

Table 3. Comparison of observed intensities and calculated amplitudes.

Intensities were estimated visually in Weissenberg and oscillation photographs using Mo  $K\alpha$  radiation ( $\lambda = 0.710 \text{ \AA}$ ).  
No correction for the observed intensities was made.

$hk^*l$	$I_{\text{obs.}}$	$F_{\text{calc.}}$	$hk^*l$	$I_{\text{obs.}}$	$F_{\text{calc.}}$	$hk^*l$	$I_{\text{obs.}}$	$F_{\text{calc.}}$	$hk^*l$	$I_{\text{obs.}}$	$F_{\text{calc.}}$
30*0	s-	36.6	50*1	vw	13.6	62*0	—	-14.6	27*1	—	2.4
22*0	w	-14.6	33*1	mw	21.0	44*1	w	-17.2	72*1	w	22.0
13*0	s	40.0	24*1	vw	17.8	70*1	vw	5.8	37*0	—	-10.8
31*0	—	-14.0	42*1	mw	26.0	35*1	—	1.0	73*0	—	-5.8
30*1	—	3.0	60*0	vw-	9.4	53*1	—	3.6	46*0	—	-2.0
40*0	m	27.2	34*0	w	-18.8	17*1	—	-9.0	64*0	—	-12.0
22*1	s	47.0	43*0	m	-20.4	71*0	—	8.0	81*1	—	0.8
23*0	s-	-33.2	15*1	vw	14.4	26*1	—	-4.0	18*1	vw	-15.4
32*0	vw	-12.0	51*1	—	-8.0	62*1	m	-22.2	55*1	—	-2.2
13*1	—	0	25*1	—	-1.0	45*0	—	-10.2	64*1	vw	-21.2
31*1	s-	-34.0	52*1	—	3.6	54*0	—	8.0	46*1	—	-18.2
14*0	—	-6.2	60*1	vw	13.8	36*0	—	10.0	28*0	—	0.1
41*0	w	-8.2	16*0	w	-21.0	63*0	—	-1.0	82*0	—	-9.0
40*1	s	39.6	61*0	—	-5.1	17*1	—	0.3	37*1	vw	-20.6
50*0	vw	5.8	34*1	—	-16.0	71*1	—	-9.0	73*1	w	22.8
23*1	—	8.8	43*1	—	15.2	80*0	—	2.2	90*1	—	0.1
32*1	ms	-30.0	25*1	—	-1.0	27*0	—	-5.8	28*1	vw	-20.6
00*2	vs	-87.2	52*1	—	3.6	72*0	—	-9.4	82*1	—	-13.6
33*0	m	21.2	44*0	—	5.2	45*1	vw	12.2	19*0	—	6.6
14*1	vw	-5.8	70*0	w	-21.0	54*1	—	10.2	91*0	—	10.6
41*1	s	-36.8	35*0	—	7.2	36*1	—	-1.0	19*1	—	-5.2
24*0	vw	8.2	53*0	w-	18.0	63*1	—	15.0	91*1	—	-1.0
42*0	m	-25.8	16*1	—	1.6	80*1	—	14.2	00*4	ms	50.8
15*0	mw-	-25.6	61*1	—	-7.2	18*0	—	-14.0	10.0*1	—	17.4
51*0	m	28.6	26*0	s	48.4	81*0	—	18.4			

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## The Probability Distribution of X-ray Intensities. II. Experimental Investigation and the X-ray Detection of Centres of Symmetry

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The probability distributions of reflected X-ray intensities have been investigated experimentally. The results are in agreement with the theory, and the possibility is demonstrated of distinguishing between centrosymmetric and non-centrosymmetric structures and projections within the limitations of the theory. Details of a convenient distinguishing test are presented and the effects upon it of absorption, extinction and experimental errors in intensities are discussed.

### 1. Introduction

The probability distribution of reflected X-ray intensities has recently been investigated theoretically by Wilson (1949). He concluded that the structure factors,  $F(hkl) = x + iy$ , of a crystal are distributed symmetrically in the complex  $x, y$  plane according to the Gaussian function

$${}_1P(x, y) dx dy = (\pi\Sigma)^{-1} \exp\{- (x^2 + y^2)/\Sigma\} dx dy, \quad (1)$$

where  $\Sigma = \sum_j f_j^2$  (2)

is the sum of the squares of the scattering powers of the atoms and is identifiable with  $\langle I \rangle$ , the local average of the calculated intensities (Wilson, 1942).

