

Fig. 4. True transmission (dashed line), approximation (full line), and approximation modified with θ -dependence of the transmission of a sphere (dotted line). $\mu = 50 \text{ cm}^{-1}$.

The first method is to use the A' and equation (9) and to solve for the wanted J^H .

The other variant is to neglect the A' and to use only the J^H , which should have a higher accuracy than the A' . For that purpose, $A_{p,s}$ has to be expressed in

the form of a multiple regression equation, using equation (2).

$$A_{p,s} \simeq b_0 + b_1 f_1 + b_2 f_2 + \dots + b_n f_n = J_{p,s}^H / J^H, \quad (10)$$

where $f_1, f_2 \dots f_n$ are non-linear functions of six variables, namely the direction-cosines of the primary-beam direction p and the secondary-beam direction s . The number and form of the f 's depend on the form of the $A_{p,s}$ in a particular case.

The coefficients $b_0, b_1, b_2 \dots b_n$ can be obtained by a least-squares method from the same measurements, which served before the determination of A' , because the right-hand side of (10) is now known. The advantage of this more complicated procedure is a certain damping effect depending on the form of the f 's, which may be desirable because of errors in the A' .

Reflexions are at present being measured on a crystal of known shape and it is planned to compare our experimental transmission values with those calculated in the normal way.

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A Semi-Empirical Method of Absorption Correction

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An extension of Furnas's method is described. The variation of intensity of an axial reflexion as the crystal is rotated about the goniometer axis is used to give a curve of relative transmission T against azimuthal angle φ for the corresponding reciprocal lattice level. Transmission coefficients for any general reflexion hkl are then given approximately by $T(hkl) = [T(\varphi_{\text{inc}}) + T(\varphi_{\text{ref}})]/2$ where φ_{inc} and φ_{ref} are the azimuthal angles of the incident and reflected beams. Equations are derived for φ_{inc} and φ_{ref} and the accuracy of the method is discussed.

1. Introduction

Although crystal structure analyses are frequently carried out with intensity measurements that have not been

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corrected for absorption of the X-rays in the crystal, it is well known that proper treatment of absorption effects is essential when great accuracy is required, particularly of thermal parameters (*cf.* Srivastava & Lingafelter, 1966), or when use is made of intensity differences in the determination of phases as in the analysis of protein structures by the method of isomorphous replacement. The determination of absorption corrections has, therefore, received a great deal of attention

and a number of ingenious methods have been suggested for dealing with the problem. The methods in use up to 1958 are summarized in *International Tables for X-ray Crystallography* (1959). In addition to the important practical method of simplifying the problem by use of a crystal of spherical or cylindrical shape, they include the computer calculation of absorption corrections, for example, by the method of Busing & Levy (1957). More recently de Meulenaer & Tompa (1965) have developed a new computer program based on the analytical method of Howells (1950) which they have extended to cover the three-dimensional problem in a general way.

Particularly in the study of complex structures, however, analytical computer methods suffer from two main disadvantages. In the first place they are uneconomical of computer time and when many thousands of measurements have to be corrected, as in the study of protein structures, the time is unacceptably long. The second and more important difficulty, however, is that these methods require precise measurement of the crystal dimensions, which may be difficult if not impossible to achieve if the crystal morphology is unfavourable. In the study of protein crystals this difficulty also is magnified because it is necessary to take into account not only the crystal but also its mounting, which usually comprises a glass capillary in which it is enclosed in contact with some mother liquor (*e.g.* King, 1954). Wells (1960) has described an extension of the Busing & Levy method designed to cope with such specimens which was used in the measurement of reflexions to 1.4 Å spacing from myoglobin crystals (Blake, Phillips & Watson, unpublished) but this still involves an oversimplification of the problem which is usually inappropriate.

There is, therefore, a need for a method suitable for routine use with complex specimens, easy to apply and quickly calculated, and the purpose of this paper is to describe such a method which we have been using for some time. It is based upon the method suggested by Furnas (1957) which makes use of the fact that the variation of absorption in a crystal can be assessed by measuring the variation in the intensity of a Bragg re-

flexion as the crystal is rotated about the normal to the corresponding reflecting planes.

