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Optimising the counting times for sample-in-container scattering experiments

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A method is given for choosing the relative counting times, for the sample-in-container and empty container parts of a fixed-duration scattering experiment, in order to minimise the statistical error on the container-corrected intensity. The method is applied to angular-dispersive diffraction experiments, and the effect on the fractional error of misestimating the relative run-times is considered.

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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 cryostat experiments. Here, a procedure is given for optimising the relative measurement times for the sample-in-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 Σ_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 $N_i \propto n_i \Sigma_i t_i = c n_i \Sigma_i t_i$ 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

$$I_{\text{req}} = \mathcal{N} (I_1 - w I_2), \quad (1)$$

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

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

It is desirable to optimise the counting times in order to minimise σ_{req}^2 , *i.e.* to find the value of t_1 for which $(1/\mathcal{N}^2) d[\sigma_{\text{req}}^2]/dt_1 = 0$. 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

$$R_{\text{opt}} \equiv t_{1,\text{opt}}/t_{2,\text{opt}} = \sqrt{a/b} = \sqrt{I_1/w^2 I_2}, \quad (3)$$

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 λ is perpendicular to the axis of symmetry, and the scattered intensity is measured as a function of the scattering angle 2θ (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} counts 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)

$$I_{\text{SC}}^{\text{E}}(\theta) = N_{\text{SC}}/t_{\text{SC}} = A_{\text{S,SC}}(\theta)I_{\text{S}}(\theta) + A_{\text{C,SC}}(\theta)I_{\text{C}}(\theta), \quad (4)$$

where $I_{\text{S}}(\theta)$ and $I_{\text{C}}(\theta)$ 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

$$I_{\text{C}}^{\text{E}}(\theta) = N_{\text{C}}/t_{\text{C}} = A_{\text{C,C}}(\theta)I_{\text{C}}(\theta). \quad (5)$$

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

$$I_{\text{S}}(\theta) = \frac{1}{A_{\text{S,SC}}(\theta)} \left[I_{\text{SC}}^{\text{E}}(\theta) - \frac{A_{\text{C,SC}}(\theta)}{A_{\text{C,C}}(\theta)} I_{\text{C}}^{\text{E}}(\theta) \right]. \quad (6)$$

By comparison with equation (1), and assuming isotropic scattering, we take $I_1 = \langle I_{\text{SC}}^{\text{E}}(\theta) \rangle \simeq c [\langle A_{\text{S,SC}}(\theta) \rangle n_{\text{S}} \Sigma_{\text{S}} + \langle A_{\text{C,SC}}(\theta) \rangle n_{\text{C}} \Sigma_{\text{C}}]$, $I_2 = \langle I_{\text{C}}^{\text{E}}(\theta) \rangle \simeq c \langle A_{\text{C,C}}(\theta) \rangle n_{\text{C}} \Sigma_{\text{C}}$ and $\mathcal{N} = 1 / \langle A_{\text{S,SC}}(\theta) \rangle$, where $\langle \dots \rangle$ represents an average over 2θ , and n_J and Σ_J ($J = \text{S}$ or 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

$$R_{\text{opt}} = \frac{t_{\text{SC,opt}}}{t_{\text{C,opt}}} \simeq \sqrt{\frac{\langle A_{\text{S,SC}}(\theta) \rangle n_{\text{S}} \Sigma_{\text{S}} + \langle A_{\text{C,SC}}(\theta) \rangle n_{\text{C}} \Sigma_{\text{C}}}{w^2 \langle A_{\text{C,C}}(\theta) \rangle n_{\text{C}} \Sigma_{\text{C}}}}, \quad (7)$$

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 $w = \langle A_{\text{C,SC}}(\theta) \rangle / \langle A_{\text{C,C}}(\theta) \rangle$. Within the small-sample limit, $A_{J,K}(\theta) \rightarrow 1$ so that equation (7) reduces to $R_{\text{opt}} = [(n_{\text{S}} \Sigma_{\text{S}} + n_{\text{C}} \Sigma_{\text{C}}) / n_{\text{C}} \Sigma_{\text{C}}]^{1/2}$.

