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Optimization of scan procedure for single-crystal X-ray diffraction intensities.

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An equation is developed for the times to be spent on the ordinates of a scan of a reflexion in order to obtain the minimum counting-statistics error in the integrated intensity for a given total scan time.

Recently several authors (Hamilton, 1967; Shoemaker, 1968; Killean, 1969; Shoemaker & Hamilton 1972; Killean, 1972) have discussed the optimization of diffractometer data collection and Werner (1972) has critically examined the modes of scan. Little attention* appears to have been given to the optimization of individual single-crystal integrated intensities. Wilson, Thomsen & Yap (1965) have developed formulae for the minimization of parameters derived from X-ray powder diffractometer line profiles. Their method is applicable to the optimum measurement of single-crystal integrated intensities and is now developed for this particular case.

The usual method of measuring an integrated intensity, N, is to measure the count rate, N_i, for a constant time at each equally spaced ordinate and define the integrated intensity as

$$N=\sum_{i=0}^{n} A_iN_i \text{ counts/unit time} \qquad (1)$$

where the constants A_i depend on the form of the numerical integration formula being used. It has been usual for the trapezoidal method to be used with $A_0=A_n=0{\cdot}5$ and, for all other i, $A_i=1$, but it should be noted that with the use of computer-controlled diffractometers in particular there is reason why more accurate forms of numerical integration with equally spaced ordinates should be used (see, for example, Grove, 1966, for details of the A_i's).

To determine the optimum time, t_i, to be spent measuring the ith ordinate, a rapid scan through the peak is used to determine R_i, the count rate. This value of R_i will be replaced in the real experiment by a more accurate count rate N_i giving a final estimate of the integrate intensity as in (1).

A time t_i spent measuring the count rate N_i gives a variance in N_i of

$$\sigma^2(N_i)=\frac{N_i}{t_i}$$

which is initially estimated as R_i/t_i.

From (1)

$$\sigma^2(N)=\sum_{i=0}^{n} A_i^2\sigma^2(N_i)$$

$$\simeq \sum_{i=0}^{n} \frac{A_i^2R_i}{t_i}\,. \qquad (2)$$

The optimization process states that the variance of N should be a minimum subject to the condition that the total time, T, is

$$T=\sum_{i=0}^{n} t_i\,. \qquad (3)$$

Minimize the function, φ with respect to the t_i's, where

$$\varphi=\sigma^2(N)-\lambda^2\,(T-\sum_{i=0}^{n} t_i)$$

$$=\sum_{i=0}^{n}\frac{A_i^2R_i}{t_i}-\lambda^2(T-\sum_{i=0}^{n} t_i)$$

and λ is a constant.

$$\frac{\partial\varphi}{\partial t_i}=-\frac{A_i^2R_i}{t_i^2}+\lambda^2=0$$

$$t_i=\frac{A_iR_i^{1/2}}{\lambda}\,. \qquad (4)$$

Let

$$\frac{\sigma(N)}{N}=k \qquad (5)$$

be the required degree of precision. The total time that must be spent measuring this reflexion is

$$T=\sum_{i=0}^{n} t_i$$

$$=\frac{1}{\lambda}\sum_{i=0}^{n} A_iR_i^{1/2}$$

and from (2)

$$\sigma^2(N)=\lambda\sum_{i=0}^{n} A_iR_i^{1/2}$$

$$=\frac{1}{T}\{\sum_{i=0}^{n} A_iR_i^{1/2}\}^2$$

$$\text{and}\quad T=\left\{\frac{\sum_{i=0}^{n} A_iR_i^{1/2}}{k\sum_{i=0}^{n} A_iR_i}\right\}^2. \qquad (6)$$

Each individual ordinate is measured for a time

$$t_i=A_iR_i^{1/2}\left(\frac{T}{\sum_{i=0}^{n} A_iR_i^{1/2}}\right). \qquad (7)$$

The practical use of (6) and (7) will depend on the strategy of the individual experimenter. It is suggested that the various R_i are obtained from a rapid step scan at large Δi and linear interpolation. Equation (6) can be evaluated for various values of k and the experimenter's criteria applied with regard to cost effectiveness. The t_i for each step are then determined from (7) and the measured integrated intensity obtained from (1). Alternatively, particularly when the background counts are relatively high, other criteria will be prefered for deciding that an intensity should be measured and then only (7) will be used to determine the optimum time, t_i, for each step (Grant, 1973).

