

Unofficial SST-1 RSoXS Chamber NEXAFS Collection and Analysis Guide

Peter Dudenas

The Resonant Soft X-ray Scattering (RSoXS) through-station on the Spectroscopy Soft and Tender-1 (SST-1) line at NSLS-II of Brookhaven National Lab was built and is operated by NIST.¹ Eliot Gann is the beamline scientist and Chief RSoXS Baron. This document is meant to serve as an informal guide for Near-Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy collection and analysis. It is mostly a recapitulation of conversations with Eliot and Dean Delongchamp (NEXAFS whisperer and grazing-incidence RSoXS skeptic) and published work (see for example the QANT publication²). It may or may not also help you understand RSoXS measurements better. No guarantees though. For more background on what RSoXS can (and can't) do for you, see the recent review by Eliot and Brian Collins.³

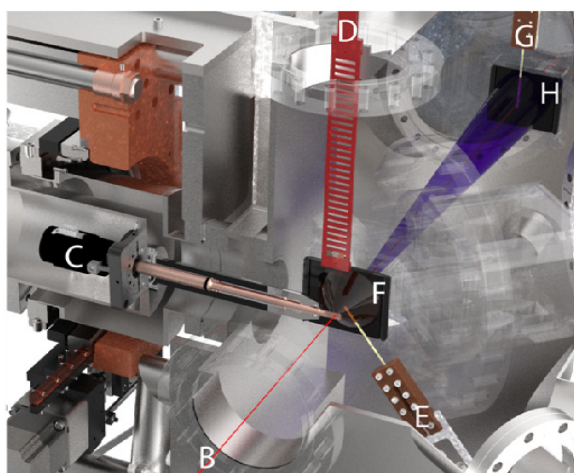


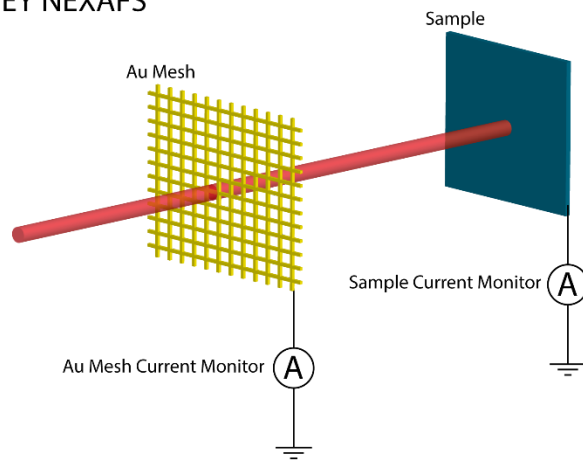
Figure 1. 3D CAD rendering of the RSoXS Measurement chamber. B) X-ray beam C) TEM load lock chamber D) High-throughput sample bar E) WAXS beamstop and photodiode F) WAXS Detector G) SAXS beamstop and photodiode H) SAXS Detector A) (not pictured) Maxwell's Demon, probably. Reproduced from Ref. 1 without permission.

Figure 1 is a fancy 3D rendering of the RSoXS chamber, illustrating the various components. Relevant to this guide are the SAXS and WAXS detectors, their respective beamstops, and the high-throughput sample bar. NEXAFS can be collected in two different modes in the RSoXS chamber-total electron yield (TEY) and transmission (see Figure 2).

In TEY mode, we derive the NEXAFS spectra by measuring current to the sample. This current results from electrons replacing ejected photoelectrons which are generated by absorption of the incoming x-ray beam. For a more detailed description see the monograph by Stohr,⁴ or this link to his website <https://www-ssrl.slac.stanford.edu/stohr/nexafs.htm>. The important takeaways here are

- 1) this requires the sample substrate to be relatively conductive. Standard P-type Si wafers with just a native oxide are a good choice and highly doped Si is even better. Don't use wafers with a thermally grown oxide since they're insulating. If the sample itself is pretty non-conductive, thick samples may also present an issue.
- 2) Because of the mean free path of ejected photoelectrons, TEY NEXAFS is only sensitive to the top 5-10 nm of the sample.

