1. Introduction

Neutron and x-ray beam-line experiments are of fixed duration and often require the sample to be held within a container, where the container wall thickness is ideally thin, but can be thick as in pressure cell or crystallography experiments. Here, a procedure is given for optimising the relative measurement times for the sample-container and empty container parts of an experiment in order to minimise the statistical error on the container-corrected intensity. The effect on the fractional error of misestimating these run-times is also considered.

2. Optimizing the relative counting-times

Consider a scattering experiment on two samples in which the instrument set-up remains constant and the total counting time \( \tau = t_1 + t_2 \) is fixed, where \( t_i \) (\( i = 1, 2 \)) is the counting time for each sample. Let \( n_i \) and \( \Sigma_i \) be the number of illuminated atoms and the mean scattering cross-section per atom, respectively. Then, within the small-sample limit where beam attenuation and multiple scattering effects can be neglected (Fischer et al., 2006), the number of detected counts for each sample will be given by \( N_i = n_i \Sigma_i t_i = c n_i \Sigma_i t_i \) if the scattering is isotropic, where \( c \) is a calibration factor that will depend on, e.g., the solid-angle subtended by the detector and the detector efficiency. Normalised intensities (or count rates) follow from the expression \( I_i = N_i / t_i = c n_i \Sigma_i \) so that, by assuming Poisson counting statistics and a negligible error on parameters other than \( N_i \), the variance associated with \( I_i \) is given by \( \sigma_i^2 = N_i / t_i^2 = I_i / t_i \). Let the required signal be given by

\[
I_{\text{req}} = N (I_1 - w I_2),
\]

where \( w \) is a dimensionless weighting factor for the intensity \( I_2 \) and \( N \) is an overall normalisation factor. Then the associated variance

\[
\sigma_{\text{req}}^2 = N^2 \left[ \frac{I_1}{t_1} + \frac{w^2 I_2}{\tau - t_1} \right].
\]

It is desirable to optimise the counting times in order to minimise \( \sigma_{\text{req}}^2 \), i.e., to find the value of \( t_1 \) for which \( (1/N^2) d(\sigma_{\text{req}}^2) / dt_1 = 0 \). This minimisation leads to a quadratic equation that solves to give \( t_1 \text{opt} / \tau = (-a \pm \sqrt{ab}) / (b-a) \) where \( a = I_1 \) and \( b = w^2 I_2 \). The solution for \( t_1 \text{opt} / \tau \) with the positive root gives \( t_2 \text{opt} / \tau = 1 - t_1 \text{opt} / \tau = (b - \sqrt{ab}) / (b-a) \), which leads to the optimal counting-time ratio

\[
R_{\text{opt}} \equiv t_1 \text{opt} / t_2 \text{opt} = \sqrt{a / b} = \sqrt{I_1 / w^2 I_2},
\]

equivalent to the findings of Sears (1985) if \( w = 1 \).

3. Sample-in-container diffraction experiments

For definiteness, consider an angular dispersive diffraction experiment on a cylindrical sample held within an annular container in which an incident beam of wavelength \( \lambda \) is perpendicular to the axis of symmetry, and the scattered intensity is measured as a function of the scattering angle \( 2 \theta \) (Fig. 1(a)) (e.g. Fischer et al., 2006). It will be assumed that detector saturation has been avoided, and that the detector counts have been corrected for dead-time. Let \( N_{SC} \) be detected in time \( t_{SC} \) for the sample (S) in its container (C). Then, provided multiple scattering events are negligible, the normalised intensity is given by (e.g. Salmon & Zeidler, 2015)

\[
N_{SC}^E(\theta) = N_{SC} / t_{SC} = \frac{A_{SC}(\theta) I_S(\theta) + A_{C,SC}(\theta) I_C(\theta)}{I_S(\theta) + I_C(\theta)},
\]

where \( I_S(\theta) \) and \( I_C(\theta) \) are the intensities for the bare sample and empty container as calculated within the small-sample limit, respectively. Similarly, let \( N_C \) counts be detected in time \( t_C \) for the empty container so that the normalised intensity is given by

\[
N_C^E(\theta) = N_C / t_C = \frac{A_{C}(\theta) I_C(\theta)}{I_C(\theta)}. \]

In equations (4) and (5), \( A_j(\theta) \) denotes an attenuation coefficient for quanta that are scattered by the sample (\( J = S \)) or container (\( J = C \)) and attenuated through absorption and scattering in either the container (\( K = C \)) or both the sample and container (\( K = SC \)) (Paalman & Pings, 1962; Kendig & Pings, 1965; Soper & Egelstaff, 1980). The required signal is given by

\[
I_S(\theta) = \frac{1}{A_{SC}(\theta)} \left[ N_{SC}^E(\theta) - \frac{A_{C,SC}(\theta)}{A_C(\theta)} N_C^E(\theta) \right]. \]

