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# Optimization of the Measuring Time in Diffraction Intensity Measurements

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In practice, there are two methods of measuring the integrated intensity of a diffraction peak. Both can be optimized, that is, performed in such a way as to give the intensity, with a given accuracy, during a minimum measuring time. These optimizing processes are described along with a third, so-called absolute optimum, method. The three methods are compared and their relative merits discussed.

## 1. Introduction

There are basically two working modes of measuring the integrated intensity of a diffraction peak. In both the measurements are made step-by-step, with the points at equal intervals in scattering angle in both the peak and background ranges of the considered reflection. At each point in one mode the number of counts during some constant time is measured; in the other, the time necessary for a constant number of counts to be reached is measured. Both are easy to perform, as modern diffractometers incorporate these two working modes.

The two methods are susceptible to optimization. That is, with the integrated intensity required to have a given accuracy (taken as its standard deviation), there will be a definite choice of the times or counts in the peak and background ranges, which make the total measuring time a minimum.

It will be seen that the total measuring time has an absolute minimum which corresponds to a third method, consisting in using at each point a different, suitable time.

Of these three optimizing processes only the constant-time method has been discussed in the literature (Szabó, 1964; Arndt & Willis, 1966). The formulae for the optimum total time and the counts or times to be used at each point will be derived here for the other two methods. However, in order to give uniformity to the discussion, first the derivation of the formulae corresponding to the constant-time method will be repeated.

Finally, by comparing the different formulae, the relative merits of the three methods will be discussed.

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## 2. Optimization

The integrated intensity may be expressed as

$$I=\int_p Y\,\mathrm{d}\theta-\int_b Y\,\mathrm{d}\theta, \qquad (1)$$

where $Y$ is the intensity in counts $\mathrm{s}^{-1}$, and the integrals are to be taken over the peak ($p$) or the background ($b$) range of the scattering angle $\theta$. Obviously, it is assumed here that these two ranges have the same width $L$. In the following the differential symbol $\mathrm{d}\theta$ will be dropped from the integrals, to simplify writing.

In fact, the integrals in (1) should be replaced by sums over the measured points. For simplicity, the same, sufficiently large, number $n$ of points will be assumed for the two ranges. This does not affect the total times, as may be easily seen. Rearranging the sums, we have

$$I=\sum_p\frac{L}{n}\,Y-\sum_b\frac{L}{n}\,Y=\sum_p\frac{L}{nt}\,Yt-\sum_b\frac{L}{nt}\,Yt, \qquad (2)$$

where $t$ is the measuring time, and $Yt$ the number of counts at each point. Assuming a Poisson distribution in counting statistics and neglecting the error in $t$, we obtain for its standard deviation $\sigma_I$ (Beers, 1957):

$$\sigma_I^2=\sum_p\frac{L^2}{n^2t^2}\,Yt+\sum_b\frac{L^2}{n^2t^2}\,Yt=\sum_p\frac{L^2}{n^2}\frac{Y}{t}+\sum_b\frac{L^2}{n^2}\frac{Y}{t}. \qquad (3)$$

### 2.1. *Constant time (c.t.) method*

In this method $t$, the time per measurement, is $t_p$ in the peak range and $t_b$ in the background range. The $t_p$ and $t_b$ are constants within their respective ranges, thus they can be removed from the summations. We want to find the minimum of the total time

$$T_{\mathrm{c.t.}}=nt_p+nt_b, \qquad (4)$$

considered as function of $t_p$ and $t_b$, with the constraint expressed by (3), which in this case reads:

$$\sigma_I^2 = \frac{1}{t_p}\sum_p \frac{L^2}{n^2} Y + \frac{1}{t_b}\sum_b \frac{L^2}{n^2} Y. \quad (3a)$$

Applying the usual (Lagrange multiplier) method of finding the minimum, and changing the sums back to integrals, we arrive at

$$t_p = \frac{1}{\sigma_I^2}\frac{L^2}{n^2}\left(\sqrt{\sum_p Y} + \sqrt{\sum_b Y}\right)\sqrt{\sum_p Y}$$
$$= \frac{1}{\sigma_I^2}\frac{L}{n}\left(\sqrt{\int_p Y} + \sqrt{\int_b Y}\right)\sqrt{\int_p Y}. \quad (5)$$

The formula for $t_b$ is obtained by interchanging the subscripts $p$ and $b$ in (5). For the optimum total time we thus have

$$T_{\text{c.t.}} = \frac{L}{\sigma_I^2}\left(\sqrt{\int_p Y} + \sqrt{\int_b Y}\right)^2. \quad (6)$$

### 2.2 *Constant count (c.c.) method*

Here we use the numbers of counts $N_p$ and $N_b$, each constant within its respective range. The measuring time at each point is

$$t = \frac{N_p}{Y} \text{ or } \frac{N_b}{Y}. \quad (7)$$

Substituting this in the constraint (3), and finding the minimum of the total time

$$T_{\text{c.c.}} = \sum_p \frac{N_p}{Y} + \sum_b \frac{N_b}{Y}, \quad (8)$$

considered as a function of $N_p$ and $N_b$, we arrive at

$$N_p = \frac{1}{\sigma_I^2}\frac{L}{n}\left(\sqrt{\int_p Y^2}\sqrt{\int_p \frac{1}{Y}} + \sqrt{\int_b Y^2}\sqrt{\int_b \frac{1}{Y}}\right)\sqrt{\int_p Y^2}\Big/\sqrt{\int_p \frac{1}{Y}}. \quad (9)$$