2. Furnas's method

The method is described most easily with reference to diffractometers with inclination-Weissenberg geometry, such as the Linear Diffractometer (Arndt & Phillips, 1961), though the diffraction geometry of a four-circle instrument operated in the usual way as a 'cone-diffractometer' (Furnas & Harker, 1955) is essentially the same (Wells, 1960; Phillips, 1964).

In these diffractometers the crystal is mounted for rotation (φ) about the main axis of the instrument which can be tilted through angles $\mu \leq 45^\circ$ towards the incident X-ray beam. When used in the equi-inclination setting the arrangement is such that the incident and reflected X-ray beams are inclined at equal angles to the axis of crystal rotation so that the mean of these two directions always lies in the plane perpendicular to the rotation axis. Furnas's method is based on the assumption that the absorption of any reflexion is the same as that suffered by an X-ray beam passing through the crystal in the mean direction of the incident and reflected beams, and hence is a function only of φ .

Suppose that the crystal has orthogonal axes and is mounted for rotation about **a**. Then by setting the inclination to the appropriate angle given by

$$\sin \mu = ha^*/2 \quad (1)$$

a reflexion $h00$ is obtained which can be observed at all values of φ since variation of this angle serves only to rotate the crystal about the normal to the reflecting planes. The intensity of such a reflexion can be studied therefore as a function of φ ; a typical result is shown in Fig. 1. Such a variation in intensity provides a measure of the relative absorption suffered by X-rays passing through the crystal in mean directions perpendicular to the rotation axis such as *AA*, *BB*, *CC* in Fig. 2(a), and according to Furnas, relative absorption corrections for general hkl reflexions are given by:

$$A(hkl) = I_{\max}(\varphi)/I(\varphi_{hkl}) = 1/T(hkl), \quad (2)$$

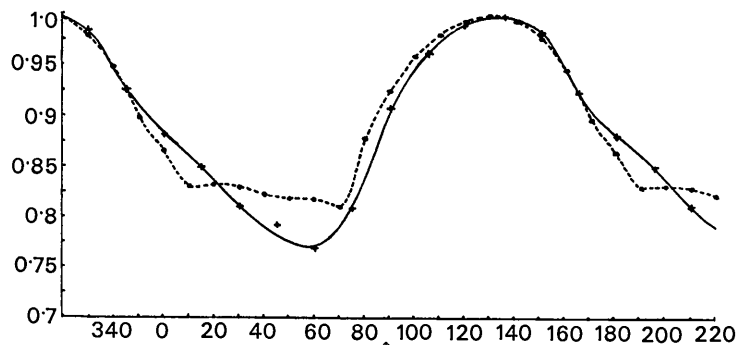


Fig. 1. Variation of relative transmission with azimuthal angle φ . Solid line, as measured; broken line, as calculated, neglecting effect of mother liquor and capillary, by the use of *ORABS*.

where I_{\max} is the maximum intensity observed for the $h00$ reflexion as φ is varied over 360° and φ_{hkl} is the angle at which the hkl reflecting planes [AA in Fig. 2(b)] are parallel to the incident X-ray beam. $T(hkl)$ is the corresponding relative transmission factor.

2.1 Calculation of φ

When the reciprocal lattice is described in spherical polar coordinates with the polar axis parallel to the axis of crystal rotation the angle φ is simply the azimuthal angle measured with reference to some convenient origin. It is useful to distinguish two types of setting. In the first of these, which has to be used with diffractometers having Weissenberg geometry, the polar axis coincides with a crystal axis so that the axis of crystal rotation is perpendicular to a principal reciprocal-lattice plane. This has the disadvantage that, unless the axis of rotation is also a reciprocal lattice axis, some general reflexion that happens to lie on or near the axis of rotation must be used in assessing the absorption corrections. In the second type of setting, commonly used with four-circle diffractometers, the axis of crystal rotation coincides with a reciprocal-lattice axis and derivation of the empirical absorption corrections is straightforward.

Let the lengths a^* , b^* , c^* and the angles α^* , β^* , γ^* define the unit-cell of a reciprocal lattice with a right-handed system of axes. The crystal is supposed to be mounted for rotation about either the a axis or the a^* axis and conveniently the origin of φ is defined as the angle at which b^* is perpendicular to the incident X-ray beam, with the c^* axis lying within the sphere of reflexion.