TEY NEXAFS



RSoXS/Transmission NEXAFS

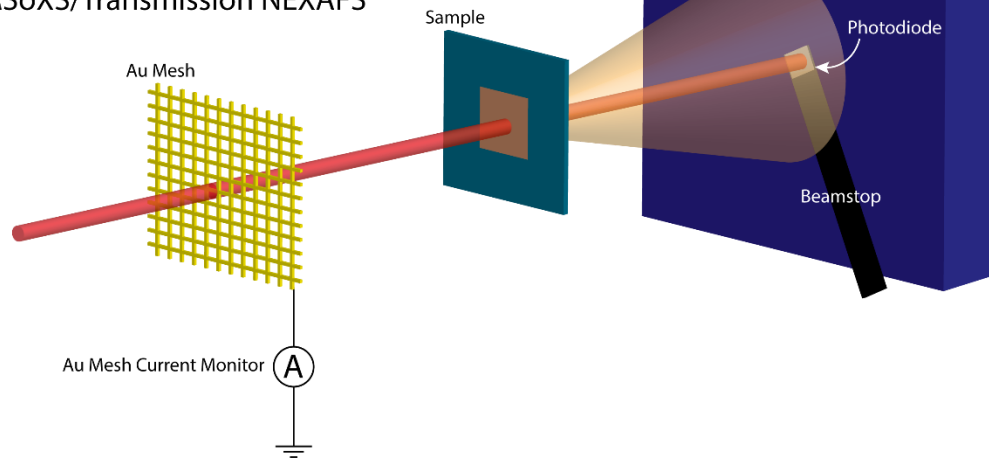


Figure 2. Schematic of TEY and transmission collection modes.

Transmission NEXAFS is the second collection mode on the RSoXS chamber. In this mode, we measure what fraction of the x-ray beam is absorbed by the sample using one of the photodiodes mounted on the SAXS and WAXS beamstops. Because this is a transmission experiment, it is sensitive to the full depth of the sample. Additionally, it requires the sample to be mounted on a transmissive

substrate such as the SiN windows used for RSoXS. In fact, when you do an RSoXS measurement you automatically measure the photodiode signal and get transmission NEXAFS for free.

Calibration Scans and Normalization

In both TEY and Transmission collection modes, we monitor the incoming beam using current generated at the Au Mesh, which is upstream from the sample. In an ideal world, this would be a perfect unchanging monitor and we would normalize directly to this signal. Unfortunately, the Au mesh is subject to contamination from adventitious carbon, and the presence of this carbon changes the current response. This makes the Au mesh current response a function of beam intensity, beam size/shape, time, and beam polarization. Because of these non-idealities, we need to calibrate the Au mesh current using the beamstop photodiode (which isn't sensitive to adventitious carbon contamination). Figure 3 shows a reference/calibration scan.

Reference/Calibration Scan

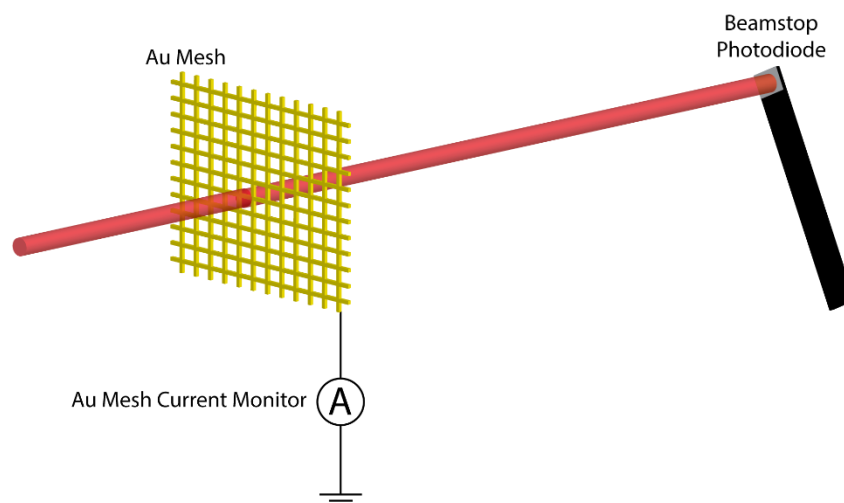


Figure 3. Schematic of a reference/calibration scan.

