess			
11	guess			
12	guess			

Use best fit
Reset all
Highlight
Import GDS
Export GDS
Discard all
Add GDS



Here is the fit performed in q and plotted in q

Artemis [GDS] Guess, Def, Set parameters

	Type	Name	Math expression	Evaluated
1	guess	amp	1	0.97053 +/- 0.04292
2	set	enot	0	
3	guess	delr	0	0.00102 +/- 0.00115
4	guess	ss	0.003	0.00150 +/- 0.00034
5	guess			
6	guess			
7	guess			
8	guess			
9	guess			
10	guess			
11	guess			
12	guess			

Use best fit
Reset all
Highlight
Import GDS
Export GDS
Discard all
Add GDS

The results fitting in R or q are pretty similar, which is reassuring.

The value for the amplitude is consistent with and close to 1, which is should be since the copper metal is 12-fold coordinate at both temperatures.

The value for $\Delta\sigma^2$ is 0.0015(3), which seems reasonable for this temperature range.

The value for ΔR fitted in q space is 0.001(1). Fitted in R space, the uncertainty is 0.002. That's kind of interesting. In either case, the uncertainty in R is smaller than for a Feff-based fit for a number of reasons. Probably the most significant is that both standard and data are of excellent quality. Were the data the sort of marginal data that comes from most research problems on difficult materials, the effects of statistical and systematic noise would be much more dramatic. Also relevant top small uncertainty is that this fitting problem has been contrived (by virtue of careful alignment and choice of E_0 back in Athena) to remove ΔE_0 from the problem. By removing the parameter most correlated with ΔR, we significantly reduces the uncertainty in ΔR.

I would not interpret all of this to mean that use of empirical standards is superior to the use of Feff. In the specific case where the first coordination shell is of known contents and can be well isolated from higher shells and where you are confident that your unknown is identical to your standard except for small changes in N, R, or σ^2, then empirical standards are a useful tool for your EXAFS toolbox.