When the structure possesses a centre of symmetry

the structure factors are confined to the real  $x$  axis, again with a Gaussian distribution

$${}_1P(x) dx = (2\pi\Sigma)^{-\frac{1}{2}} \exp\{-x^2/2\Sigma\} dx. \quad (3)$$

The corresponding distribution functions in terms of the intensities ( $= |F|^2$ ) are

$${}_1P(I) dI = \Sigma^{-1} \exp(-I/\Sigma) dI \quad (4)$$

and  ${}_1P(I) dI = (2\pi\Sigma I)^{-\frac{1}{2}} \exp(-I/2\Sigma) dI. \quad (5)$

The difference led Wilson to suggest as a distinguishing ratio

$$\rho = \langle |F|^2 \rangle^2 / \langle I \rangle, \quad (6)$$

which takes the values  $\pi/4 (\doteq 0.785)$  for (1) and  $2/\pi (\doteq 0.637)$  for (5).

A consideration of the effects of centring and of symmetry elements other than a centre of symmetry

has shown that only those causing systematic absences can modify the intensity distributions and thus the numerical value of this ratio. If, however, the systematic absences are omitted from the statistical survey, all cases reduce to one or other of the two treated above.

He has also shown that centrosymmetric unit cells may be detected in this way by a survey of the general  $hkl$  reflexions, whereas centrosymmetric projections are identified by surveying the corresponding zone of reflexions only.

The present authors undertook an experimental investigation of the possibility of using the ratio  $\rho$  (equation (6)) to detect centres of symmetry. Wilson's criteria were verified, but another test has been developed which has provided detailed verification of both the predicted distribution functions. It is more informative, and is also quicker to apply since it involves a survey of intensities only. These will normally be the observed intensities, but the procedure is equally applicable to a set of calculated intensities.

Each intensity is expressed as a fraction  $z (= I/\langle I \rangle)$  of the local average intensity\* so that the distributions (4) and (5) become

$${}_1P(z) dz = \exp(-z) dz \quad (7)$$

$$\text{and} \quad {}_1P(z) dz = (2\pi z)^{-\frac{1}{2}} \exp(-\frac{1}{2}z) dz. \quad (8)$$

The fractions,  $N(z)$ , of the reflexions whose intensities are less than or equal to  $z$  are

$${}_1N(z) = 1 - \exp(-z) \quad (9)$$

$$\text{and} \quad {}_1N(z) = \text{erf}(\frac{1}{2}z)^{\frac{1}{2}}, \quad (10)$$

where  $\text{erf } x$  is the 'error function' (Jahnke & Emde, 1938).

These two functions are compared in Fig. 1, from which it is evident that the distinction must be sought among the weak and accidentally absent reflexions. In favourable circumstances the difference may be evident on inspection of Weissenberg photographs; those corresponding to non-centrosymmetric pro-

jections have a greater uniformity of intensity. Generally, however, this is not fully apparent until allowance is made for the rapid decline of  $\langle I \rangle$  with increase of  $\sin \theta$ .

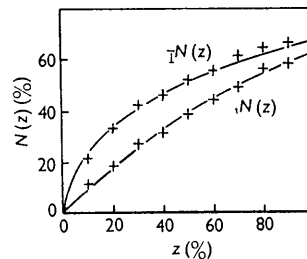


Fig. 1. Graphical comparison of functions  ${}_1N(z)$  and  ${}_1N(z)$ . Experimental points for the  $l$ -ephedrine hydrochloride [001] and [010] projections.

## 2. Procedure

The intensity data required will ordinarily be those prepared for structure determinations. In some circumstances, discussed in the next section, partially or wholly uncorrected intensities may be used.

A set of fully corrected intensities will exhibit a rapid decline in  $\langle I \rangle$  with increase in  $\sin \theta$  due to the decrease in atomic scattering factors and to thermal motion. This complication may conveniently be allowed for in the following way.

