of this nature is responsible for the value $c \sim 18$ Å given by Neuhaus and Kitaijgorodskij, particularly since both of them experienced difficulty with the c-axis photographs (§ 2). The true length of the c axis should be revealed, of course, in the process of indexing general reflexions hkl with l odd in the oscillation photographs taken by Kitaijgorodskij; but the c axis in β-naphthol is so long that the spacing of a plane (h, k, l) is nearly the same as that of a plane $(h, k, l\pm 1)$ and indexing is not easy if the crystal is slightly mis-set; in any case Kitaijgorodskij does not appear to have indexed general reflexions.

We have presented two independent lines of evidence suggesting that crystals of β-naphthol are polar (§ 3). If the validity of the evidence is accepted then the centrosymmetrical space group $P2_1/a$ determined by Kitaijgorodskij is unacceptable.

It is possible that the material which we have examined has a structure different from that of the crystals examined by Neuhaus and Kitaijgorodskij; thus our material, with two non-equivalent molecules in the unit cell, may be built from molecules closely associated in pairs by hydrogen bonding between the hydroxyl groups whilst that examined by Neuhaus and Kitaijgorodskij may consist of single molecules. We believe this suggestion is unlikely for two reasons. First, our material closely resembles that described by Kitaijgorodskij; both materials are crystallized from carbon disulphide in the form of rhombic plates with $a \sim 8{\cdot}1$ Å parallel to the long diagonal and $b \sim 5{\cdot}95$ Å parallel to the short diagonal of the rhomb and $\beta \sim 119°\ 50'$. Secondly, we have grown crystals under a variety of conditions from six different solvents and find that powder photographs of all specimens are apparently identical.

Kitaijgorodskij has deduced a structure for β-naphthol, largely from geometrical considerations, which is said to give satisfactory intensities for the $hk0$ and $00l$ reflexions. Some of the geometrical arguments are not valid, however, if applied to our unit cell and space group, and no details are given of the agreement between observed and calculated intensities. We are continuing our X-ray examination of β-naphthol with a view to obtaining full details of the crystal structure.

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The Fourier Transform Method for Normalizing Intensities

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A method for bringing experimental intensities to an absolute scale, based on the value of the electron distribution function in $\mathbf{r} = 0$, is described. Formulas for the normalization constant are given for crystals and samples of spherical and cylindrical symmetry. The formulas represent approximate values. As an example, the percentage error in the normalization constant for cellulose is calculated as a function of the radius of the limiting sphere in reciprocal space, and the calculations are compared with experimental results.

Introduction

The method outlined by Krogh-Moe (1956) for converting experimental X-ray intensities to an absolute scale has been in use for some years at the University of Oslo. The method is described in a study of the cylindrically symmetrical distribution method in X-ray analysis (Norman, 1954*a*, *b*). As the original work is not well known, the formulas for the normalization constant will be given below. For crystals the method leads to the formulas derived by Kartha (1953).

Theory

The coherently scattered radiation $I(\mathbf{r}^*)$, measured in units of the scattering from a free electron, and the electron distribution function $D(\mathbf{r})$, are combined in the following equation:

$$D(\mathbf{r}) = \int \varrho(\mathbf{u})\varrho(\mathbf{u}+\mathbf{r})d\mathbf{u} = \int I(\mathbf{r}^*) \exp\,[-2\pi i\mathbf{r}\mathbf{r}^*]d\mathbf{r}^* . \tag{1}$$

ϱ is the electron density in e.Å^{-3} and $\mathbf{r}^*$ the scattering vector. $D(\mathbf{r})$ can be split into two terms, $D_{\text{at.}}(\mathbf{r})$ and $D_m(\mathbf{r})$, $D_{\text{at.}}(\mathbf{r})$ including that part of the first integral in (1) where $\varrho(\mathbf{u})$ and $\varrho(\mathbf{u}+\mathbf{r})$ are the electron densities at two points within the same atom. $D_m(\mathbf{r})$ thus represents the structure-dependent part of the distribution function. It will further be necessary to introduce the function $D_0(\mathbf{r})$ corresponding to a uniform distribution of the scattering matter.

