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Further Remarks Concerning Optimization of Counting Times in Single-Crystal Diffractometry: Rebuttal to Killean; Considerations of Background Counting and Slewing Times

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The objections raised by Killean [*Acta Cryst.* (1969), B**25**, 977] to the validity and applicability of the optimization presented by Hamilton [ACA Summer Meeting (1967), Abstract E6] and Shoemaker [*Acta Cryst.* (1968), A**24**, 136] are discussed, and shown to be not entirely substantial; it is concluded that optimized distribution of a fixed total counting time for the determination among the various reflections may still prove useful under commonly encountered experimental conditions. Modifications of the equations of Hamilton and of Shoemaker are presented. It is shown that, within the context of fixed total counting time, the addition of background to which a portion of that counting time must be allocated (in optimized ratios; see Shoemaker, 1968) results in an increase in the optimum counting time t_j (scan plus background) per reflection to be assigned to relatively weak reflections that are highly sensitive to the parameters being determined, and a decrease in optimum counting time for weak reflections of low sensitivity and for all strong reflections. When *a priori* estimates of optimum counting times t_j (without consideration of slewing between reflections) are available, as from a previous rough determination, the question may arise as to whether a low-weight reflection k should be counted at all since its omission releases not only its optimum t_k, but also the slewing (circle-setting) time t_s as well, for distribution among the remaining reflections. It is shown for fixed *total* time (counting plus slewing) that if $t_k < t_k^*$ where $t_k^* \simeq (t_s t_k^0)^{1/2}$, the weight of the determination is increased by omitting the operations of slewing to and counting reflection k. [Here t_k^0 is defined (Shoemaker, 1968) as a counting time that would give a variance contribution due to counting statistics equal to the variance contribution due to all other sources.]

Hamilton (1967) has presented an equation giving relative counting times t_j for the various reflections j when, under certain conditions, the weight of a single parameter ξ_i is to be maximized under the constraint of a fixed total counting time for the structure determination:

$$t_j \propto (\mathrm{Lp})^{-1/2} \cdot \left| \frac{\partial |F_j|^2}{\partial \xi_i} \right| \cdot \frac{1}{|F_j|^3} \qquad (1)$$

(where the Lp factor is defined in the usual way, rather than the reciprocal as given originally by Hamilton). Shoemaker (1968) has independently derived more general equations, and has shown that they specialize to Hamilton's equation under the conditions specified, which include the condition that background counts be negligible and the condition that random error contributions to F^2 from counting statistics be small compared to those from all other sources (the latter being assumed proportional to F^2 itself). Recently Killean (1969) has claimed to demonstrate that Hamilton's equation is invalid as an optimizing condition, and that Shoemaker's equations are likely to be of rather limited applicability, particularly in regard to 'X-ray diffractometry aimed at normal stereochemical work.'

Killean's remarks concerning equation (1) apparently assume incorrectly that the range of applicability claimed for that equation includes *the limit* at which relative error contributions from counting statistics are not merely small but effectively negligible. His analysis, based on his equation (3), contains essentially nothing that cannot be found in equations (9), (10), (18) and (25) of Shoemaker and the associated discussion, other than expression of the more or less obvious fact that optimization by variation of counting times is impossible under conditions in which the weights cannot in fact depend on those counting times. Short of that limit there is an important range in which equation (1) may be regarded as valid at least as a reasonable working approximation.

In amplification, it may be helpful to present Shoemaker's equation (34) in a modified form:

$$t_j = t_j^0 \left[\left(1 + \frac{T}{T^0}\right) \frac{(\Omega_j/\lambda_j)^{1/2}}{\langle(\Omega_j/\lambda_j)^{1/2}\rangle_{j,t0}} - 1 \right]. \qquad (2)$$

The notation (Shoemaker, 1968) will be only partially reviewed here. The total time allowed for counting is T. The 'point of diminishing returns' is given by

$$T^0 = \sum_j t_j^0 \qquad (3)$$

where

$$t_j^0 \equiv \lambda_j/\kappa_j^2 \qquad (4)$$

is the counting time for reflection j that would be necessary to make the variance in the intensity for that reflection due to counting statistics equal to the variance due to all other sources of random error. The subscripts j and t^0 on the mean in equation (2) indicate that it is a weighted mean taken over all j with weights proportional to the t_j^0. κ_j^2 is the contribution to the variance in $\Delta F = F_o - F_c$ due to sources other than counting statistics [Shoemaker, 1968, equations (10) and (20)]. When background count is negligible (a case denoted by a zero subscript), then

$$\lambda_j = \lambda_{0j}$$

where

$$\lambda_{0j} \propto (\text{Lp})^{-1}. \quad (5)$$

If we further assume that

$$\kappa_j^2 \propto |F_j|^2 \quad (6)$$

and if we write for the one parameter ξ_i that is being optimized in Hamilton's treatment