The reflexions and their intensities are tabulated in order of increasing  $\sin \theta$ , giving each its appropriate multiplicity (zone or general as the case may be). Systematic absences are ignored, as are reflexions having  $\sin \theta \leq \lambda/a$ , where  $a$  is the shortest cell dimension (Wilson, 1949), but those accidentally absent must be retained. The list is then divided into several nearly equal groups. Ideally each should contain a large number of reflexions within a small range of  $\sin \theta$ , but a reasonable compromise is sometimes necessary. For each group  $\langle I \rangle$  is calculated and the values of  $N(z)$  for  $z = 10, 20, \dots, 100\%$  are determined. Finally, for each  $z$  the mean of  $N(z)$  over all  $\sin \theta$  groups is compared graphically with the theoretical values. Details of the calculation for the [010] projection of ephedrine hydrochloride are shown in Table I.

As an alternative to the foregoing technique in which each intensity is compared with the average of a batch

\* Any difference between  $\langle I_{\text{obs.}} \rangle$  (used for grading observed intensities) and  $\langle I_{\text{calc.}} \rangle$  will be due to inadequacies in the  $f$ 's assumed for the latter, e.g. anisotropic thermal vibrations, non-spherical electron densities in the atoms, and sometimes inaccurate allowances for hydrogen atoms.

Table I. Details of the examination of the intensity distribution of the [010] projection of  $l$ -ephedrine hydrochloride

Group	$M^*$	Limits of $\sin \theta$		$\langle I \rangle$	Wilson's ratio	$N(z)$ (%)												
						$N(10)$	$N(20)$	$N(30)$	$N(40)$	$N(50)$	$N(60)$	$N(70)$	$N(80)$	$N(90)$				
A	18	0.000	0.200		Discarded for theoretical reasons													
B	106	0.200	0.515	270	0.545	34.0	47.3	49.1	54.9	56.7	64.1	68.0	69.8	69.8				
C	116	0.515	0.712	60	0.696	17.3	24.2	34.5	43.2	46.5	48.4	60.5	65.6	69.0				
D	118	0.712	0.875	27	0.715	18.7	32.3	42.5	44.0	44.0	47.5	54.2	61.0	66.0				
E	46	0.200	0.362	399	0.620	21.8	26.1	43.5	47.9	56.6	61.0	61.0	65.3	65.3				
F	118	0.362	0.625	126	0.531	28.9	47.5	52.6	62.8	66.1	68.0	74.6	74.6	76.5				
G	120	0.625	0.790	42	0.762	10.0	20.0	33.3	35.0	45.0	48.4	51.8	53.3	53.3				
		Weighted average				0.647	21.8	33.5	42.5	46.2	52.1	55.8	61.7	64.9	66.8			
		Theoretical average				0.637	24.81	34.53	41.87	47.38	52.05	56.14	59.72	62.89	65.72			

\*  $M$  denotes the number of reflexions in a group.

it is possible, at the expense of a little more time, to compare each intensity with the appropriate value of  $\langle I \rangle$  obtained from a graph of  $\langle I \rangle$  against  $\sin \theta$ . This conversion of the intensities is analogous to the derivation from structure factors of the 'unitary structure factor assuming atoms',  $\hat{F} = F / \sum_j f_j$  (Harker & Kasper, 1948). In practice, however, results so obtained are not better than those given by the quicker method of batching, especially when the list of reflexions is divided into several overlapping sets of contiguous batches. The alternative sliding-scale procedure, however, may well prove useful when dealing with sparsely populated zones or central reciprocal-lattice rows (Rogers, 1949).

It should be noted that although the  $P(z)$  distributions give a wider margin for discrimination at the low intensities, yet the use of the  $N(z)$  distribution is preferred because it provides a smoother plot in more obvious agreement with the theoretical curves.

### 3. Conditions for valid statistical treatment

The assumptions underlying the theory are

(i) that there should be a large number of atoms all occupying general positions in the unit cell and such that one or a few atoms do not dominate the intensity distribution, and

(ii) that a sufficiently large number of intensities should be used in calculating the averages.