It bears repeating that the Au mesh current response is a function of beam intensity, beam size/shape, time, and beam polarization. What this means practically is that you should take calibration scans for each set of unique beam conditions/parameters. As an example, if you take NEXAFS at 0 and 90 polarization directions on both the SAXS and WAXS detectors, you need 4 calibration scans to accompany the 4 unique sets of parameters: [[0 pol, WAXS], [90 pol, WAXS], [0 pol, SAXS], [90 pol, SAXS]]. Continuing, if you take 5 different polarizations at normal incidence, then you need 5 calibration scans total, one for each of the polarizations.

I don't think the adventitious carbon's temporal behavior has been thoroughly characterized, but we assume it changes relatively slowly. So, you don't need new calibration scans before every sample measurement, but it would be good practice to make your calibration scans close to your sample measurements. At the very least, you should take calibration scans the day of your sample measurements.

To beat a dead horse, here's some hypothetical questions and answers:

Q1 – “Can I use a SAXS calibration scan to normalize my NEXAFS spectra taken in the WAXS configuration?”

A1 – No. The WAXS configuration has a larger beam than the SAXS configuration. The Au mesh current response is likely non-linear with beam size due to non-uniform adventitious carbon deposition and identity (e.g., graphitic vs non-graphitic).

Q2 – “Can I use a calibration scan from 11/19/20 to normalize my NEXAFS I collected on 9/30/21?”

A2 – No. Not only is the adventitious carbon probably different, beamline parameters such as slit sizes, grating offset, and EPU look-up table values might be different. Mercury also went into retrograde in between the two measurements, so that's no good.

Q3 – “If I take NEXAFS spectra at various sample rotation angles, do I need calibrations for each one?”

A3 – No. You are changing the sample orientation, but the beam itself is unchanged.

Q4 – “What if I'm using Eliot's slick fixed-incident angle, variable polarization scan to get angle-dependent NEXAFS?”

A4 – Astute question. In this case you should take calibration scans for each polarization.

Q5 – “Well I don't have any calibration scans. Is all my data useless?”

A5 – No, your data isn't useless, but you should explicitly state it is uncorrected data and make sure you collect calibration scans next time. The preferred order of how to present your data is as follows:

1. Double normalized from a calibration measured in the exact same setting on the same day
2. Double normalized from a similar calibration scan (e.g., perhaps it is a couple weeks old)
3. No normalization

TEY NEXAFS calibration

So now that you have a calibration scan which has the same measurement parameters as your sample, we can calculate the “double normalization” and use it to normalize/correct your spectra. Your TEY NEXAFS measurement signals may look something like Figure 4.

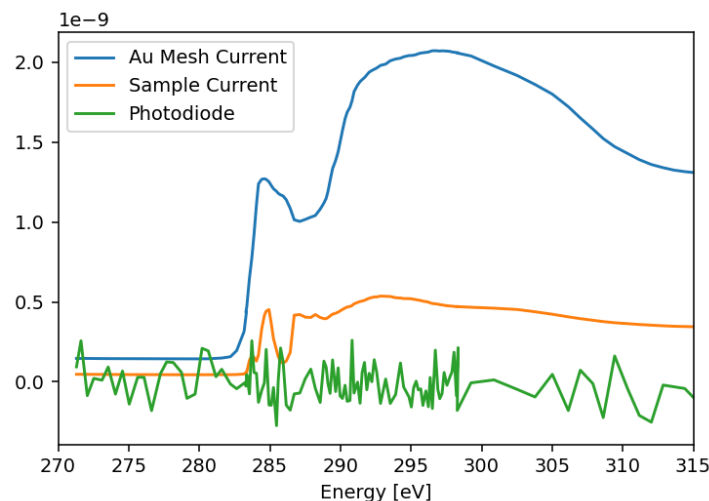


Figure 4. Various signals from a TEY NEXAFS measurement.

Notice that while we still collect the photodiode response, because this is TEY NEXAFS and the sample is on a non-transmissive substrate, we have no real photodiode signal. From a TEY sample measurement, we only use the Au mesh current and sample current. This is in contrast to the calibration scan (Figure 5).

