XAS Sample Optimizer and Measurement Time Estimator

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1 Theory

1.1 Sample optimization

According to the Beer-Lambert law, the intensity I transmitted through the sample is given by

$$I = I_0 e^{-\mu x}, \tag{1}$$

where I_0 is the incident intensity, μ is the attenuation coefficient, and x is the thickness of the sample. Taking into account that in measurements we have non-negligible background for incident and transmitted signals, the Beer-Lambert law translates to measured counts N and N_0 so that

$$\frac{N - B}{T} = \frac{N_0 - B_0}{T_0} e^{-\mu x}, \tag{2}$$

where B and B_0 are the background contributions to the measured counts of transmitted signal N and the incident signal N_0, respectively. T and T_0 are the corresponding measurement times. Typically the sample is mixed with a low-Z filling material, which will contribute an additional $(\mu x)_0$ to the attenuation coefficient. In the presence of filler, the previous equation reads

$$\frac{N - B}{T} = \frac{N_0 - B_0}{T_0} e^{-\mu x - (\mu x)_0}, \tag{3}$$

An optimal XAS sample is prepared so that the signal-to-noise ratio (SNR) of the edge jump $\Delta \mu x$ or a quantity proportional to that is maximized. For now on, let us denote the attenuation coefficient below the edge as μ and above the edge μ'. Thus the edge jump can be written as $\Delta \mu x = \mu' x - \mu x$. Utilizing the Eq. (3), the edge jump is obtained from the measured signals followingly:

$$\Delta \mu x = -\ln \frac{(N' - B')T_0'}{(N_0' - B_0')T'} + \ln \frac{(N - B)T_0}{(N_0 - B_0)T}, \tag{4}$$

or

$$\Delta \mu x = \ln(N_0' - B_0') + \ln(N - B) - \ln(N' - B') - \ln(N_0 - B_0) + \ln \frac{T_0 T'}{T T_0'}. \tag{5}$$

Therefore the uncertainty of $\Delta \mu x$ is obtained using the propagation of error:

$$\sigma_{\Delta \mu x} = \sqrt{\left(\frac{\sigma_{N_0'}}{N_0' - B_0'}\right)^2 + \left(\frac{\sigma_N}{N - B}\right)^2 + \left(\frac{\sigma_{N'}}{N' - B'}\right)^2 + \left(\frac{\sigma_{N_0}}{N_0 - B_0}\right)^2}, \tag{6}$$

where σ_k are the uncertainties of the quantities k. Uncertainties of the background signals are neglected a they are assumed to smoothed out by fitting.

Since photon counting is a Poisson process, we know that $\sigma_k = \sqrt{k}$. However, to get a useful result, we need to make some further assumptions. For example, σ_{N_0} can be written as

$$\sigma_{N_0} = \sqrt{N_0} = \sqrt{\frac{N_0}{N_0 - B_0}} \sqrt{N_0 - B_0} \equiv \sqrt{\beta} \sqrt{N_0 - B_0}. \tag{7}$$

$\beta \geq 1$ is now the ratio of the total recorded counts to the useful signal. Assuming that the incident beam intensity and its background does not change considerably over the edge step we may write

$$\left(\frac{\sigma_{N_0'}}{N_0' - B_0'}\right)^2 + \left(\frac{\sigma_{N_0}}{N_0 - B_0}\right)^2 \approx \frac{2\beta}{N_0 - B_0} \tag{8}$$

On the other hand for σ_N we find

$$\begin{aligned}\left(\frac{\sigma_N}{N - B}\right)^2 = \left(\frac{\sqrt{N}}{N - B}\right)^2 &= \frac{\frac{T}{T_0}(N_0 - B_0)e^{-\mu x - (\mu x)_0} + B}{\left(\frac{T}{T_0}\right)^2 (N_0 - B_0)^2 e^{-2\mu x - 2(\mu x)_0}} \\ &= \frac{1}{N_0 - B_0}\left(1 + \gamma e^{\mu x}\right)\frac{T_0}{T} e^{\mu x + (\mu x)_0},\end{aligned} \tag{9}$$

where Eq. (3) has been used and

$$\gamma \equiv \frac{T_0}{T}\frac{B e^{(\mu x)_0}}{N_0 - B_0}. \tag{10}$$

Similarly when we assume that the filler attenuation and the background do not change much over the edge (*i.e.* $B' \approx B$) we would get

$$\left(\frac{\sigma_N'}{N' - B'}\right)^2 = \frac{1}{N_0 - B_0}\left(1 + \gamma e^{\mu' x}\right)\frac{T_0}{T} e^{\mu' x + (\mu x)_0} \tag{11}$$