The formula for $N_b$ is obtained by interchanging here the subscripts $p$ and $b$. For the optimum total time we obtain

$$T_{\text{c.c.}} = \frac{1}{\sigma_I^2}\left(\sqrt{\int_p Y^2}\sqrt{\int_p \frac{1}{Y}} + \sqrt{\int_b Y^2}\sqrt{\int_b \frac{1}{Y}}\right)^2. \quad (10)$$

### 2.3. *Absolute optimum (abs.) method*

Now we take all the times $t$ as independent variables, *i.e.* we allow at each point different measuring times, related only by the constraint (3). In this case we search the minimum of the total time

$$T_{\text{abs.}} = \sum_p t + \sum_b t, \quad (11)$$

considered as a function of all the $t$ values. We arrive at

$$t = k\sqrt{Y}, \text{ with } k = \frac{1}{\sigma_I^2}\frac{L}{n}\left(\int_p \sqrt{Y} + \int_b \sqrt{Y}\right) \quad (12)$$

valid for all the points in both ranges. For the optimum total time we have now

$$T_{\text{abs.}} = \frac{1}{\sigma_I^2}\left(\int_p \sqrt{Y} + \int_b \sqrt{Y}\right)^2. \quad (13)$$

## 3. Discussion

As to the selection between the different methods, there is confusion in the literature. Klug & Alexander (1974) show no preference, and Cullity (1956) expressly recommends the method which will be shown to be the least suitable.

In order to choose between the three methods, the following points must be taken into account.

(1) *The total time.* It is important to note that the ratios of the optimum total times obtained for the three cases are independent of the vertical ($Y$) or the horizontal ($\theta$) scale used, and that they are also independent of $\sigma_I$.

By using the well-known formulae

$$\bar{f}^2 \leq \overline{f^2} \quad \text{and} \quad 1/\bar{f} \leq \overline{(1/f)}, \quad (14)$$

valid for any positive function $f$, where the bars denote mean values, it is easy to show that

$$T_{\text{abs.}} \leq T_{\text{c.t.}} \leq T_{\text{c.c.}}. \quad (15)$$

It is not so easy to give the ratios of our optimum times in the general case. We may rather evaluate them for a convenient peak form, for which the integrals are elementary. Of the commonly used peak forms, the most satisfactory are the 'square peak', for which all these optimum times are equal, and the 'triangular peak' (Fig. 1), for which we give in Table 1 the calculated time ratios.

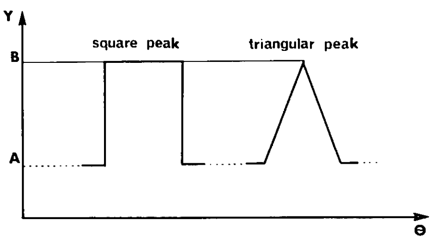


Fig. 1. Two commonly used peak forms.

Table 1. *Time ratios for the triangular peak*

| $(B-A)/A$ | $T_{c.t.}/T_{abs.}$ | $T_{c.c.}/T_{abs.}$ |
|---|---|---|
| 0 | 1 | 1 |
| 1 | 1·005 | 1·05 |
| 10 | 1·05 | 1·60 |
| 100 | 1·10 | 3·07 |
| 1000 | 1·12 | 4·92 |
| ∞ | 1·125 | $\infty\left(=0{\cdot}75 \ln \dfrac{B-A}{A}\right)$ |

(2) *Calculations required.* In this respect the constant-time method is the best, as only the intensity integrals appear, which must be calculated anyway for finding $I$. Next is the absolute optimization, where in each range one integral, that of $\sqrt{Y}$, is needed. The worst is the constant-count method, where in each range two integrals, those of $Y^2$ and of $1/Y$, must be calculated.

(3) *Experimental feasibility.* We have also to keep in mind that the constant-time and the constant-count methods are equally easy to perform, whereas the measurements corresponding to the absolute optimization would be rather laborious.

## 4. Conclusions

The constant-time should always be preferred to the constant-count method, as the latter is in no respect better than the former. The selection between the constant time and the absolute methods is somewhat arbitrary, as in some respects one or the other is favoured. For most practical cases, however, we would use the constant-time method.

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### References

ARNDT, U. W. & WILLIS, B. T. M. (1966). *Single Crystal Diffractometry*. Cambridge Univ. Press.
BEERS, Y. (1957). *Theory of Error*. New York: Addison-Wesley.
CULLITY, B. D. (1956). *Elements of X-ray Diffraction*. New York: John Wiley.
KLUG, H. P. & ALEXANDER, L. E. (1974). *X-ray Diffraction Procedures*. New York: John Wiley.
SZABÓ, P. (1964). *Rep. Centr. Res. Inst. Phys. Budapest*, **12**, 257–261.

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# Complete List of Subgroups and Changes of Standard Setting of Two-Dimensional Space Groups

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To illustrate the efficiency of a systematic method of derivation of subgroups [Billiet, *Bull. Soc. Fr. Minéral. Cristallogr.* (1973), **96**, 327–334], the authors have tabulated the complete list of standard settings of every subgroup of any two-dimensional space group.

In other papers (Billiet, 1973; Billiet, Sayari & Zarrouk, 1978), we have given much information, concerning a systematic method of deriving subgroups (which are space groups again) of space groups. This method has enabled us to find all the subgroups of the triclinic and monoclinic space groups (Sayari & Billiet, 1977).

Here a new example of the efficiency of this method is given. We have listed the subgroups and the changes of standard setting of the two-dimensional space

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