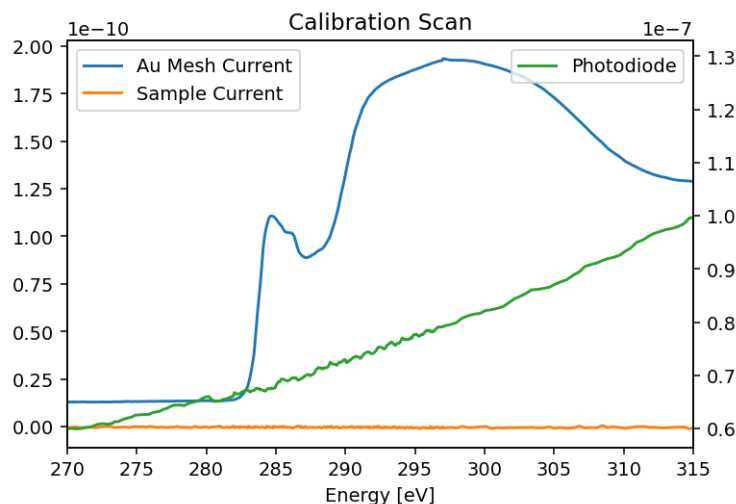


Figure 5. Various signals from a calibration scan.

The calibration scan has no sample blocking the beam and generating current. Thus, we record a photodiode response and zero sample current. From the calibration scan, we divide the Au mesh current by the photodiode signal to calculate our “Double Normalization” (Eqn. 1). The Double Normalization for this example is plotted in Figure 6.

$$\text{Double Normalization} = \frac{[\text{Au Mesh Current}]_{\text{calibration}}}{[\text{Photodiode}]_{\text{calibration}}} \#(1)$$

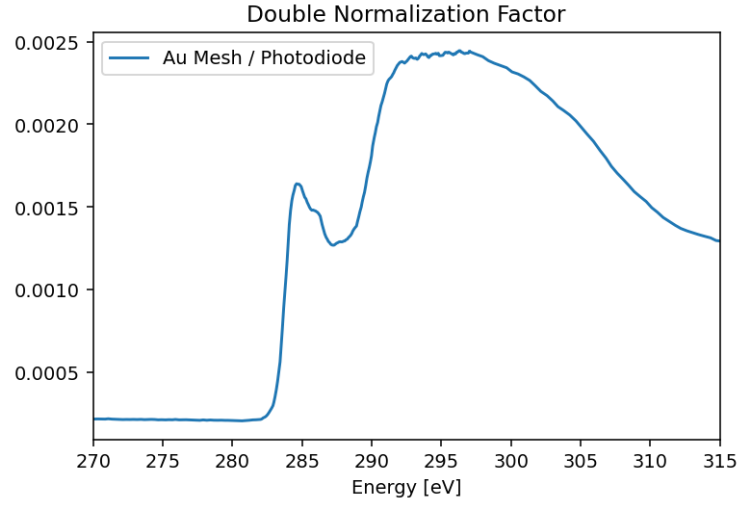


Figure 6. Double Normalization Factor

To correct the raw TEY NEXAFS spectra, we divide by the Au mesh current from the sample measurement and multiply by the double normalization (Eqn. 2). The raw sample current and corrected spectra are shown in Figure 7.

$$\text{Corrected TEY NEXAFS} = \frac{\text{Sample Current}}{[\text{Au Mesh Current}]_{\text{sample}}} * \frac{[\text{Au Mesh Current}]_{\text{calibration}}}{[\text{Photodiode}]_{\text{calibration}}} \#(2)$$

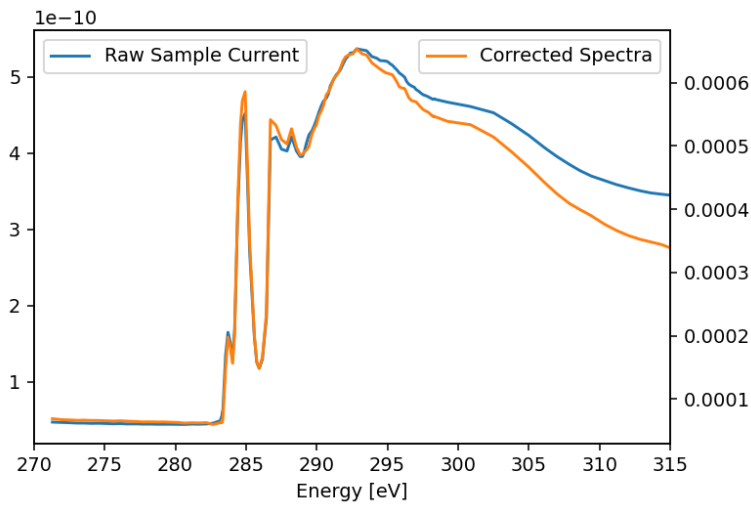


Figure 7. Raw sample current and the corrected NEXAFS plotted versus energy.

