International Tables for Crystallography (2006). Vol. C, References, pp. 668–673.

function of the measured intensities, say $F(I_1, I_2, \ldots, I_j, \ldots)$. General statistical theory gives the usual approximation

$$\sigma^2(F) = \sum_{i,j} \frac{\partial F}{\partial I_i}\frac{\partial F}{\partial I_j}\operatorname{cov}(I_i, I_j), \quad (7.5.7.1)$$

where $\operatorname{cov}(I_i, I_j)$ is the covariance of I_i and I_j if $i \neq j$, and is the variance of I_j, $\sigma^2(I_j)$, if $i = j$. There is very little correlation* between successive intensity measurements in diffractometry, so that $\operatorname{cov}(I_i, I_j)$ is negligible for $i \neq j$. Equation (7.5.7.1) becomes

$$\sigma^2(F) = \sum_j \left(\frac{\partial F}{\partial I_j}\right)^2 \sigma^2(I_j). \quad (7.5.7.2)$$

These equations are strictly accurate only if F is a linear function of the I's, a condition satisfied for the integrated intensity, but for few other quantities of interest. In most applications in diffractometry, however, the contribution of each I_j is sufficiently small in comparison with the total to make the application of equations (7.5.7.1) and (7.5.7.2) plausible. Any proportionality factors c_j (Section 7.5.1) can be absorbed into the functional relationship between F and the I_j's.

The object is to minimize $\sigma^2(F)$ by varying the time spent on each observation, subject to a fixed total time

$$T = \sum_j t_j. \quad (7.5.7.3)$$

It is simplest to regard the total intensity and the background intensity as separate observations, so that in (7.5.7.2) the sum is over n 'background' and n 'total' observations. With I_j expressed as a counting rate, its variance is I_j/t_j [equation (7.5.3.8)], so that (7.5.7.2) becomes

$$\sigma^2(F) = \sum_j G_j^2 I_j/t_j, \quad (7.5.7.4)$$

where for brevity G has been written for $|\partial F/\partial I|$. The variance of F will be a minimum if, for any small variations $\mathrm{d}t_j$ of the counting times t_j,

* Exceptions to this statement may be important for line and area detectors, or if an interpolation function is used to estimate background. Wilson (1967) has discussed some features of the powder diffractometry case.

$$0 = -\sum_j G_j^2 I_j t_j^{-2}\,\mathrm{d}t_j, \quad (7.5.7.5)$$

subject to the constancy of the total time T. There is thus the constraint

$$0 = \sum_j \mathrm{d}t_j. \quad (7.5.7.6)$$

These equations are consistent if for all j

$$G_j^2 I_j t_j^{-2} = k^{-2}, \quad (7.5.7.7)$$

$$t_j = kG_j I_j^{1/2}, \quad (7.5.7.8)$$

where k is a constant determined by the total time T:

$$T = k\sum_j G_j I_j^{1/2}. \quad (7.5.7.9)$$

The minimum variance is thus achieved if each observation is given a time proportional to the square root of its intensity. A little manipulation now gives for the desired minimum variance

$$\sigma^2_{\min}(F) = \frac{1}{T}\left[\sum_j \left(\partial F/\partial I_j\right) I_j^{1/2}\right]^2. \quad (7.5.7.10)$$

The minimum variance is found to be a perfect square, and the standard uncertainty takes a simple form.

Here, the optimization has been treated as a modification of fixed-time counting. However, the same final expression is obtained if the optimization is treated as a modification of fixed-count timing (Wilson, Thomsen & Yap, 1965).

Space does not permit detailed discussion of the numerous papers on various aspects of optimization. If the time required to move the diffractometer from one observation position to another is appreciable, the optimization problem is affected (Shoemaker & Hamilton, 1972, and references cited therein). There is some dependence on the radiation (X-ray *versus* neutron) (Shoemaker, 1968; Werner 1972*a*,*b*). A few other papers of historical or other interest are included in the list of references, without detailed mention in the text: Grant (1973); Killean (1972, 1973); Mack & Spielberg (1958); Mackenzie & Williams (1973); Szabó (1978); Thomsen & Yap (1968); Zevin, Umanskii, Kheiker & Panchenko (1961).

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