

(B) leading to the same value of the absolute scale obtained in that work and is also identical with the sample on which the relative measurements were carried out. It is worth noting that the pressure values given in that work were the values of total forces on a sample of area of 2 cm². The corrected values, f_{ps}^c , are given in Table 1. As the result of the correction, the small amount of reduction which was found in the previous study does not seem to exist, or at least it is comparable to the experimental errors.

A careful treatment of the effects of porosity and surface roughness is important in order to give more reliability to the experimental values of X-ray structure factors obtained

with powders. An effort to correct for these effects by a parameter determined by measurements of fluorescent intensity from copper powder samples of different particle size is in progress.

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Simplified method of computing centroids of X-ray profiles. By JOHN S. THOMSEN, *Department of Physics, The Johns Hopkins University, Baltimore, Maryland 21218, U.S.A.* and F. Y. YAP, *Department of Physics, Wilson College, Chambersburg, Pennsylvania 17201, U.S.A.*

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One definition employed by crystallographers in fixing the centroid of an X-ray diffraction profile has previously involved in its application the use of successive approximations. A simplified method, sufficiently accurate to eliminate such iterations in most cases, is given, based on the Thomsen & Yap analysis of statistical errors in centroid, median, and peak. Certain differences between the above error analysis and Wilson's recent work are discussed briefly.

Crystallographers have frequently employed the centroid of experimentally observed diffraction profiles in the determination of crystal grating constants (Pike & Wilson, 1959; Taylor, Mack & Parrish, 1964). From a mathematical standpoint it would be desirable to deal with the centroid of the entire profile, *i.e.* with integration limits $\pm\infty$; in this case, the convolution theorem for the addition of centroids would be rigorously applicable. In practice, of course, the use of some finite truncation limits is unavoidable.

Taylor, Mack & Parrish considered several possible conventions for defining such limits and recommended the following: An angular range which is large compared with the width of the aberration functions is selected and located symmetrically about the centroid of the observed curve to establish the truncation range. Since this centroid position is obviously not known *a priori*, they suggest the use of successive approximations.

In the present note we describe a simplified procedure which usually eliminates the need for any iterations. We have recently completed a comprehensive analysis of statistical errors in various possible wavelength criteria – centroid, median, and peak (Thomsen, 1965; Wilson, Thomsen, & Yap, 1965; Thomsen & Yap, 1968). The simplified technique for locating the centroid constituted a relatively minor part of the rather lengthy Thomsen & Yap paper. Hence it seems useful to give a slightly modified derivation here.

Let us denote the abscissa variable (wavelength, energy, or angle) by v and the ordinate (counts or intensity) by $f(v)$. We will take the initial guess (zeroth approximation) for the centroid of the truncated profile as the origin of v . Let the result of the first iteration (first approximation) be c_1 and the true centroid position be c . The specified truncation range will be taken as $2V$; initially this range is simply $-V \leq v \leq V$. Thus the first approximation c_1 is given by

$$c_1 = \frac{\int_{-V}^V vf(v)dv}{\int_{-V}^V f(v)dv} \quad (1)$$

The true centroid is defined in terms of the range $c - V \leq v \leq c + V$, which involves the as yet unknown position c . The integrand in the denominator of equation (1) is always positive and is relatively small for large v ; hence the denominator will be only slightly affected if the range of integration is translated by the small displacement c . On the other hand, the numerator will be quite sensitive to such a shift; in fact it will differ from zero only because $c \neq 0$, *i.e.* only because of the inaccuracy of the initial guess. Thus, with a slight approximation, we may rewrite equation (1) as

$$c_1 \approx \frac{\int_{c-V}^{c+V} vf(v)dv}{\int_{c-V}^{c+V} f(v)dv} = \frac{\int_V^{c+V} vf(v)dv - \int_{-V}^{c-V} vf(v)dv}{\int_{-V}^V f(v)dv} \quad (2)$$

The first term on the right hand side is, by definition, the true centroid c . Thus, with an obvious additional approximation, we may rewrite the above expression as

$$c_1 \approx c - rc, \quad (3)$$

where

$$r \equiv \frac{V[f(V) + f(-V)]}{\int_{-V}^V f(v)dv} \quad (4)$$

This parameter r contains only experimentally determined quantities. Physically it represents the ratio of the average heights at the end points $\pm V$ to the average height over the entire range $-V \leq v \leq V$. Hence it will obviously be less than unity for all cases of interest.