If you plan to merge the NEXAFS spectra with the bare atom data and perform a Kramer-Kronig (KK) transform, you can proceed from here using your favorite KK transform program. QANT² has the KK transform built in if you like Igor, and `kkcalc`⁵ is python library specifically for this task. Why would you want to do a KK transform you ask? To calculate the real and imaginary components of the index of refraction, of course! Those are required if you want to do more advanced analysis of RSoXS data, like using the Cy-RSoXS simulation engine (publication and software repository are forthcoming).

If you want to perform composition fitting or analyze the angular dependence of the NEXAFS spectra, then we need to proceed with pre-edge normalization (absolutely necessary) and potentially post-edge normalization (this will be situation dependent). For pre-edge normalization we fit a line to the pre-edge data, subtracting this as a baseline, and for post-edge normalization we then divide by post-edge data (~340 eV). Figure 8 shows these procedures.

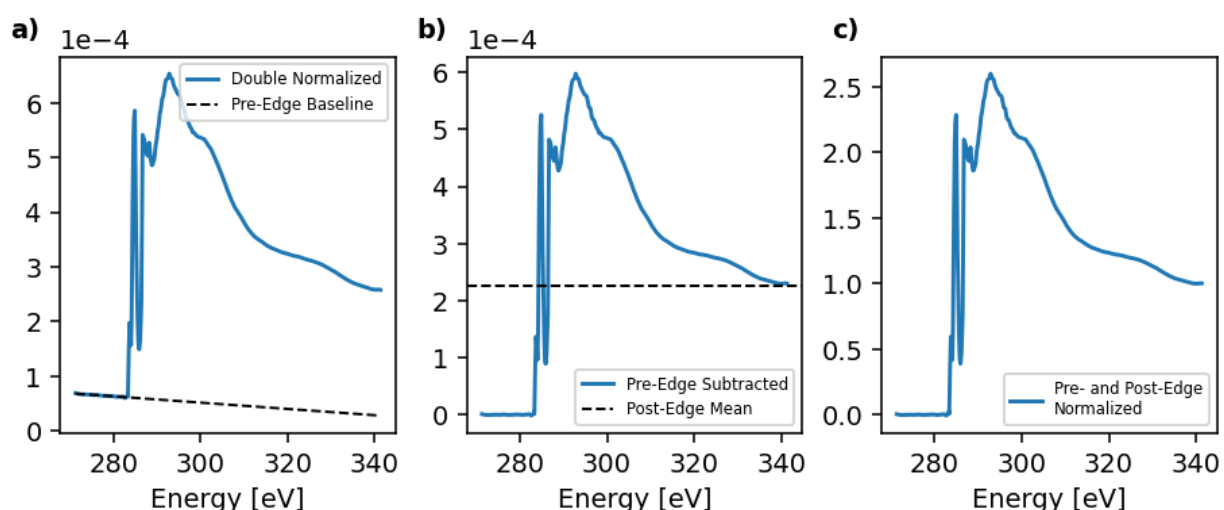


Figure 8. Stepwise plotting of the pre- and post-edge normalization. a) A pre-edge baseline is fit to the double normalized NEXAFS spectra and subtracted. b) The pre-edge subtracted data is divided by the post-edge mean to yield the pre- and post-edge normalized spectra in c).

A natural question to ask is “In what situations should I do the post-edge normalization?” Well, the post-edge contains information about how much carbon is present; post-edge normalization places the spectra on a per-carbon atom basis and there are instances where this will or won’t be useful. “The most common reason to do post-edge normalization is to normalize for different spot sizes in variable incident angle measurements.” (Direct quote from Dean). So, if you’re analyzing the angular dependence of a specific resonance peak, you will probably need to post-edge normalize. Another instance where post-edge normalization is useful is comparing spectra from different beamlines or collection conditions (e.g., different grid biases for partial electron yield (PEY) NEXAFS). An example of where you should not post-edge normalize is magic angle composition analysis. Here, we would want to know the relative amounts of two or more materials in a multicomponent system, and post-edge normalization would remove some of that information. When in doubt, email Eliot or Dean for advice. Or consult a Magic 8-Ball. That might work too.