Then in the

a-axis mounting,

$$\tan \varphi_{hkl} = \frac{(lc^* + ha^* \cos \beta^*) \sin \alpha^*}{kb^* + ha^* \cos \gamma^* + (lc^* + ha^* \cos \beta^*) \cos \alpha^*}, \quad (3)$$

and in the

*a**-axis mounting

$$\tan \varphi_{hkl} = \frac{lc^* \sin \beta^* \sin \alpha^*}{kb^* \sin \gamma^* + lc^* \sin \beta^* \cos \alpha^*} \quad (4)$$

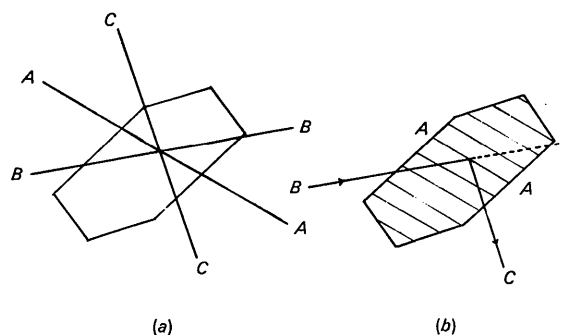


Fig. 2. Cross section of crystal; AA represents one of the reflecting planes, B the incident ray, C the reflected ray.

both of which expressions reduce to

$$\tan \varphi_{hkl} = lc^*/kb^* \quad (5)$$

when the crystal axes are orthogonal.

By taking into account the signs of both the numerator and the denominator in these expressions for $\tan \varphi$ it is possible to determine the correct quadrant for φ .

2.2 Discussion of the Furnas method

The efficacy of the method depends to a great extent upon the shape of the crystal and the θ -range of the measurements, which determine the validity of the underlying assumption that the absorption correction is a function of φ alone. Clearly needle-shaped crystals mounted for rotation about the needle axis are best suited to this approximation, but even with crystals of this kind it is best to use an absorption curve derived from an axial reflexion in the same reciprocal lattice level (*i.e.* at the same value of μ) as the reflexions that are being measured (*cf.* Fig. 5). For crystals of less suitable habit the end effects are more important and failure to use an appropriate axial reflexion can introduce serious errors. The method is unsatisfactory also in correcting the intensities of reflexions at high angles, clearly because the corrections are invariant with θ whereas the absorption, even in regularly shaped crystals, varies significantly over the normal range of angles.

Nevertheless this method has been used to advantage in a number of investigations, most particularly in the study of proteins at low angles when the variations of the absorption corrections with θ are of little importance. It was used in the work on sperm-whale myoglobin at 6 Å resolution (Kendrew, Bodo, Dintzis, Parrish, Wyckoff & Phillips, 1958). Again, in the study of horse oxyhaemoglobin (Cullis, Muirhead, Perutz, Rossmann & North, 1961), application of the corrections substantially improved the agreement between equivalent reflexions measured on the diffractometer and also the agreement between diffractometer and photographic measurements. Furthermore, these empirical corrections were more successful than calculated corrections (Wells, 1960) in improving the agreement between diffractometer and photographic measurements, though it is not clear whether this was because the assumption that absorption on the diffractometer depends only upon φ is exactly equivalent to the assumption that absorption is constant over a single precession photograph, or whether it was because the empirical method is the more faithful when the specimen system is complicated. The Furnas method was also used successfully in the preliminary study of hen egg-white lysozyme (Blake, Fenn, North, Phillips & Poljak, 1962).

These successes of the method and its ease of application led us to consider whether it could be improved and hence to the method now proposed in which account is taken of the different directions of the incident and reflected rays.

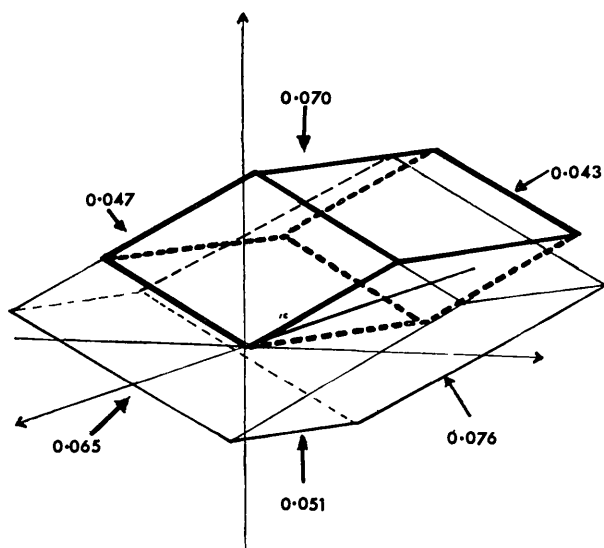


Fig. 4. Composite clinographic projection of the two crystals used for the test calculations. Heavy lines, crystal 116; light lines, crystal 126. Dimensions in mm.