The coherently scattered radiation can be written as the sum of the structure-independent intensity $I_{\text{at.}}(\mathbf{r}^*)$, and the structure-dependent intensity $I_m(\mathbf{r}^*)$. If the homogeneous regions of the scattering substance are large enough (James, 1950, p. 508), the intensity will decrease towards small angles of scattering. The high peak around $\mathbf{r}^* = 0$, corresponding to a uniform distribution of the scattering matter, cannot be observed. Thus it is natural to extrapolate the intensity to zero for $\mathbf{r}^* = 0$; and the observed intensity, $I_{\text{obs.}}$, can be written

$$KI_{\text{obs.}} = I_{\text{at.}} + I_m + I_{\text{inc.}} - I_0 \,. \tag{2}$$

K is the normalization constant, $I_{\text{inc.}}$ is the incoherently scattered intensity, and I_0 is the small-angle scattering intensity which is omitted. $I_{\text{at.}}$ and $I_{\text{inc.}}$ can be taken as independent of the direction of $\mathbf{r}^*$. If each scattering unit consists of n atoms, and the total number of units is N, the sum of the two intensities is

$$I_{\text{at.}}(s) + I_{\text{inc.}}(s) = N\sum_{j=1}^{n}(f_j^2(s)+S_j(s)) = NB(s) \,. \tag{3}$$

Here $s = 2\pi|\mathbf{r}^*|$, f_j is the atomic form factor and S_j is the incoherent factor. $B(s)$ is often called the background, and can be calculated from theoretical values of f_j and S_j when the composition of the substance is known.

From equations (1), (2), and (3) and the splitting of the coherently scattered radiation and the distribution function, the following equations are derived:

$$D_m(\mathbf{r}) - D_0(\mathbf{r}) = K\int I_{\text{obs.}}(\mathbf{r}^*) \exp\,[-2\pi i\mathbf{r}\mathbf{r}^*]d\mathbf{r}^* - N\int B(s) \exp\,[-2\pi i\mathbf{r}\mathbf{r}^*]d\mathbf{r}^* \,, \tag{4}$$

and

$$D_m(0) - \frac{N}{V_0}\left(\sum_{j=1}^{n} Z_j\right)^2 = K\int I_{\text{obs.}}(\mathbf{r}^*)d\mathbf{r}^* - N\int B(s)d\mathbf{r}^* \,. \tag{5}$$

V_0 is the volume of the n atoms in the scattering unit. The theory requires that the integration in (4) and (5) should be carried out throughout the whole reciprocal space. In practice the intensities can be measured only within a limited (often approximately spherical) volume of reciprocal space. As a consequence the calculated $D_m(\mathbf{r})$ will show false details. Neglecting these so-called diffraction effects and assuming there is no overlap of the electron densities for neighbouring atoms, the normalization constant can be expressed by the formula

$$\frac{K}{N} = \frac{\int B(s)d\mathbf{r}^* - \frac{1}{V_0}\left(\sum_{j=1}^{n} Z_j\right)^2}{\int I_{\text{obs.}}(\mathbf{r}^*)d\mathbf{r}^*} \,. \tag{6}$$

Formulas for the normalization constant

In the following three sections the formula for the normalization constant will be specialized for spherical and cylindrical symmetry of the observed intensity, and for crystals.

(i) *Liquids*

If the distribution and intensity functions show spherical symmetry, and the volume element in reciprocal space is expressed in spherical polar coordinates, the expression for K/N becomes

$$\frac{K}{N} = \frac{\frac{1}{2\pi^2}\int_0^{s_0} s^2B(s)ds - \frac{1}{V_0}\left(\sum_{j=1}^{n} Z_j\right)^2}{\frac{1}{2\pi^2}\int_0^{s_0} s^2I_{\text{obs.}}(s)ds} \,, \tag{7}$$

where s_0 is the upper limit for s.

(ii) *Fibres*

For cylindrically symmetrical systems with x^* and z^* as cylinder coordinates in reciprocal space, formula (6) takes the form

$$\frac{K}{N} = \frac{\frac{1}{2\pi^2}\int_0^{s_0} s^2B(s)ds - \frac{1}{V_0}\left(\sum_{j=1}^{n} Z_j\right)^2}{2\pi\iint x^*I_{\text{obs.}}(x^*, z^*)dx^*dz^*} \,. \tag{8}$$

(iii) *Crystals*

In the structure determination of crystals, only the intensities at the reciprocal-lattice points are registered. Under the assumption that the atoms in the crystal vibrate independently, all with the same mean-square amplitude in a direction parallel to the scattering vector $\mathbf{r}^*$, the expression for the coherently scattered intensity can be written (James, 1950, p. 24)

$$I(\mathbf{r}^*) = N\sum_{j=1}^{n} f_j^2(1-\exp[-2M]) + \exp[-2M]\sum_{j}\sum_{k} f_j f_k \exp[-2\pi i \mathbf{r}_{jk}\mathbf{r}^*]\,. \qquad (9)$$