$$\Omega_j^{1/2} = \Omega_{i,j}^{1/2} = \left|\frac{\partial |F_j|}{\partial \xi_i}\right| = \frac{1}{2|F_j|}\left|\frac{\partial |F_j|^2}{\partial \xi_i}\right| \quad (7)$$

then equation (2) reduces to

$$(t_j + t_j^0)_0 = \text{const.}\ (\text{Lp})^{-1/2} \cdot \left|\frac{\partial |F_j|^2}{\partial \xi_i}\right| \cdot \frac{1}{|F_j|^3} \quad (8)$$

which differs from Hamilton's equation [equation (1)] only in the presence of the added term t_j^0 on the left side, and the zero subscript which explicitly indicates the absence of background. Hamilton's equation may be regarded as a suitable working approximation if the t_j^0 are generally small in comparison to the t_j. The smaller the t_j^0 are relative to the t_j, however, the smaller effect a given variation of the t_j will have on the weight ω_i of ξ_i, and in the limit where $t_j^0 \simeq 0$ there will be no significant effect and therefore no optimization, in agreement with Killean's conclusions. To show this explicitly, we first rearrange Shoemaker's equation (18) and combine it with our equation (4) to give for the weight w_j of reflection j

$$w_j = \frac{1}{\lambda_j}\left(\frac{t_j t_j^0}{t_j + t_j^0}\right) = \frac{1}{\lambda_j}\left(\frac{1}{t_j} + \frac{1}{t_j^0}\right)^{-1}. \quad (9)$$

Differentiation gives

$$\frac{\mathrm{d}w_j}{\mathrm{d}t_j} = \frac{1}{\lambda_j}(1 + t_j/t_j^0)^{-2}. \quad (10)$$

With

$$\Omega_{i,j} \equiv \frac{\partial \omega_i}{\partial w_j}$$

[Shoemaker, equation (25)], we obtain

$$\frac{\partial \omega_i}{\partial t_j} = \frac{\Omega_{i,j}}{\lambda_j}(1 + t_j/t_j^0)^{-2} \quad (11)$$

which for finite t_j vanishes as $t_j^0 \to 0$. The optimization condition [Shoemaker, equation (32)] may be written in the present instance in the form

$$\frac{\partial \omega_i}{\partial t_j} - \alpha^2 = 0 \quad (12)$$

which for vanishing t_j^0 leads to a zero value for the Lagrangian parameter α^2, and no optimization. At the other extreme, where the non-counting random errors κ_j tend to vanish and the t_j^0 become indefinitely large, equation (12) gives

$$\frac{\Omega_{ij}}{\lambda_j} - \alpha^2 \stackrel{?}{=} 0 \quad (13)$$

as a condition of optimization, and since that condition is in general impossible of fulfillment for all j there is again no optimization, as already pointed out (Shoemaker, p. 141). Between these limits, equations (11) and (12) lead to the equations already given by Shoemaker, and to equation (2).

Equations (1) and (8) assume negligible background count; if the background count is not negligible, the counting times should be optimally divided between reflection and background [Shoemaker, equations (4–6)]. If this condition is fulfilled, the effect of adding a background scan rate R_B to a reflection that would have a scan rate R_0 without background, to give a new scan rate $R_S = R_0 + R_B$, is to increase λ_j from the value λ_{0j} that obtains in the absence of background by the factor

$$\frac{\lambda_j}{\lambda_{0j}} = [(1+\beta)^{1/2} + \beta^{1/2}]^2 \geq 1 \quad (14)$$

where $\beta = R_B/R_0$; when β is large $\lambda_j/\lambda_{0j} \to 4\beta$. Let us represent by $\bar{\lambda}$ and $\bar{\Omega}$ the appropriate kinds of means of λ and Ω over all reflections, and use a zero subscript to indicate the case where background is absent. Neglecting unity in comparison to T/T^0 (since $T \gg T^0$ is the usual case), we may rewrite equation (2) as

$$t_j = \frac{\bar{\lambda}_0}{\kappa_j^2}\left[\frac{T}{T_0^0}\left(\frac{\Omega_j}{\bar{\Omega}}\right)^{1/2}\left(\frac{\lambda_j}{\bar{\lambda}}\right)^{1/2} - \frac{\lambda_j}{\bar{\lambda}_0}\right]. \quad (15)$$

For a strong reflection, addition of background to all reflections has the effect that $\bar{\lambda}$ increases more than λ_j, while of course $\bar{\lambda}_0$ does not change at all, and the equation predicts that the t_j will invariably decrease. For a weak reflection, addition of background increases λ_j more than $\bar{\lambda}$, and t_j may increase or decrease depending on the relationship between the two terms. If a weak reflection is already one with a relatively small optimum counting time, the optimum time may go to zero and the reflection excluded; the sensitivity of the parameter to the reflection is low enough that the added time for counting background is not worth while. If a weak reflection is already one with a large optimum counting time, being a reflection that is very sensitive to the parameters, an increase in t_j (to include background counting time and also perhaps to counteract partially the resulting decrease in precision) may be indicated.