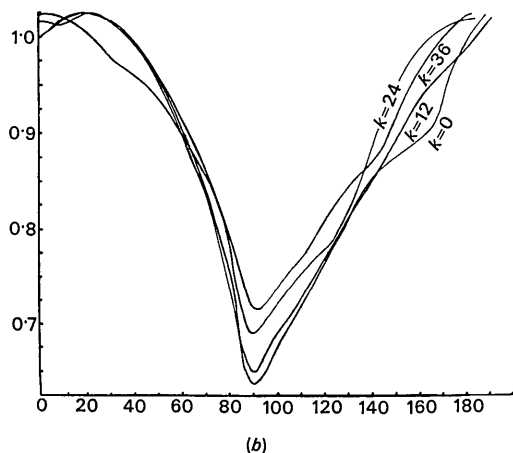
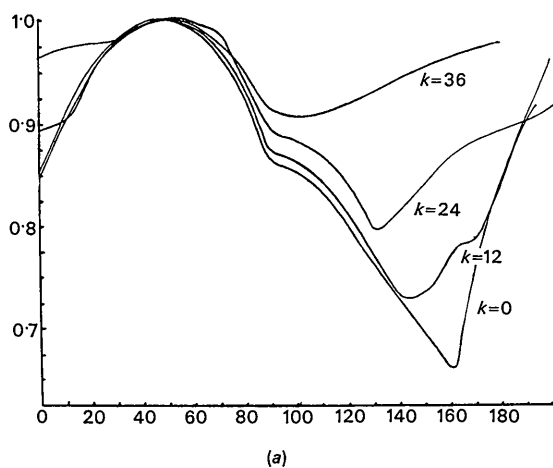


Fig. 5. Calculated transmission curves for axial reflexions with $k=0, 12, 24, 36$. (a) Crystal 116, (b) Crystal 126.

intensities of a reflexion corresponding to a reciprocal lattice point on the axis of rotation. The intensity is measured at regular intervals, say 5 or 10° , as the crystal is rotated about the φ axis.

In making the measurement it is necessary strictly to rock the crystal about some axis other than φ , otherwise only a measure of the peak intensity is obtained rather than the required integrated intensity. This distinction can be most important when the crystal is distorted. Clearly four-circle diffractometers are best suited for this purpose, since the $\omega(\theta)$ - and χ -circles can be used for rocking the crystal, but such an instrument is not always available and, in any case, it is often inconvenient to move the specimen from one diffractometer to another. For these reasons we have often used careful measurements of the peak intensity in deriving the corrections. It is evident that the measured transmission factors at φ and $\varphi + 180^\circ$ should be identical; any differences indicate either missetting of the crystal and diffractometer or some type of specimen distortion leading to focusing/defocusing effects. In the latter event integrated intensities are satisfactory but peak intensities are not. R. D. Diamond (unpublished) has modified the linear diffractometer so as to permit variation of μ , the inclination angle, during these measurements.

The measurements are plotted conveniently, as in Fig. 1, to show the variation of the relative transmission factor with φ , and the origin and sense of rotation of φ are determined from measurements of appropriate reference reflexions. The computer, at present an Elliott 803B, is programmed to calculate the required angles from the reflexion indices and to derive the corresponding transmission and absorption factors by interpolation from a list tabulated at 7.5° intervals.

4. Tests of the method

The method has been tested numerically against the computer program *ORABS* of Wehe, Busing & Levy (1962) in a number of ways.

4.1 Comparison of observed and calculated transmission curves

In addition to the transmission curve observed for the 080 reflexion of a representative haemoglobin crystal, Fig. 1 shows the curve calculated from measurements of that crystal by means of the *ORABS* program. The calculated curve, which takes into account only the crystal and not its mounting, agrees well with the observed except near the minimum where the measured transmission is less than the computed. Examination of the specimen showed that at the corresponding angle the X-ray beam was nearly tangential to the wall of the capillary tube in which the crystal was mounted. Thus, where the two curves differ, the observed transmission curve is most probably a truer representation of the absorption of the sample as a whole and corrections derived from it are likely to be more satis-

factory than those calculated from the crystal dimensions alone.