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* After submission of this note and during a visit to the Division of Chemical Physics, CSIRO, Melbourne the author's attention was drawn to a research programme carried out by J. K. Mackenzie and F. J. Williams at the CSIRO Divisions of Tribophysics and Mathematical Statistics some fifteen years ago but unpublished because of the state of diffractometer instrumentation at that time. Mackenzie and Williams's (1973) treatment which is more extensive as it considers profile shapes and background measurements leads to equations (6) and (7) in this note and is in complete agreement with the present results.

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Single-crystal diffractometer data: the on-line control of the precision of intensity measurement.

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A method is described for single-crystal data collection to a prestated counting-statistics precision. Procedures for dealing with weak and accidentally absent reflexions are included.

Four-circle diffractometer systems with on-line computer control provide an opportunity for measuring each reflexion in a data collection to a prestated (counting statistics) precision. The required precision will depend on the type of problem under investigation (and the precision of the results required) and could be the same for every reflexion or a function of θ and $|F_o|$. If, before each reflexion is measured, an estimate of its integrated intensity is found by measurement for a short trial time q, then the least time T needed to ensure the required precision can be calculated. The mode of integration is not considered here (Killean, 1973). There will, however, be a maximum time T_m that can reasonably be spent measuring any one reflexion and it will not be possible in this time to achieve the required precision for some weak reflexions. A predicted precision for such a reflexion, if measured for the maximum time, can be found and if the precision does not satisfy a criterion for the precision of weak reflexions, then the reflexion is deemed to be 'accidentally absent' and not measured.

If the fractional precision required for a given reflexion is k, then

$$k=\frac{\sigma(C)}{C}$$

where C is the net integrated counts. If I and B are the peak and background counts, B being measured for a time $1/n$th of that for I, then

$$k=\frac{(I+n^2B)^{1/2}}{(I-nB)}\,.$$

For the trial time q, the corresponding counts are I_q and B_q, $C_q=I_q-nB_q$ and $\sigma(C_q)=(I_q+n^2B_q)^{1/2}$. To ensure that a reflexion is almost certainly being measured to at least the precision of k,

$$C'_q=C_q-2\sigma(C_q)$$

is used instead of C_q to calculate T.

If $f=\frac{T}{q}$ then

$$k=\frac{\{f(I_q+n^2B_q)\}^{1/2}}{fC'_q} \tag{1}$$

and

$$f=\frac{(I_q+n^2B_q)}{(kC'_q)^2}\,.$$

A further remeasurement of the reflexion for a time $q(f-1)$ when added to the trial measurement will give the required k. If $T<q$, then no further measurement is necessary for such a strong reflexion.

If $T>T_m$, a decision has to be taken whether or not the weak reflexion is to be measured. The predicted precision k', if the reflexion were measured for T_m, would be from (1):

$$k'=\frac{\{f_m(I_q+n^2B_q)\}^{1/2}}{f_mC'_q} \tag{2}$$

where $T_m=f_mq$. A criterion for measuring this reflexion would be $k'<k_c$ where k_c is a prestated acceptable precision for weak reflexions. Almost all such reflexions satisfying this criterion when measured for T_m would have at least the precision k_c. Very weak reflexions for which $k'>k_c$ would not be acceptable in the data set, would not be further measured and would be considered to be accidentally absent. It is possible if q is made too small, that C'_q could become negative for some very weak reflexions. Then it would be preferable to use C_g in equation (2) for the weak-reflexions criterion. However, a better choice of q at the outset of the experiment can confine the negative C'_q to those very weak reflexions which would anyway be considered accidentally absent.

This method of data collection has the advantages (i) of economy in the use of diffractometer time by measuring each reflexion for the least time necessary to ensure a certain precision and (ii) of a further saving in time by measuring only those weak reflexions for which a satisfactory precision can be predicted (an important consideration when collecting data from crystals with high temperature factors).

This measuring routine has been incorporated into the on-line control by an IBM 1130 computer of a Siemens AED diffractometer. The preset parameters for a data collection include k, k_c, q and T_m. Typically q is made $\frac{1}{25}$th to $\frac{1}{50}$th of T_m which itself is chosen by considering k in relation to the intensity expected from weak reflexions and the time available for the experiment.

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