Therefore we obtain

$$\sigma_{\Delta\mu x} = \frac{1}{\sqrt{N_0 - B_0}}\sqrt{2\beta + \frac{T_0}{T}\left[e^{\mu x} + e^{\mu' x} + \gamma\left(e^{2\mu x} + e^{2\mu' x}\right)\right] e^{(\mu x)_0}}, \tag{12}$$

or, in terms of count rates $n_0 = N_0/T_0$, $b_0 = B_0/T_0$, and $b = B/T$:

$$\sigma_{\Delta\mu x} = \frac{1}{\sqrt{n_0 - b_0}}\sqrt{\frac{2\beta}{T_0} + \frac{1}{T}\left[e^{\mu x} + e^{\mu' x} + \gamma\left(e^{2\mu x} + e^{2\mu' x}\right)\right] e^{(\mu x)_0}}, \tag{13}$$

where

$$\beta = \frac{n_0}{n_0 - b_0} \qquad \text{and} \qquad \gamma = \frac{b e^{(\mu x)_0}}{n_0 - b_0}. \tag{14}$$

Thus the relative uncertainty of $\Delta\mu x$ is

$$\delta \equiv \frac{\sigma_{\Delta\mu x}}{\Delta\mu x} = \frac{1}{\sqrt{n_0 - b_0}}\frac{\sqrt{\frac{2\beta}{T_0} + \frac{1}{T}\left[e^{\mu x} + e^{\mu' x} + \gamma\left(e^{2\mu x} + e^{2\mu' x}\right)\right] e^{(\mu x)_0}}}{\mu' x - \mu x} \tag{15}$$

Optimal sample thickness is thus found by maximizing Equation (15) *i.e.* finding the sample thickness x for which

$$\frac{\partial\delta}{\partial x} = 0. \tag{16}$$

Note that the filler contribution $(\mu x)_0$ is now considered constant. Differentiating Equation (15) gives us a condition

$$\frac{4T}{T_0}\beta e^{-(\mu x)_0} + 2\gamma\left[(1 - \mu x)\, e^{2\mu x} + \left(1 - \mu' x\right) e^{2\mu' x}\right] + (2 - \mu x)\, e^{\mu x} + \left(2 - \mu' x\right) e^{\mu' x} = 0 \tag{17}$$

It is clear that the equation above needs to be solved numerically. In terms of mass attenuation coefficients, we may write

$$\mu x = \left(\frac{\mu}{\rho}\right)\rho x = \left(\frac{\mu}{\rho}\right)\frac{m}{A} \tag{18}$$

and solve the equation with respect to mass to sample container cross-section ratio m/A for practical applications.

The problem with Eq. (17) is that it leaves T/T_0 as a free parameter. However, in practice there is always limited time to conduct the measurement. Therefore we need to make the decision how the total measurement time $T_{tot} = T + T_0$ is allocated between the direct beam and transmitted beam measurements. By writing $T_0 = T_{tot} - T$, we may make the decision by maximizing δ by requiring that

$$\frac{\partial \delta}{\partial T} = 0 \tag{19}$$

simulaneously with Eq. (17). Straightforward derivation gives a condition

$$\tau \equiv \left(\frac{T}{T_0}\right)_{\text{optimal}} = \sqrt{\frac{e^{\mu x} + e^{\mu' x} + \gamma(e^{2\mu x} + e^{2\mu' x})}{2\beta e^{-(\mu x)_0}}} \tag{20}$$

Thus Equation (17) to be solved becomes

$$\sqrt{8\beta e^{-(\mu x)_0}}\sqrt{e^{\mu x} + e^{\mu' x} + \gamma(e^{2\mu x} + e^{2\mu' x})} \\ +2\gamma\left[(1-\mu x)\, e^{2\mu x} + \left(1-\mu' x\right) e^{2\mu' x}\right] + (2-\mu x)\, e^{\mu x} + \left(2-\mu' x\right) e^{\mu' x} = 0 \tag{21}$$