4.2 Analysis of corrections derived from calculated transmission curves

In order to test the suggested method against *ORABS* without introducing complications due to the specimen mounting the following procedure was adopted. Transmission curves were calculated for a number of axial reflexions by means of *ORABS* and these curves were used to derive absorption corrections for various general reflexions by the new method for comparison with those computed directly by *ORABS*.

The model crystals used in these tests had the shape of horse oxyhaemoglobin crystals, which is not ideally suited to the use of our method since they have a diamond-shaped cross-section in the plane perpendicular to the goniometer axis (see *Discussion* below). Fig. 4 is a composite clinographic projection drawing of two model crystals showing their dimensions and the axis of rotation. The corresponding reciprocal lattice dimensions are $a^*=0.01515$, $b^*=0.0244$, $c^*=0.0304$, $\beta^*=69^\circ$. Calculated transmission curves for axial reflexions with $k=0, 12, 24$ and 36 are shown in Fig. 5.

Clearly the shape of the transmission curve varies with the axial reflexion in a way that is strongly dependent upon the crystal size and shape. The transmission curves for crystal 116 vary to an important extent as k changes from 0 to 36 but, even though the non-prismatic habit of these crystals is unfavourable, it is clear that the curves for crystal 126 are relatively constant.

Each of these calculated transmission curves was used to derive absorption corrections for all of the reflexions in the reciprocal-lattice levels with $k=0, 12, 24$ and 36 , and the general results obtained for crystal 116 are shown in Fig. 6. Fig. 6 shows that the average differences between absorption corrections derived in this way and those calculated directly by *ORABS* are small and well-behaved when an appropriate transmission curve is used and that they can be unacceptably large when inappropriate transmission curves are used. As might be expected from Fig. 5, the results obtained with crystal 126 were subject to much less extreme errors so that the choice of transmission curves is much less critical than it is for 116.

The detailed agreement of the absorption corrections calculated in these two ways is illustrated in Fig. 7, which shows the variation of the corrections over the zero reciprocal lattice level. The zero-level transmission curve, which is strictly unobservable, was used in deriving the semi-empirical corrections which clearly agree closely with those calculated by *ORABS*. It may be noted, incidentally, that the contours of constant absorption calculated by the Furnas method are simply radial lines to which the contours derived by the improved method are asymptotic at low values of θ .

It is apparent in Figs. 6 and 7 that although the two methods give results in satisfactorily close agreement

there is a progressive increase in the discrepancy between them as θ increases. This clearly arises from the fact that the semi-empirical method described here does not take into account the progressive reduction in average path length in the crystal as θ rises. But it is just this reduction in path length that is considered in calculating the absorption corrections for reflexions from a cylindrical crystal, and the general differences between the two methods can be accounted for quite closely as the contribution to the absorption of a cylindrically shaped crystal with the mean thickness of the crystal as diameter. Fig. 6 shows also how the agreement is improved by combining the semi-empirical correction with those listed in *International Tables* (1959) for the equivalent cylinder, the diameter of which can be estimated quite simply. The mean difference between corrections calculated by the two methods is now less than 2% over the full range of θ -values.