Killean's critique of Shoemaker's (1968) equations seems to be based on the assumption that for normal stereochemical X-ray work counting statistics are not usually a significant source of random error, relative to other sources. It is interesting to note in this connection that many authors of structure papers still find it necessary in refinement to employ weights based to an important degree on counting statistics, particularly when diffractometer data extend to high scattering angles where there are many weak reflections. It is also important to note in this connection that the weak reflections are usually the ones most favorable to optimization, and these are moreover the ones for which background counts are more likely to be relatively important. Killean's assumed typical conditions – ultimate G or R index 0·04 or 0·05 without including counting-statistical error – may be realistic in many cases, but if accepting them, under conditions of negligible background count, we would argue that counting-statistical error should not become really unimportant as a contributor to uncertainty until the count is at least several times his figure of 150. In the event of high background, this limit should be disproportionately higher.

Killean's remark that '... there is something suspect in limiting the counts in order to minimize the variances of the parameters' seems to miss the point of Hamilton's and Shoemaker's treatments that counts of some reflections are limited to small values so that counts of others, more sensitively related to the parameters to be refined, may have larger values so as to maximize the weight of the determination. His further remark 'It would be better to eliminate the $\sigma_1^2\{|F_{0j}|\}$ term by increasing the counts, particularly as with $I_j=150$ most of the time on the X-ray diffractometer would be spent setting the circles rather than measuring reflections' again seems to miss the point of optimization; the total counting time T is by hypothesis fixed, and cannot be increased across the board. However, since Killean has raised the matter of slewing time (setting circles), let us pursue this subject further.

If – as in the usual case in a structure determination – there is no way of knowing, before making even the first pass on a reflection, whether it should be counted or not, then the total slewing time for all reflections $T_s=nt_s$ (n = number of reflections, t_s = slewing time per reflection) is fixed and already committed, and neither affects nor is affected by what is done with the actual counting time $T=T_{\rm tot}-T_s$. If on the other hand, within the context of a fixed total time $T_{\rm tot}$, estimates of optimized w_j (and t_j) are available ahead of time, perhaps from a previous rough determination, it may be that certain low-weight reflections (k) should not be counted because, through neglecting them, not only their counting times t_k but also their slewing (circle-setting) times t_s become available to be distributed among the remaining reflections to increase the overall weight Ω of the determination. For a given reflection k there is presumably a limiting value for the previously optimized t_k [as given, for example, by equation (2)] – call it t_k^* – such that, if $t_k<t_k^*$, it is not worthwhile slewing to that reflection and counting it. Precise estimation of t_k^* would be difficult, but by the approach summarized in an Appendix to this paper it can be surmized that t_k^* is very roughly the geometric mean of t_k^0 and t_s:

$$t_k^*\simeq(t_k^0t_s)^{1/2}. \qquad (16)$$

If the condition $t_k<t_k^*$ as based on *a priori* estimates of t_k is met by only one or a very few reflections, the decision whether or not to slew to each such reflection or count it at all may be based on these *a priori* estimates and use of equation (16). If, however, the condition is met by a large number of reflections, perhaps a 'renormalization' should be involved similar to that already discussed by Shoemaker for the case $w_j<0$, since dropping some reflections will change the averages that are involved in the computation of the remaining t_k and in the derivation of equation (16). The problem of renormalization is beyond the scope of this paper, but with the advent of modern automatic diffractometers that slew rapidly on all circles simultaneously (*e.g.* Syntex $P\bar{1}$) the problem may be academic.

It remains for the present authors to acknowledge: (1) that the actual *degree* of optimization of parameter weight possible through the use of our equations under various conditions has not yet been estimated theoretically or determined experimentally; and (2) that the effect of systematic errors is largely unexplored and potentially damaging to the valid and effective application of these equations. In conclusion, we feel that the ultimate test of these equations will be only through actual experimentation with them.