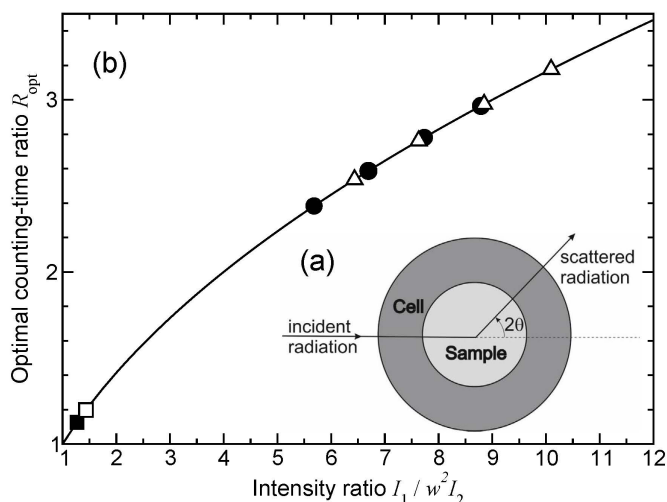


Figure 1

(a) Geometry for an angular dispersive diffraction experiment on a sample in its container. (b) The dependence of R_{opt} on $I_1 / w^2 I_2$, where $I_1 = \langle I_{\text{SC}}^{\text{E}}(\theta) \rangle$ and $I_2 = \langle I_{\text{C}}^{\text{E}}(\theta) \rangle$, for neutron diffraction experiments performed with an incident beam of width 11 mm and $\lambda = 0.5 \text{ \AA}$ on (i) powdered glassy SiO_2 (●) or Se (△), each with a packing fraction of 60%, held within a vanadium container of wall thickness $t_{\text{wall}} = 0.1 \text{ mm}$ and (with increasing intensity ratio) outer diameter ϕ of 5, 6, 7 or 8 mm; and (ii) a solid pellet of either glassy SiO_2 (■) or crystalline vanadium (□) in a $\text{Ti}_{0.676}\text{Zr}_{0.324}$ container with $\phi = 14.5 \text{ mm}$ and $t_{\text{wall}} = 4.25 \text{ mm}$, corresponding to the ambient conditions geometry for a high-pressure experiment using a Paris-Edinburgh press with single-toroid anvil geometry (Salmon & Zeidler, 2015). The scattering cross-sections per atom are 3.544, 8.30, 5.10 and 5.034 barn for SiO_2 , Se, V and $\text{Ti}_{0.676}\text{Zr}_{0.324}$ (Sears, 1992), respectively, and the corresponding atomic number densities are 0.0660, 0.0321, 0.0722 and 0.0510 \AA^{-3} , respectively. The absorption cross-sections used in the calculation of $A_{J,K}(\theta)$ were taken from Sears (1992).

Figure 1(b) shows a plot of R_{opt} versus the intensity ratio $I_1 / w^2 I_2$ 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 τ .

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 σ_{req} and I_{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_{opt} . For each of the curves given in Fig. 2, R_{opt} corresponds to the minimum where $F_{\text{req}} / F_{\text{req,opt}} = 1$. If in the performance of an experiment $R = (\tau - t_{\text{C}}) / t_{\text{C}}$ 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_{C} by 50% will increase $F_{\text{req}} / F_{\text{req,opt}}$ by $\simeq 14\%$. 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_{C} will increase $F_{\text{req}} / F_{\text{req,opt}}$ by $\simeq 8\%$.

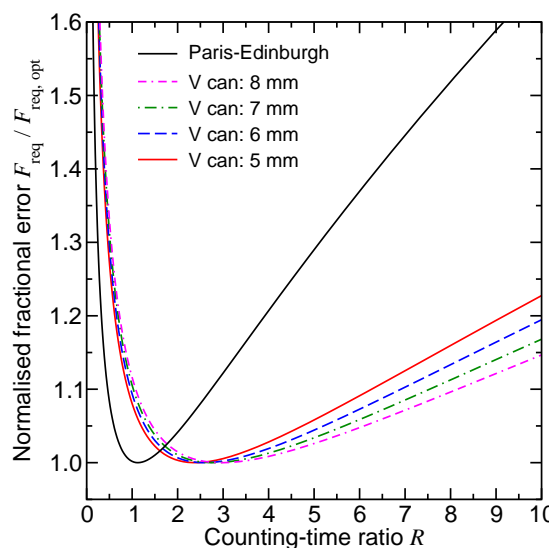


Figure 2

The dependence of the normalised fractional error $F_{\text{req}} / F_{\text{req,opt}}$ on $R = t_{\text{SC}} / t_{\text{C}}$ for glassy SiO_2 in the pressure cell or vanadium container experiments of Fig. 1.

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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