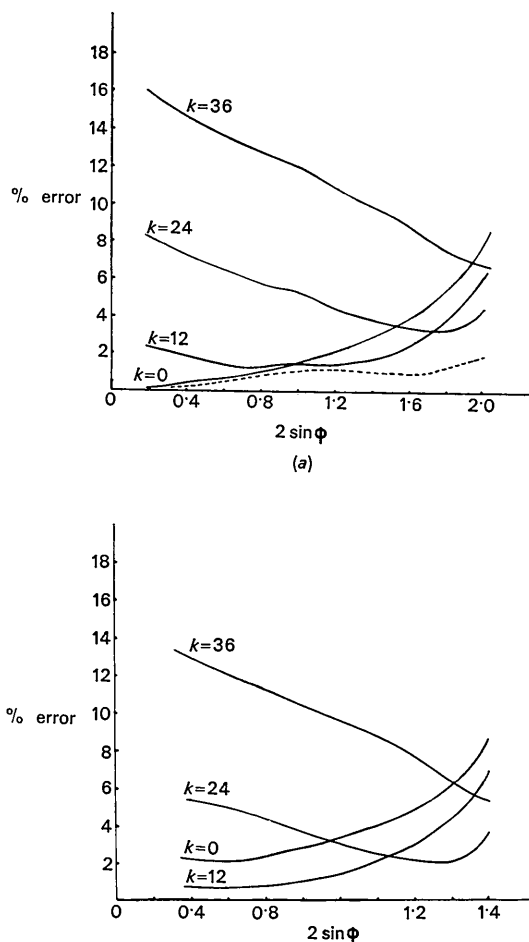


Fig. 6. Average errors for crystal 116 between absorption corrections calculated exactly by *ORABS* and those derived from the transmission curves $k=0, 12, 24, 36$; for the reciprocal lattice levels (a) $k=0$ (b) $k=12$. In (a) the broken line shows the error when the $k=0$ curve is used in combination with the correction for the equivalent cylinder.

5. Discussion

It must be emphasized that the empirical method only gives relative values of absorption correction so that, usually, corrections are made relative to the direction

of least absorption in the crystal. The corrected intensities then differ by a constant factor (representing the transmission in the direction of least absorption) from the values that would be obtained by an analytical method but this may be treated as an additional con-

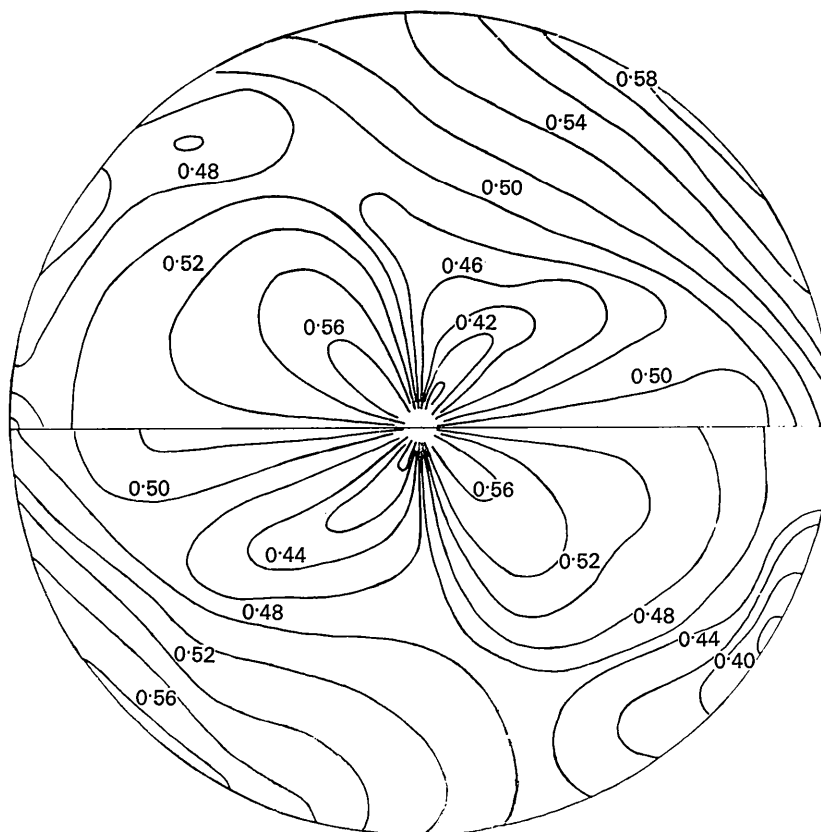


Fig. 7. Contour plot of relative transmission over the zero reciprocal lattice level for crystal 116. Upper half, calculated by use of *ORABS*; lower half derived from $k=0$ curve of Fig. 5. Note that the contours become radial at low $\sin \theta$ and that the contours of the Furnas corrections would be radial lines asymptotic to those in the figure.