The first term, representing the temperature diffuse scattering, $I_{\text{t.d.}}$, varies continuously in reciprocal space and has a very broad maximum at moderate angles. The second term represents the lattice spectra. Except for the temperature factor $\exp[-2M]$, it is equal to the intensity scattered from the undisplaced lattice. The integrated intensities are measured above the background of incoherent and temperature diffuse scattering, and the new expression which has to replace equation (2) for the observed intensity becomes

$$KI'_{\text{obs.}} = I'_{\text{at.}} + I'_m - I_0\,. \qquad (10)$$

The primes distinguish the intensities from the former $I_{\text{obs.}}$, $I_{\text{at.}}$, and I_m. Introducing the interference function $Q(\xi, \eta, \zeta)$ (James, 1950, p. 9), the observed intensity and the structure factor in arbitrary units are combined in

$$I'_{\text{obs.}}(\xi, \eta, \zeta) = |F_{\text{obs.}}(\xi, \eta, \zeta)|^2 Q(\xi, \eta, \zeta)\,. \qquad (11)$$

Using this expression for the observed intensity, the formula for the normalization constant becomes

$$K = \frac{\int I'_{\text{at.}} d\mathbf{r}^* - \frac{N}{V_0}\left(\sum_{j=1}^{n} Z_j\right)^2}{\frac{N}{V_0}\sum_{h}\sum_{k}\sum_{l}{}' |F_{\text{obs.}}(hkl)|^2}\,. \qquad (12)$$

The primed summation sign indicates that the term for which $h = k = l = 0$ is not included in the observed intensities.

$I'_{\text{at.}}$ is the structure independent scattering from the atoms 'modified' owing to the temperature vibrations in the crystal. Two different points of view may be used to derive the expression for this intensity. Either only the real independent scattering from the atoms can be considered, giving

$$I'_{\text{at.}} = N\sum_{j=1}^{n} f_j^2 \exp[-2M]\,; \qquad (13)$$

or the interaction between the atoms in the Bravais lattice can be included, leading to

$$I'_{\text{at.}} = \sum_{j=1}^{n} f_j^2 \exp[-2M] Q(\xi, \eta, \zeta)\,. \qquad (14)$$

Equations (13) and (14) give the following two formulas for the normalization constant:

$$K = \frac{\int \sum_{j=1}^{n} f_j^2 \exp[-2M] d\mathbf{r}^* - \frac{1}{V_0}\left(\sum_{j=1}^{n} Z_j\right)^2}{\frac{1}{V_0}\sum_{h}\sum_{k}\sum_{l}{}' |F_{\text{obs.}}(h, k, l)|^2}\,, \qquad (15)$$

and

$$K = \frac{\sum_{h}\sum_{k}\sum_{l}{}'\sum_{j=1}^{n} f_j^2 \exp[-2M] - \left(\sum_{j=1}^{n} Z_j\right)^2}{\sum_{h}\sum_{k}\sum_{l}{}' |F_{\text{obs.}}(h, k, l)|^2}\,. \qquad (16)$$

These equations correspond to the formulas given by Kartha (1953). The formulas contain the temperature factor $\exp[-2M]$, which has to be determined before the calculation of the normalization constant can be carried out.

In the original work referred to (Norman, 1954*a*), the normalization constant was also determined for a periodic fibre structure. The intensity was measured above the background of temperature diffuse and incoherent scattering. In this case formula (8) for the normalization constant had to be replaced by formulas similar to (15) and (16).

The influence of the omitted term $D_m(0)$ on the normalization constant

The formulas for the normalization constant in the previous section were deduced on the assumption that the term $D_m(0)$ in equation (5) could be neglected. If the electron density drops to zero between neighbouring atoms and the diffraction effect is small, the approximation is good. In the structure investigation of cellulose by means of the cylindrically symmetrical distribution method, the normalization constant was calculated for different upper limits of $\mathbf{r}^*$. When the intensity was expanded into a series of even Legendre polynomials, formula (7) could be used to determine K/N. $I_{\text{obs.}}$ was replaced by the first term in the Legendre series. The result is shown in Table 1.