Data Issues

There are two common-ish data issues to look out for when analyzing NEXAFS data from SST-1: Photodiode saturation and energy offsets. Photodiode saturation occurs when the gain on the photodiode is set too low. A saturated photodiode signal is shown in Figure 9.

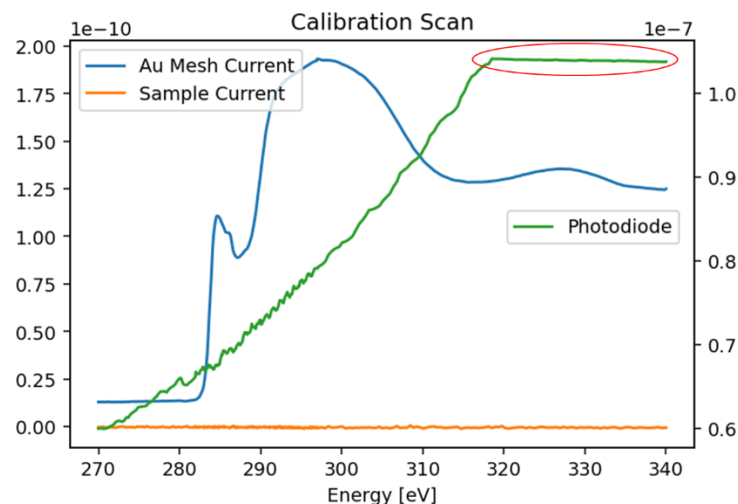


Figure 9. A calibration scan with photodiode saturation (circled in red).

Above ~ 317 eV, the photodiode saturates, and we no longer have a reliable way to normalize our calibration Au mesh current. Ideally, you will catch this at the beamline, adjust the photodiode gain, and retake the measurement. As a backup, you can fit and extrapolate the photodiode signal to circumvent this issue. I do this by fitting a straight line to a small region before saturation and replace the saturated data with the extrapolated fit (Figure 10). I've also tried a 2nd order polynomial, but that doesn't seem to work as well. Again, this is a backup when you don't have the option to re-collect the data. Figure 11 shows the difference between using the saturated and extrapolated photodiode signals.

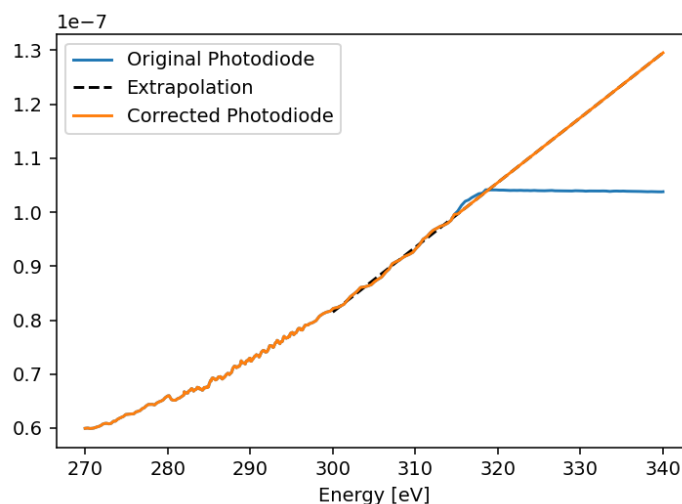


Figure 10. The photodiode signal before and after extrapolation.