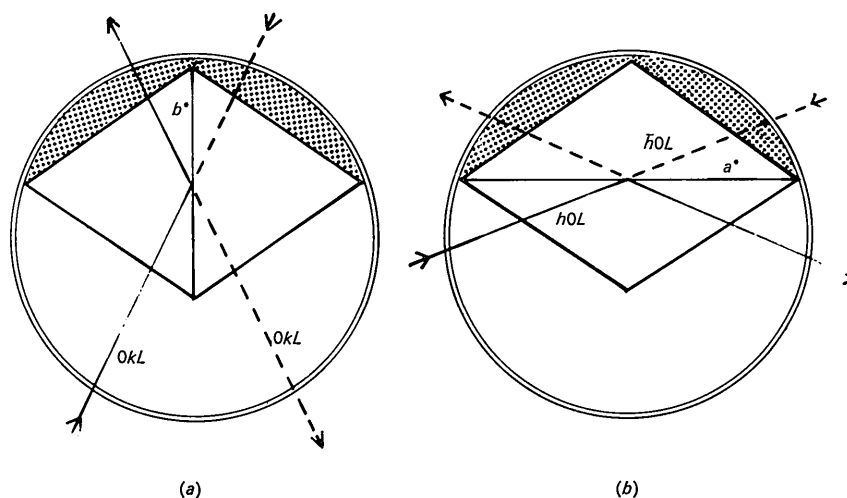


Fig. 8. Asymmetric mounting of protein crystal with mother liquor in capillary. Anomalous scattering differences would be seriously affected in (b) but not in (a).

stant scale factor and is not important unless absolute intensities are required.

We have been using the method routinely to correct the intensities of reflexions from protein crystals measured by means of the linear diffractometer. The results obtained, for example in the study of lysozyme at 2 Å resolution (Blake, Mair, North, Phillips & Sarma, 1967) have been most satisfactory. The method takes less than 1/20 of the computing time taken by *ORABS*, and we are convinced that, for specimens of complicated shape, the empirical absorption curves give a more faithful representation of the effective shape of the specimen than can be obtained by measurement and that this more than compensates for the approximation introduced by the method of computing the corrections.

It is clearly most important that the empirical corrections should be based upon an appropriate transmission curve and the best curve to use for any reciprocal lattice level is the one obtained from the axial reflexion in that level, as Fig. 6 shows. Such treatment corrects for variations in absorption relative to the direction of least absorption in that level, but the intensities in one level differ from those in another by a constant factor, the unknown ratio between the minimum absorptions suffered by the two axial reflexions. This factor can be treated as a scale factor for each level which can be determined if there are equivalent reflexions in different levels. Alternatively, an intersecting reciprocal lattice plane, itself corrected for internal absorption variations, may be used for scaling purposes. In the case of high resolution protein work, it is common to measure each reciprocal lattice level from a different crystal so that the absorption factor is automatically included in the scaling procedure.

However, a conveniently intense axial reflexion is rarely available on each level, particularly when there are space group absences. In practice, as Fig. 5 shows, this difficulty may be overcome if the crystal habit is favourable. If the crystals are prismatic and mounted to rotate about the major zone axis, there is no problem; the mean path length varies only slowly as $\sec \mu$ and this factor may be used to relate the desired correction to the nearest available transmission curve so that there is not now an unknown scale factor between levels corrected from the same axial reflexion. If the crystals are not prismatic, it is usually possible to choose a specimen such as crystal 126 above (Figs. 4 and 5) for which one would not anticipate a serious variation of transmission curve over the range of levels being considered. Reflexions within one level may again be corrected by use of the nearest available axial reflexion, but it may be preferable, rather than using the $\sec \mu$ factor, to treat the layer scale factor as unknown and to determine it by the use of equivalent reflexions or intersecting levels, as described above.

There remains a difficulty that arises when the specimens are markedly asymmetric and which may be serious. It is clear that this semi-empirical method gives

equal absorption corrections for the reflexions hkl and $\bar{h}\bar{k}l$ (for a crystal rotating about \mathbf{c}^*) for which the projected directions of the incident and reflected beams are simply reversed. But the actual absorption suffered in these two reflexions will only be the same if the shape of the specimen is symmetrical about the reflecting planes. This condition often is not satisfied, particularly in the study of protein crystals where the glass and liquid components of the mount must be taken into account as well as the shape of the crystal itself. Thus, the reflexions illustrated in Fig. 8(a) suffer the same absorption whereas those shown in Fig. 8(b) do not.