After the determination of the cell contents and space group of a substance it is usually known if either of these assumptions is violated. If atoms are in special positions, or some have relatively larger scattering powers, the simple technique of the last section should be replaced by a special treatment appropriate to the material concerned. Paucity of intensities is a different problem for which the sliding-scale procedure already discussed may help. It is also possible to utilize for the derivation of the  $\langle I \rangle$  versus  $\sin \theta$  graph intensities other than the few to which the statistical analysis is applied.

The theory also assumes the use of fully corrected values of  $I$ . This is not always strictly necessary, since the observed values of  $\langle I \rangle$  may be allowed to include any factors which are regular functions of  $\theta$ , like the variation of the  $f$ 's and the temperature factor already considered. Thus, while it is necessary to allow for the irregular absorption corrections in single-crystal work, it is not necessary to do so in powder work, since the correction is then a regular function of  $\theta$ . It is, however, advisable to make corrections when their omission would exaggerate the decline in  $\langle I \rangle$ . Errors in the intensity data due to extinction cannot be allowed for satisfactorily, but inasmuch as they affect only the strongest intensities the shape of the significant low-intensity end of the  $N(z)$  plot is unaltered. The plotted points will lie on a curve slightly below the theoretical one, and can be brought into coincidence with it by means of a uniform contraction parallel to the  $z$  axis.

This may furnish some indication of the seriousness of the extinction errors in individual problems. It is clear, however, that the powers of the test are not impaired by the presence of extinction errors among the intensities.

It is also evident from the nature of the problem that random errors in the intensities have to be severe before producing any marked effect on the experimental  $N(z)$  plots. The irregular absorption in organic single crystals is generally small and so may be regarded as introducing small random errors which can be ignored without detriment to the test. Systematic errors responsible for consistently false relative intensities will, however, produce deviations, but as in practice these may be superimposed on other deviations due to minor departures from conditions (i) and (ii) above, they should be interpreted with caution.

### 4. Examples of the application of the statistical method

The substances treated here range from the favourable *l*-menthol to eucryptite, in which pseudosymmetry severely affects the intensity distribution.

#### A. *l*-Menthol

Unpublished data by D. Rogers.

Space group  $C3_1$ ;  $a = 21.5$ ,  $c = 6.10$  A.;  $Z = 9$ .

The asymmetric unit consists of three unrelated molecules of  $C_{10}H_{19}OH$ , in which all scattering units have an  $f$  between 7 and 9. The  $hk0$  zone extends only to a Bragg angle of  $30^\circ$  with Cu  $K\alpha$  radiation (the melting-point of the crystal is  $42^\circ$  C.), but there are available

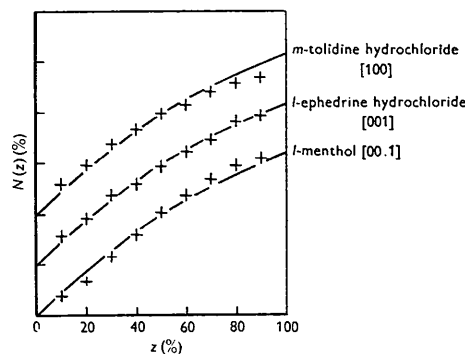


Fig. 2.  $N(z)$  curves for non-centrosymmetric projections. Successive curves displaced 20% vertically.

492 reflexions, i.e. 82 different intensities. These were utilized without correcting by geometrical factors or for absorption. The latter is small for menthol, and the cross-section of the crystal was a regular hexagon with corners rounded by evaporation.

The  $N(z)$  points are given in Fig. 2 and are in close agreement with the theoretical curve. The absence of a centre of symmetry from the projection is consistent with the space group and the optical activity of the crystal.

## B. 1:2:3:4-Tetraphenylcyclobutane

Data published by Dunitz (1948).

Space group  $P2_1/a$ ;  $a=17.02$ ,  $b=5.775$ ,  $c=12.35$  Å.;  $\beta=127^\circ$ ; two centrosymmetric molecules of  $C_4H_4(C_6H_5)_4$  per unit cell.

The statistics of the  $h0l$  zone are derived for both the observed and calculated  $F$ 's (Fig. 3). The observed data have a distribution agreeing more closely with the theoretical curve, but both are consistent with the centrosymmetric projection.