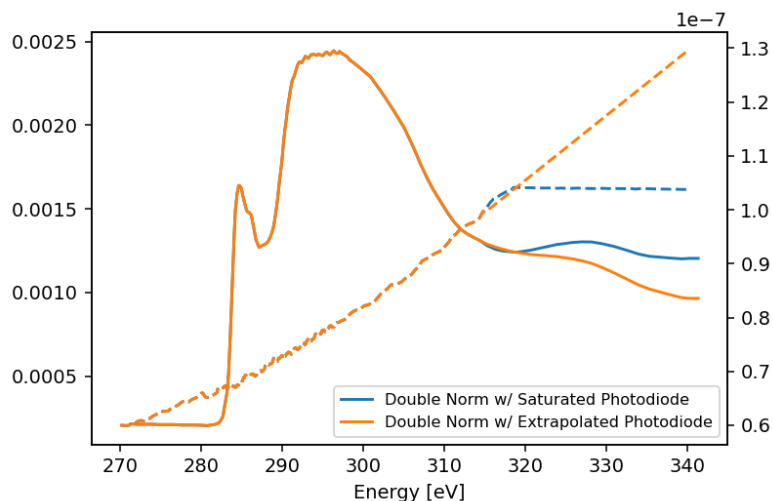


Figure 11. Double Normalization factor calculated with the saturated and extrapolated photodiode signals.

The next issue you may run into is an energy offset between calibration and sample measurements. This is caused by inconsistent positioning of the line grating. There are three line gratings on the beamline, which are optimized for different measurement modes and energies. For example, when we switch between RSoXS and NEXAFS measurements we change the line grating used. So, if you took a calibration scan, moved onto RSoXS, and then came back to the NEXAFS line grating to measure your samples, the line grating may be in a slightly different position and result in a 1-2 eV offset between the two measurements. If you go through the double normalization procedure and see a weird dip pre-edge in your data (Figure 12), you likely have an energy offset.

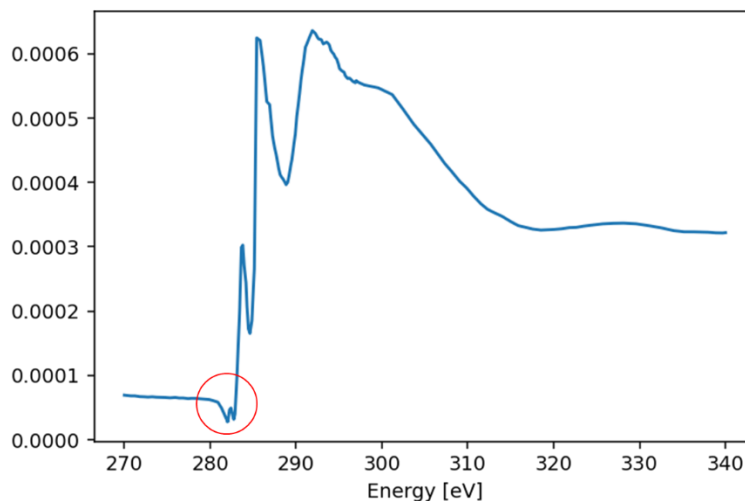


Figure 12. Double Normalized NEXAFS spectra showing symptoms of sample-calibration energy offset.

If we plot the Au mesh current for the Sample and Calibration scans, the energy offset is obvious (Figure 13). We'd ideally have an HOPG scan to calibrate the correct energy offset to apply to each of these scans. But if you're lazy, the first peak in the data should occur at ~ 285 eV. Here, it appears that the calibration scan is correct, so a 1.3 eV offset is added to the sample scan energies.

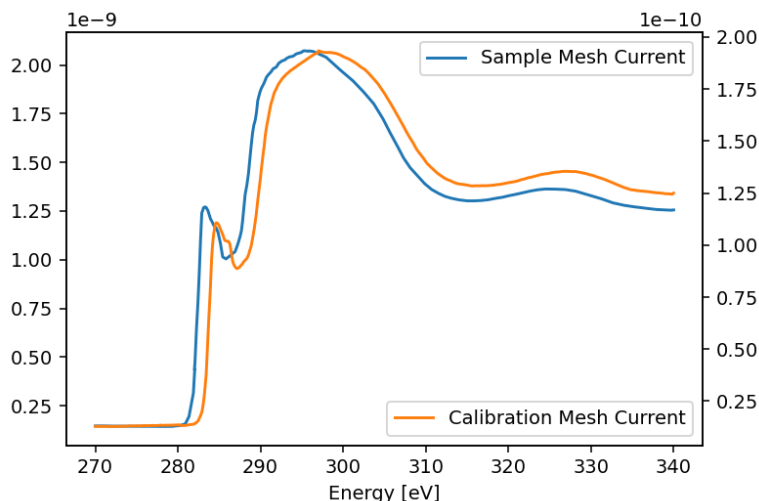


Figure 13. Au mesh current for sample and calibration scans. An energy offset exists between the two measurements.

