Citation for published version:

Salmon, PS, Zeidler, A & Fischer, HE 2016, 'Optimising the counting times for sample-in-container scattering experiments', *Journal of Applied Crystallography*, vol. 49, no. 6, pp. 2249-2251.
<https://doi.org/10.1107/S160057671601493X>

DOI:

[10.1107/S160057671601493X](https://doi.org/10.1107/S160057671601493X)

Publication date:

2016

Document Version

Peer reviewed version

[Link to publication](#)

University of Bath

Alternative formats

If you require this document in an alternative format, please contact:
openaccess@bath.ac.uk

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

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

Philip S. Salmon,^{a*} Anita Zeidler^a and Henry E. Fischer^b

^aDepartment of Physics, University of Bath, Bath BA2 7AY UK, and ^bInstitut Laue-Langevin, 71 Avenue des Martyrs, F-38042 Grenoble Cedex 9, France. Correspondence e-mail: p.s.salmon@bath.ac.uk

© 0000 International Union of Crystallography
Printed in Singapore – all rights reserved

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.

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 $I_1 = \langle I_{\text{SC}}^E(\theta) \rangle$ and $I_2 = \langle I_{\text{C}}^E(\theta) \rangle$, 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 $0.0510 \text{ \AA}^{-3}$, 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).

Acknowledgements: AZ is supported by a Royal Society–EPSRC Dorothy Hodgkin Research Fellowship.

References

- Fischer, H. E., Barnes, A. C. & Salmon, P. S. (2006). *Rep. Prog. Phys.* **69**, 233–299.
- Kendig, A. P. & Pings, C. J. (1965). *J. Appl. Phys.* **36**, 1692–1698.
- Paalman, H. H. & Pings, C. J. (1962). *J. Appl. Phys.* **33**, 2635–2639.
- Salmon, P. S. & Zeidler, A. (2015). *J. Phys.: Condens. Matter* **27**, 133201.
- Sears, V. F. (1985). *Nucl. Instrum. Meth. Phys. Res. B* **12**, 430–433.
- Sears, V. F. (1992). *Neutron News* **3**, No. 3, 26–37.
- Soper, A. K. & Egelstaff, P. A. (1980). *Nucl. Instrum. Methods* **178**, 415–425.
- Zeidler, A., Salmon, P. S., Martin, R. A., Usuki, T., Mason, P. E., Cuello, G. J., Kohara, S. & Fischer, H. E. (2010). *Phys. Rev. B* **82**, 104208.