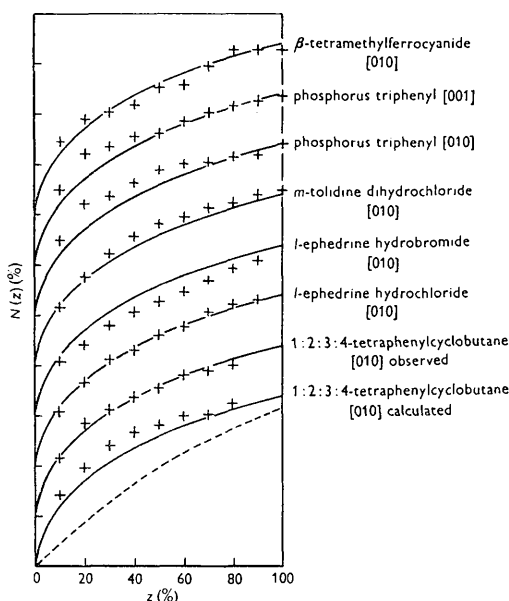


Fig. 3.  $N(z)$  curves for centrosymmetric projections. Successive curves displaced 20% vertically.

C. *l*-Ephedrine hydrochloride

Unpublished intensity data by D. C. Phillips.

Space group  $P2_1$ ;  $a=12.64$ ,  $b=6.15$ ,  $c=7.34$  Å.;  $\beta=102^\circ 6'$ ; two molecules of  $C_{10}H_{15}ON \cdot HCl$  per unit cell (Gossner & Neff, 1933).

The chlorine atoms are in general positions and contribute to all reflexions. The distributions for the centrosymmetric [010] and the non-centrosymmetric [001] projections are plotted in Fig. 1 in relation to the theoretical curves. The agreement is good and the distinction obvious. Wilson ratios appear in Table 2.

Table 2. Some values of the Wilson ratio  $\rho$

Substance (Theoretical values)	Projection	Wilson ratios	
		(I)	(I)
<i>m</i> -Tolidine	[100]	—	0.794
dihydrochloride	[010]	0.639	—
<i>l</i> -Ephedrine	[001]	—	0.761
hydrochloride	[010]	0.647	—
<i>l</i> -Ephedrine	[010]	0.695	—
hydrobromide			
$\beta$ -Tetramethyl ferrocyanide	[010]	0.632	—

AC 3

D. *l*-Ephedrine hydrobromide

Unpublished intensity data by D. C. Phillips.

Space group  $P2_1$ ;  $a=12.74$ ,  $b=6.20$ ,  $c=7.62$  Å.;  $\beta=100^\circ 48'$ ; two molecules of  $C_{10}H_{15}ON \cdot HBr$  per unit cell (Gossner & Neff, 1933).

This substance is isomorphous with *l*-ephedrine hydrochloride, and the difference in the intensity distributions for the [010] projection (Fig. 3) is probably due to the presence of the heavier bromine atoms.

E. *m*-Tolidine dihydrochloride

The structure determination was performed by Hargreaves & Taylor (1941), but the intensities employed here are those recently estimated by Fowweather & Hargreaves (1950).

Space group  $I2$ ;  $a=4.948$ ,  $b=6.18$ ,  $c=23.25$  Å.;  $\beta=91^\circ 20'$ ; two molecules of  $(CH_3 \cdot C_6H_3 \cdot NH_2 \cdot HCl)_2$  per unit cell.

The molecules lie on twofold axes and each possesses two chlorine atoms. Despite this slight lack of generality the  $N(z)$  points for the [010] and [100] projections (Figs. 3 and 2 respectively) leave no doubt that only the former is centrosymmetric; the space group is therefore  $I2$  uniquely and its choice by Hargreaves & Taylor is thus confirmed.

Full details of the derivation of the  $N(z)$  values have already been published (Howells, Phillips & Rogers, 1949); only the Wilson ratios are quoted here in Table 2.

## F. Phosphorus triphenyl

Unpublished data by E. R. Howells.

Space group  $P2/a$ ;  $a=11.6$ ,  $b=15.1$ ,  $c=8.57$  Å.;  $\beta=93^\circ$ ; four molecules of  $(C_6H_5)_3P$  per unit cell.