Using the optimized T/T_0 we can also write Eq. (15) in the following compact manner in terms of T_0 which is useful for estimating the measurement time:

$$\delta = \frac{1}{\sqrt{n_0 - b_0}}\sqrt{\frac{2\beta}{T_0}}\frac{\sqrt{1+\tau}}{\mu' x - \mu x} \tag{22}$$

1.2 Measurement time estimation

To estimate the measurement time required to obtain $\Delta\mu x$ with required precision from the measured photon count rates, we turn back to Equation (6). Given in terms of count rates following the nomenclature introduced previously, Eq. (6) becomes

$$\sigma_{\Delta\mu x} = \sqrt{\left(\frac{\sigma_{N_0'}}{(n_0' - b_0')T_0'}\right)^2 + \left(\frac{\sigma_N}{(n-b)T}\right)^2 + \left(\frac{\sigma_{N'}}{(n'-b')T'}\right)^2 + \left(\frac{\sigma_{N_0}}{(n_0-b_0)T_0}\right)^2}. \tag{23}$$

Assuming that the photon counting is a Poisson process, this becomes

$$\begin{aligned}\sigma_{\Delta\mu x} &= \sqrt{\left(\frac{\sqrt{n_0' T_0'}}{(n_0' - b_0')T_0'}\right)^2 + \left(\frac{\sqrt{nT}}{(n-b)T}\right)^2 + \left(\frac{\sqrt{n'T'}}{(n'-b')T'}\right)^2 + \left(\frac{\sqrt{n_0 T_0}}{(n_0-b_0)T_0}\right)^2} \\ &= \sqrt{\frac{n_0'}{(n_0'-b_0')^2 T_0'} + \frac{n}{(n-b)^2 T} + \frac{n'}{(n'-b')^2 T'} + \frac{n_0}{(n_0-b_0)^2 T_0}}\end{aligned} \tag{24}$$

Since the direct beam, its background, and the sample background levels are approximately equal below and above the edge, $\sigma_{\Delta\mu x}$ can be reduced to

$$\sigma_{\Delta\mu x} = \sqrt{\frac{2n_0}{(n_0-b_0)^2 T_0} + \frac{n}{(n-b)^2 T} + \frac{n'}{(n'-b)^2 T}}, \tag{25}$$

where it was assumed that the measurement times $T = T'$ and $T_0 = T_0'$. Now utilizing the Beer-Lambert law, we find that

$$\Delta\mu x = \mu' x - \mu x = -\ln\frac{n'-b}{n_0-b_0} + \ln\frac{n-b}{n_0-b_0} = \ln(n-b) - \ln(n'-b). \tag{26}$$

Therefore the relative uncertainty $\delta = \sigma_{\Delta\mu x}/\Delta\mu x$ becomes

$$\delta = \frac{1}{\ln(n-b) - \ln(n'-b)} \sqrt{\frac{2n_0}{(n_0-b_0)^2 T_0} + \frac{1}{T}\left[\frac{n}{(n-b)^2} + \frac{n'}{(n'-b)^2}\right]} \tag{27}$$

As before, we may optimize the ratio T/T_0 by defining the total measurement time $T_{tot} = T_0 + T$, writing $T_0 = T_{tot} - T$ and finding T for which

$$\frac{\partial\delta}{\partial T} = 0. \tag{28}$$

A straightforward derivation gives

$$\tau \equiv \left(\frac{T}{T_0}\right)_{\text{optimal}} = \sqrt{\frac{\frac{n}{(n-b)^2} + \frac{n'}{(n'-b)^2}}{\frac{2n_0}{(n_0-b_0)^2}}}. \tag{29}$$

Substituting this back into Eq. (27) gives

$$\delta = \frac{1}{\ln(n-b) - \ln(n'-b)} \frac{1}{n_0-b_0} \sqrt{\frac{2n_0}{T_0}}\sqrt{1+\tau}, \tag{30}$$

from which T_0 can be solved for required precision δ.

2 Implementation

The equations presented are implemented in Python. The required mass attenuation coefficients and edge energies obtained using XRAYLIB. For installation of XRAYLIB, see `https://github.com/tschoonj/xraylib`. Other dependencies are standard libraries.

The current version of the sample optimizer assumes $\beta = 1.1$ and $\gamma = 0.03e^{(\mu x)_0}$, which may vary depending on the measurement setup and settings. The filler is assumed to be 1 mm of $Z = 7$ with $\rho = 1.5$ g/cm^3 which is a good approximation for often used boron nitride and starch.