This effect is particularly important when measurements are being made of the effects of anomalous scattering. In the study of lysozyme (Blake *et al.*, 1967) they were corrected in an approximate way. From Fig. 8(a) and (b) it is clear that the absorption error from the asymmetric distribution of mother liquor is zero for reflexions with $h=0$ and becomes increasingly serious as h increases. The assumption was made, therefore, that the required correction was a function only of h and the reflexions hkl with constant l were divided into groups with constant h and \bar{h} . The ratios $\Sigma_k I(h)/\Sigma_k I(\bar{h})$ were then plotted against h , as shown in Fig. 9. These plots were frequently found to be linear and in such cases the corresponding linear correction was applied to each row on the more highly absorbed side to bring its mean intensity up to that of the other. Where the plots were not linear, so that a simple form of correction was not applicable, the entire set of measurements was usually rejected. It is clear that in general a better treatment of this effect is still required.

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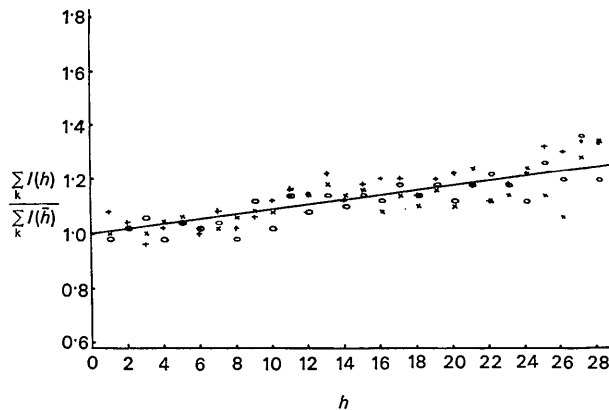


Fig. 9. Plot of ratio $\frac{\sum_k I(h)}{\sum_k I(\bar{h})}$ against h . In this example a linear correction may be safely applied to equalize the average intensities on opposite rows.

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Approximate Location of Centres of Molecules from Morphological and Unit-cell data

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Centres of molecules can sometimes be located approximately from morphology, unit-cell dimensions, number of molecules per unit cell and space group. This is possible when the observed morphology is not in accordance with the morphology predicted from the law of Donnay and Harker applied to the known unit-cell dimensions and space group. Additional information about the centers can be obtained by the periodic-bond-chain method.

Introduction

In the course of a crystal-structure determination any information about particular structural features may be helpful. In this paper it will be shown how sometimes the centres of molecules can be located from the following data: morphology, cleavage, unit-cell dimensions, number of molecules per unit cell and space group.

The method is based on the application of a reversed Donnay-Harker law and of the periodic-bond-chain method. For several molecular compounds approximate coordinates of the centres of molecules are predicted and compared with the coordinates known from crystal structure determinations.

Before entering into the details of the method the use of some terms and symbols will be discussed.

(a) *Centres of molecules*. The crystal structure is considered as a packing of molecules. The proposed method gives essentially some information about the packing, not in detail, but rather the coordination of one molecule by its neighbours. For convenience the molecules are indicated by the coordinates x_m , y_m and z_m of their geometrical centres, because these are most easily computed by giving each atom the same weight. In the examples the hydrogen atoms are ignored.

(b) *Sublattice and pseudolattice*. The method gives idealized coordinates of the centres of molecules. Sometimes the points that occupy these idealized positions have a lattice which differs from the real lattice by having shorter periods, namely submultiples (for instance, by centring a face or by halving an axis). The lattice belonging to the points that occupy the *idealized* positions is called a *sublattice**. The *actual* centres of molecules have a *pseudolattice* with a certain *pseudosymmetry*. In some cases (see example 3) *partial pseudosymmetry* occurs, that is, the particular pseudosymmetry is valid for a certain projection only and not for the three-dimensional structure.

(c) The symbol d_{hkl} stands for the interplanar spacing of planes (hkl), which are not necessarily lattice planes. Whenever h , k and l have a common factor, this arises either from the space group extinction, or from extra extinctions that find their origin in the idealized positions of centres of molecules.

(d) The symbol $[uvw]$ not only indicates a zone axis or a lattice row, but also the length of its period. For example, in a lattice of type C the distance between the points $(0,0,0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$ is indicated by $[\frac{1}{2}\frac{1}{2}0]$ or by $\frac{1}{2}[110]$.

* The relation between a sublattice and a lattice is therefore the same as that between a lattice and a superlattice.