Table 1. *The normalization constant for ramie*

s_0	4·0	5·0	6·0	7·0
K/N	5·78	6·43	6·32	6·37

The calculations show that the variation in K/N is small when $s_0 = 5$ or larger, but that the value drops by 10% when s_0 decreases from 5 to 4. This can be taken as an indication of the usefulness of the method for $s_0 = 5$ or larger. The tendency of K/N to decrease as s_0 gets smaller is understandable. When s_0 decreases, the diffraction phenomena will be more pronounced. $D_m(0)$ can have both positive and negative values, and the diffraction effect will thus bring out fluctuations in the normalization constant determined from (6). The other effect of a decrease in s_0 is a broadening of the peaks. This will systematically lead to a positive value of $D_m(0)$. When K/N is determined from one of the formulas in the previous section, the value of the normalization constant will come out too small.

Finally, the influence of the term $D_m(0)$ on the normalization constant will be illustrated by the example of cellulose (Norman, 1954*a*). The first term in the Legendre series for a cylindrically symmetrical distribution function $D(\mathbf{r})$ corresponds to a spherical symmetry in the sample. If the interaction between the glucose groups is neglected, the intensity $I_m(s)$ is equal to

$$I_m(s) = N \sum_{j \neq k} \sum \exp\left[-2M\right] f_j f_k \frac{\sin s r_{jk}}{s r_{jk}}. \quad (17)$$

The summation should be taken over the atoms in the glucose unit. $D_m(0)$ can be written

$$D_m(0) = \frac{N}{2\pi^2} \int_0^{s_0} s^2 \exp\left[-2M\right] \sum_{j \neq k} \sum f_j f_k \frac{\sin s r_{jk}}{s r_{jk}} ds. \quad (18)$$

It can be expected that only the contribution from nearest neighbours will influence the value of $D_m(0)$. To simplify the calculations, the O–C and the C–C distances were set equal to 1·5 Å and the O–H and C–H distances equal to 1 Å. For M the value $0{\cdot}01 s^2$ was chosen.

From equation (5), the correct formula for the normalization constant in case of spherical symmetry can be written

$$\frac{K}{N} = \frac{\int_0^{s_0} s^2 B(s) ds - \frac{2\pi^2}{V_0}\left(\sum_{j=1}^{n} Z_j\right)^2}{\int_0^{s_0} s^2 I_{\text{obs.}}(s) ds} \times \left[1 - \frac{\frac{2\pi^2}{N} D_m(0)}{\int_0^{s_0} s^2 B(s) ds - \frac{2\pi^2}{V_0}\left(\sum_{j=1}^{n} Z_j\right)^2}\right]. \quad (19)$$

The first factor is identical with the expression for the normalization constant in (7). The last term in the bracket will thus give the error due to the fact that $D_m(0)$ is omitted in formula (7).

For cellulose the error has been calculated numerically in the interval $s_0 = 2$ to $s_0 = 10$, and the result is shown by the curve in Fig. 1. The percentage error drops from several hundreds for $s_0 = 2$ to 30 for $s_0 = 3$ and to 5 for $s_0 = 5$. Above $s_0 = 7$ the error is less than 3%. In Fig. 1 the errors based on the values in Table 1 are indicated by circles. It was assumed that the error in the experimentally determined normalization constant was 2·9% for $s_0 = 7$.

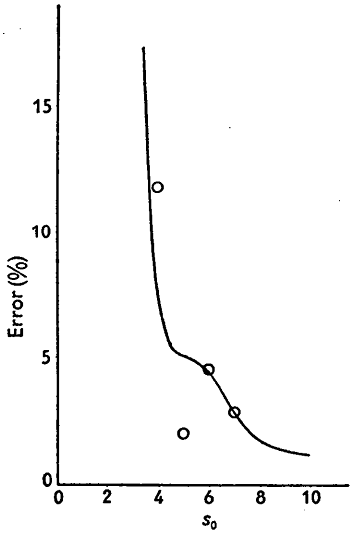

Fig. 1.

Apart from the low value at $s_0 = 5$, the agreement between experimental and theoretical values is satisfactory. Calculations have shown that the shape of the curve for the percentage error varies considerably with the assumed interatomic distances and temperature factors in the region $s_0 = 4$ to $s_0 = 6$. Thus the curve would show a pronounced minimum at $s_0 = 4{\cdot}5$ if only C–C distances were considered. Therefore too much weight should not be put on the discrepancy between the experimental and calculated value at $s_0 = 5$.

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