Equation (4) now yields immediately

$$c = c_1 / (1 - r). \quad (5)$$

This expression gives the true centroid c in terms of experimentally known quantities without the need of successive approximations. If data are recorded at reasonably closely spaced abscissa intervals, the integrals in equations (1) and (4) can, of course be replaced by the corresponding sums. Furthermore the zeroth approximation and the range may usually be chosen so as to eliminate the use of fractional abscissa intervals at the end points.

While the above derivation involves certain approximations, the resulting errors will normally be small. It can be shown that the *fractional* error in c will usually be of the order of $(c/w)^2 + |sc/w|$, where w is the full width of the profile at half intensity and s is the index of asymmetry as defined by Sauder (1966). In our error calculations we employed the model given by equation (II. 9) of Thomsen & Yap (1968), which we termed an 'asymmetric witch'. For this model, with $s = 0.25$, $c = 0.05 w$, and a total truncation range of only $2w$, we compute a fractional error of 0.5% in c . For wider truncation ranges the error becomes still smaller.

Very recently Wilson (1967) published a paper which also includes a treatment of the statistical errors in the centroid, median, and peak. Aside from superficial aspects, his results for centroid and median differ from ours in one significant respect, *i.e.* he ignores any statistical error in the determination of the truncation limits. Clearly, if we use the centroid definition recommended by Taylor, Mack & Parrish, the random intensity fluctuations responsible for the statistical error in c_1 also produce an error in the truncation limits. For this case, it can be shown (Thomsen &

Yap, 1968) that the net effect is to multiply Wilson's error by a factor $(1-r)^{-1}$. Another interesting consequence of employing the Taylor, Mack & Parrish definition is to eliminate any error due to uncertainty in the correction for a *constant* background.

Admittedly the factor $(1-r)^{-1}$ is quite close to unity (~ 1.05) for the large truncation ranges generally used by crystallographers. However, if we consider a Lorentzian profile with a truncation range of twice the full width, this factor increases the error by more than 50%. Other methods of truncation also involve additional statistical error, although the analysis may be less straightforward. Similar considerations apply to the median.

It should also be noted that Wilson's equation (27) (for the standard deviation of the peak as determined by a parabolic fit) is dimensionally correct only if the quantity I in his equation (26) represents counts rather than intensity (counts per unit time). With this modification it becomes a special case of our result for a polynomial fit. Wilson (1965) had previously derived this equation with all terms properly defined, but neglected to transform the notation when quoting it in his recent paper.

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Notes and News

Announcements and other items of crystallographic interest will be published under this heading at the discretion of the Editorial Board. The notes (in duplicate) should be sent to the General Secretary of the International Union of Crystallography (G. Boom, Laboratorium voor Fysische Metaalkunde der Rijksuniversiteit, Universiteitscomplex Paddepoel, Groningen, The Netherlands). Publication of an item in a particular issue cannot be guaranteed unless the draft is received 8 weeks before the date of publication.

International Union of Crystallography

Structure Reports

The Executive Committee has pleasure in announcing that Volume 22 of *Structure Reports*, covering the literature for 1958, was published in August. Volume 23 (1959) had been published earlier. Volumes 24 (1960), 26 (1961), 27 (1962) and Volume 25 (the cumulative index for 1951-60) are now with the press and will be ready in 1968-69.

Volumes 22, 24 and 26 each consist of 800-900 pages. Their prices are (Netherlands Guilders) f140 (or at present rates of exchange \$39 or £16.8s.). The price of Volume 25 (Index) will be f90 (\$25.00 or £10.10s.).

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