After correcting for the energy offset, the double normalized TEY NEXAFS data looks much better (Figure 14).

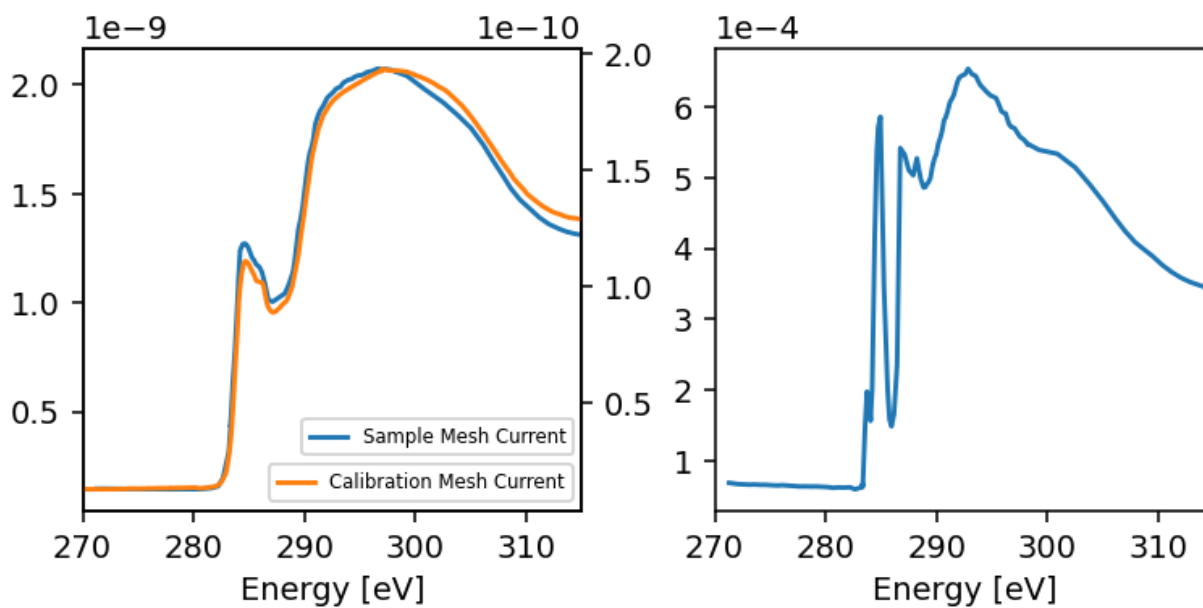


Figure 14. a) Au mesh current for the sample and calibration scans, corrected for energy. b) Double normalized NEXAFS spectra after correcting for energy offset. No pre-edge dip is observed.

References

- (1) Gann, E.; Crofts, T.; Holland, G.; Beaucage, P.; McAfee, T.; Kline, R. J.; Collins, B. A.; McNeill, C. R.; Fischer, D. A.; DeLongchamp, D. M. A NIST Facility for Resonant Soft X-Ray Scattering Measuring Nano-Scale Soft Matter Structure at NSLS-II. *J. Phys.: Condens. Matter* **2021**, 33 (16), 164001. <https://doi.org/10.1088/1361-648X/abdffb>.
- (2) Gann, E.; McNeill, C. R.; Tadich, A.; Cowie, B. C. C.; Thomsen, L. Quick AS NEXAFS Tool (QANT): A Program for NEXAFS Loading and Analysis Developed at the Australian Synchrotron. *J Synchrotron Rad* **2016**, 23 (1), 374–380. <https://doi.org/10.1107/S1600577515018688>.
- (3) Collins, B. A.; Gann, E. Resonant Soft X-Ray Scattering in Polymer Science. *Journal of Polymer Science n/a* (n/a). <https://doi.org/10.1002/pol.20210414>.
- (4) Stohr, J. *NEXAFS Spectroscopy*; Springer Series in Surface Sciences; 1992.
- (5) Watts, B. kkalcalc <https://github.com/benajamin/kkalcalc>.