APPENDIX
Derivation of equation (16)

For a given value of t_k, we will assess the change $\Delta\Omega$ in the total weight $\Omega=\sum W_i\omega_i$ of the determination [Shoemaker, 1968, equation (14)] resulting from (I) deleting the counting of reflection k altogether, followed by (II) adding t_k+t_s to the total time available for *counting* the remaining reflections under optimized conditions. We define a limiting time t_k^* such that if $t_k=t_k^*$, then $\Delta\Omega=\Delta\Omega_{\rm I}+\Delta\Omega_{\rm II}=0$; if on the other hand $t_k<t_k^*$, then $\Delta\Omega>0$, and both slewing and counting of reflection k should be eliminated. For the first step

$$\Delta\Omega_{\rm I}=\frac{\partial\Omega}{\partial w_k}\Delta w_k=-\Omega_k w_k$$

since w_k decreases to zero. [The definition of Ω_k is given by Shoemaker, equation (31).] Combination of this equation with equation (9) gives

$$\frac{1}{t_k^*}+\frac{1}{t_k^0}=-\frac{\Omega_k/\lambda_k}{\Delta\Omega_{\rm I}}=\frac{\Omega_k/\lambda_k}{\Delta\Omega_{\rm II}}\,. \qquad (17)$$

In the second step we increase the total time available *for counting* the remaining reflections by t_k+t_s. If optimization is maintained, the changes in counting times for reflections j are, from equation (2),

$$\Delta t_j = t_j^0 \left[\frac{t_k+t_s}{T_0'} \frac{(\Omega_j/\lambda_j)^{1/2}}{\langle(\Omega_j/\lambda_j)^{1/2}\rangle'_{j,t^0}}\right] \quad (18)$$

where the primes here and elsewhere indicate omission of the term $j=k$ from sums and averages. The increased reflection weights are, from equation (10),

$$\Delta w_j = \frac{\Delta t_j}{\lambda_j(1+t_j/t_j^0)^2} \; . \quad (19)$$

The increase in the weight of the determination in this step is

$$\Delta\Omega_{11} = \sum_j{}' \Omega_j \Delta w_j$$

$$= (t_k+t_s)Q_k \quad (20)$$

where

$$Q_k = \frac{\langle(\Omega_j/\lambda_j)^{3/2}/(1+t_j/t_j^0)^2\rangle'_{j,t^0}}{\langle(\Omega_j/\lambda_j)^{1/2}\rangle'_{j,t^0}} \; . \quad (21)$$

(We drop the primes and the subscript k henceforth because Q should be very nearly independent of the one term omitted in the averaging.) Thus t_k^* is defined by

$$\frac{1}{t_k^*} + \frac{1}{t_k^0} = \frac{\Omega_k/\lambda_k}{(t_k^*+t_s)Q} \; . \quad (22)$$

To get this into a useful form we must resort to approximations. We start by rewriting equation (21) as

$$Q \simeq C\,[\langle(\Omega_j/\lambda_j)^{1/2}\rangle_{j,t0}]^2/(1+T/T^0)^2 \quad (23)$$

where (at least for a given T/T_0) C is a constant presumably of order of magnitude unity. Equation (2) can be written in the form

$$\frac{(\Omega_j/\lambda_j)^{1/2}}{\langle(\Omega_j/\lambda_j)^{1/2}\rangle_{j,t0}} = \frac{1+t_j/t_j^0}{1+T/T^0} \; . \quad (24)$$

Thus, with $t_k = t_k^*$

$$\frac{\Omega_k/\lambda_k}{Q} \simeq C^{-1}\,(1+t_k^*/t_k^0)^2 \quad (25)$$

and equation (22) becomes

$$\frac{1}{t_k^*} + \frac{1}{t_k^0} \simeq C^{-1}\,(1+t_k^*/t_k^0)^2/(t_k+t_s)$$

or

$$t_k^* + t_s \simeq C^{-1} t_k^*(1+t_k^*/t_k^0) \; .$$

For the case $t_s=0$ this equation becomes

$$C \simeq 1 + t_k^*/t_k^0 \, .$$

For this case we must adjust C so that t_k^* vanishes, since the t_j have been optimized without any consideration of slewing. Hence $C=1$ and we obtain

$$t_k^* \simeq (t_k^0 t_s)^{1/2}. \quad (16)$$

Note that no assumption has been made regarding the magnitude of T relative to T^0.

To understand the operation of this equation, consider a not far from marginal reflection k for which $t_k > t_k^*$, meaning that we should slew to the reflection and count it. Suppose now that something happens that increases κ_k and thus decreases the attainable precision of the reflection intensity (*e.g.* a noisy electronic circuit). This results in a decrease in t_k^0, and therefore by equation (16) also a *decrease* in t_k^*, which momentarily runs against intuition. However t_k^* decreases only as $(t_k^0)^{1/2}$ while t_k itself decreases with the first power, by equation (2); thus, while both are decreasing, t_k may overtake t_k^* and the condition $t_k < t_k^*$ may result, so that the reflection should be omitted.

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