By comparison with equation (1), and assuming isotropic scattering, we take \( I_1 = \langle N_{SC}^E(\theta) \rangle \approx c \langle A_{SC}(\theta) \rangle n_S \Sigma_S + \langle A_{C,SC}(\theta) \rangle n_C \Sigma_C \), \( I_2 = \langle N_C^E(\theta) \rangle \approx c \langle A_C(\theta) \rangle n_C \Sigma_C \) and \( N = 1 / \langle A_{SC}(\theta) \rangle \), where \( \langle \cdots \rangle \) represents an average over \( 2 \theta \), and \( n_S \) and \( n_C \) are the
number of illuminated atoms and the mean scattering cross-section per atom, respectively. Hence, from equation (3), the optimal counting-time ratio is given by
\[
R_{\text{opt}} = \frac{t_{\text{SC, opt}}}{t_{\text{C, opt}}} \approx \sqrt{\frac{\langle A_{\text{SC}}(\theta) \rangle n_S \Sigma_S + \langle A_{\text{C, SC}}(\theta) \rangle n_C \Sigma_C}{w^2 \langle A_{\text{C}}(\theta) \rangle n_C \Sigma_C}}, \tag{7}
\]
where \(t_{\text{SC, opt}}\) and \(t_{\text{C, opt}}\) are the desired counting times for the sample-in-container and empty container measurements, respectively, and \(w = \frac{\langle A_{\text{C, SC}}(\theta) \rangle}{\langle A_{\text{C}}(\theta) \rangle}\). Within the small-sample limit, \(A_{\text{C}}(\theta) \rightarrow 1\) so that equation (7) reduces to
\[
R_{\text{opt}} = \left[\frac{n_S \Sigma_S + n_C \Sigma_C}{n_C \Sigma_C}\right]^{1/2}.
\]

Figure 1(b) shows a plot of \(R_{\text{opt}}\) versus the intensity ratio \(I_1 / w I_2\) for a typical neutron diffraction set-up and experiments ranging from those in which a large sample (of glassy SiO\(_2\) or Se) is held within a thin-walled vanadium container, to those in which a small sample (of glassy SiO\(_2\) or crystalline vanadium) is held within a thick-walled pressure cell. In each case \(R_{\text{opt}} \lesssim 3\), i.e., the optimal counting time for the empty container is a substantial fraction of the total counting time \(\tau\).

Figure 2 shows the dependence of the normalised fractional error \(F_{\text{req}} / F_{\text{req, opt}}\) on the counting-time ratio \(R \equiv t_1 / t_2 = t_{\text{SC}} / t_{\text{C}}\) for the experiments on glassy SiO\(_2\) held within a vanadium container or pressure-cell. Here, the fractional error \(F_{\text{req}} = \sigma_{\text{req}} / I_{\text{req}}\), where \(\sigma_{\text{req}}\) and \(I_{\text{req}}\) are given by equations (2) and (6), respectively, and \(F_{\text{req, opt}}\) is the value corresponding to the optimal counting-time ratio \(R_{\text{opt}}\). For each of the curves given in Fig. 2, \(R_{\text{opt}}\) corresponds to the minimum where \(F_{\text{req}} / F_{\text{req, opt}} = 1\).

If in the performance of an experiment \(R = (\tau - t_1) / t_{\text{C}}\) whereas \(R_{\text{opt}} = (\tau - t_{\text{C, opt}}) / t_{\text{C, opt}}\), it follows that \(t_{\text{C}} / t_{\text{C, opt}} = (1 + R_{\text{opt}}) / (1 + R)\). For example, if in the pressure-cell experiment \(R = 3.252\) versus \(R_{\text{opt}} = 1.126\), then \(t_{\text{C}} / t_{\text{C, opt}} = 0.5\), and Fig. 2 shows that this underestimate of \(t_{\text{C}}\) by 50% will increase \(F_{\text{req}} / F_{\text{req, opt}}\) by \(\pm 14\%\). In comparison, if in the 5 mm vanadium container experiment \(R = 5.767\) versus \(R_{\text{opt}} = 2.3835\), then \(t_{\text{C}} / t_{\text{C, opt}} = 0.5\) and Fig. 2 shows that this underestimate of \(t_{\text{C}}\) will increase \(F_{\text{req}} / F_{\text{req, opt}}\) by \(\pm 8\%\).

4. Conclusions
A simple method is provided for estimating the optimal counting-times for the sample-in-container and empty container parts of a fixed-duration scattering experiment. The approach can be used to minimise the statistical error in, e.g., diffraction experiments that employ pair-distribution function (PDF) methods (Fischer et al., 2006, Zeidler et al., 2010).

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References