The  $N(z)$  values for both the [001] and [010] projections (Fig. 3) indicate the presence of symmetry centres. The departures from the theoretical curves which do occur are similar in both projections and are probably due to the comparatively heavy phosphorus atoms which are situated so that they make only small contributions to half the reflexions.

G.  $\beta$ -Tetramethylferrocyanide

Data by Powell & Stanger (1939).

Space group  $Pbca$ ;  $a=8.46$ ,  $b=13.24$ ,  $c=11.64$  Å.; four molecules of  $Fe(CH_3 \cdot NC)_4(NC)_2$  per unit cell. Intensity data shortly to be published by H. M. Powell & R. Hulme.

The heavy iron atoms are in special positions and the symmetry elements reduce the number of reflexions available in each zone. The experimental distribution (Fig. 3), however, leaves little doubt that the [010] projection is centrosymmetric.

## H. Mercury diphenyl.

Unpublished data by R. Gwynne Howells.

Space group  $P2_1/c$ ;  $a=5.56$ ,  $b=8.36$ ,  $c=11.66$  Å.;  $\beta=112\frac{1}{2}^\circ$ ; two centrosymmetric molecules of  $(C_6H_5)_2Hg$  per unit cell.

The very heavy mercury atoms lie at symmetry centres and dominate half the reflexions while making no contribution to the remainder. These latter should conform to the theoretical distributions since they are due to the phenyl groups only. They are, however, so very much weaker than the 'mercury' reflexions that their intensities and the average are on the extreme lower limit measurable. As a result it is not possible in this case to derive the significant low-intensity end of the  $N(z)$  curves.

It is hoped to discuss elsewhere the way in which the present statistical treatment should be modified to deal with the group of strong reflexions; this being a typical case of the general problem of the effects on the normal Gaussian functions produced by heavy atoms and pseudosymmetry.

### I. *Eucryptite*

Intensities from powder data by Winkler (1948).

Space group  $C6_22$ ;  $a = 5.27$ ,  $c = 11.25$  Å.; three molecules of  $LiAlSiO_4$  per unit cell.

The experimental distribution does not agree with either of the two theoretical possibilities; the substance produces an unusually high proportion of accidental absences, attributable to the structural pseudosymmetry. The top and bottom halves of the cell differ only in that one contains Al+Li where the other contains Si. Thus all reflexions with  $l$  odd are extremely weak.

### 5. Conclusions

The results confirm the Gaussian distribution found empirically by Hughes (1949) for the structure amplitudes of a centrosymmetric structure; they also provide quantitative verification of Wilson's theoretical distributions.

Only drastic departures from the conditions (i) and (ii) (§ 3) seem to disturb the distributions sufficiently to cause doubt in interpretation. The method may, therefore, be applied to a wide range of substances, being particularly suitable for the more complex organic compounds.

As a consequence of the ability to decide whether a unit cell or its projection possesses a centre of symmetry, the number of space groups distinguishable by X-ray means alone is considerably increased (Rogers, 1949).

Finally, it seems profitable to adopt the statistical survey of intensities as part of the routine procedure leading to Patterson and Fourier syntheses; in addition to the space-group information obtained, large systematic errors in the intensities may be revealed, and the data derived are of immediate use in converting the intensities to the absolute scale (Wilson, 1942).

We wish to record our appreciation of the interest of Dr A. J. C. Wilson in this work and our indebtedness to J. D. Dunitz, F. Fowweather, A. Hargreaves, R. Gwynne Howells, R. Hulme, H. M. Powell and G. B. Stanger who were consulted on matters relating to the materials and data used for the tests and who readily agreed to their inclusion in this study.

Two of us (E.R.H., D.C.P.) are indebted to the Department of Scientific and Industrial Research for financial assistance and to the University of Wales for the award of Research Studentships.

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## On the Derivation of Harker-Kasper Inequalities

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Group theory leads to an easy and straightforward method of finding Harker-Kasper inequalities.

1. In deriving inequality relations between structure factors, Harker & Kasper (1948), in their well-known

paper, applied Schwarz's inequality to the so-called simplified structure factor, which is written as far as