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Absorption and Other Errors in the Measurement of the Intensities of X-ray Reflexions from Single Crystals

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The origins of the tendency to underestimate absorption errors are discussed and the statement made that 'In most cases where accurate measurements are made, either photographically or by counter methods, the errors due to absorption in the crystal are greater than recording errors'.

Calculations for a square prism and experimental results for approximately spherical crystals are given to justify the statement.

These experimental results on a number of crystals combined with the tabulated values of A^*, the absorption correction factor for spherical crystals, permit calculation of a factor, β, which relates the coefficient of variation of intensity, $\nu(I)$, to the coefficient of variation of the crystal radius, $\nu(r)$. $\nu(r)$ is obtained from photomicrographs of the crystal. For values of μr less than 0·4, $\nu(I)$ is independent of θ, but for crystals above this value it varies in a somewhat complicated way with the Bragg angle.

$\nu(I)$ is calculated for a number of typical cases and the relative advantages of counter and photographic recording are discussed in the light of these results, together with the considerations leading to the choice of Mo or Cu radiation.

The values of $\nu(I)$ can be used to form weights for least-squares correlation of photographs of different reciprocal lattice layers or for the refinements of structure parameters. The calculations involved can be simply programmed for an electronic computer.

1. Introduction

With the advent of accurate recording methods, both photographic and counter, for measuring X-ray intensities, absorption errors assume a greater, and in many cases an overriding, importance. In many structure determinations they are the main factor limiting the accuracy with which bond lengths and electron density can be evaluated. But the importance of the absorption error is not yet sufficiently recognized, largely because of the long period during which eye estimation against a standard scale was the normal method of intensity measurement and absorption errors were only one of a number of contributions to the total error. The justification for ignoring or making inadequate corrections for these various errors is evident in the great advance of structural knowledge which has been achieved in this period. It is clear that a large collection of rather inaccurate data is usually sufficient to enable a reasonable approximation to a structure to be found. For many purposes such an approximation will be sufficient and a great deal of structural work is likely to continue to be carried out in this way.

Photographic recording has the great advantage that the primary record is permanent and the relationship between intensities is exhibited on the record together with other indications, such as shadows in the background, the effects of white radiation, *etc.*, which allow checks on the functioning of the apparatus to be made by inspection of the primary record. These visual checks are lost with counter recording and very elaborate instrumental checks are required as a substitute. A blind man might photometer a photograph and obtain indications of errors as well as records of spot densities, but the apparatus and checking procedures would be much more complicated than if man's most important sense were available. In the country of the blind there would be no alternative, but before the inherent advantages of photographic recording are abandoned for counter methods it is as well to weigh them in the balance. There is no doubt that for some problems the speed of automatic counter recording is imperative if the problem is to be solved at all. But there will continue to be many problems where this is not an overriding consideration and, in particular, accurate structure determinations of all kinds — to establish key structures beyond all reasonable doubt, to obtain accurate bond lengths and angles and electron densities, to study thermal vibration effects — will require certainty and accuracy rather than speed. It is true that counter recording is inherently more accurate than photographic methods, but if the errors from absorption in the crystal are greater than the recording errors in both cases, there is nothing to choose between them on the score of accuracy. The comparatively effortless certainty and the easy checking of suspect results which photographic recording provides may then well outweigh the greater speed and discrimination of counter methods.

Thus the question of the size of absorption errors, in relation to those of the recording method, is of crucial significance and the object of this paper is to estimate their relative importance under various conditions and to discover the best means of minimizing the total error in intensity.

On the basis of the evidence given in this and related papers the following statements can be made.

(i) In most cases where accurate measurements are made, either photographically or by counter methods, the errors due to absorption in the crystal are greater than recording errors.

(ii) For copper radiation (i) is almost invariably true, but, for organic crystals with no atom heavier than oxygen (*i.e.* $\mu \sim 10\ \text{cm}^{-1}$) and with linear dimensions less than 0·1 mm, absorption errors should not be greater than 0·5%, which is less than photographic recording errors in all cases. However, the introduction of a sodium atom, giving $\mu \sim 30\ \text{cm}^{-1}$, or the increase in size of the specimen, will bring absorption errors above recording errors for a considerable proportion of reflexions. For example, the benzil $(C_6H_5CO)_2$ crystal No. 4 (Fig. 1) had a diameter of 0·3 mm, $\mu = 12{\cdot}9\ \text{cm}^{-1}$, and gave a variation in intensity for symmetry-related reflexions of nearly 3%. This is for an approximation to a sphere; not a very good approximation, but the best that could be ground with such soft crystals. Unground shapes would certainly give greater errors and if the linear absorption coefficient had been $30\ \text{cm}^{-1}$, the errors would have increased to 8–10%.

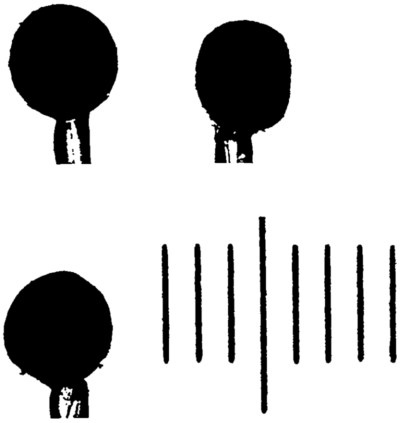

Fig. 1. Photomicrographs of one of the benzil crystals(No. 4) used for intensity measurements. Scale div. = 0·1 mm.

(iii) For molybdenum radiation, absorption errors can be ignored for a larger class of crystals. For those with no atom heavier than oxygen, crystals up to 0·5 mm can be used without introducing errors greater than 0·5%. For organic materials containing sodium ($\mu \sim 5\ \text{cm}^{-1}$) the crystals should not be larger than 0·1–0·2 mm for errors to be within this limit, and when the linear absorption coefficient gets beyond $10\ \text{cm}^{-1}$, then absorption errors, as for copper radiation, begin to become greater than photographic recording errors.

There are two groups of elements for which the linear absorption coefficients for Mo $K\alpha$ are only slightly less than for Cu $K\alpha$ radiation. Organic bromides, as a particular example, will have absorption errors nearly as large for Mo $K\alpha$ as for Cu $K\alpha$ for this reason.

Apart from the historical reason for ignoring absorption errors, there appears to be another reason for underestimating their importance resulting from fallacious reasoning from the absorption correction (A^*) tables. In a number of papers the following justification has been given for ignoring absorption errors. If half the average linear dimension of the crystal is taken as r, and the A^* tables for a cylinder with the corresponding value of μr show very little variation with θ, then the error due to absorption can be ignored. This is an almost complete fallacy. If the crystal were a perfect cylinder then, in such cases, absorption could be ignored, but no crystal is a perfect cylinder, despite all efforts to make it so. Consequently, for each reflexion there is an equivalent perfect cylinder, the radius of which varies from reflexion to reflexion, depending on the aspect of the crystal presented to the X-rays. What matters is not how A^* varies with θ, but how it varies with r. Thus it is the variation in the vertical columns (rather than the horizontal row) of the table which is significant, and this is quite large everywhere. At $\mu r = 0{\cdot}1$ the slope is still half as great as it is at 1·0. This explains why a crystal may have no significant variation of the absorption correction with θ, but nevertheless have quite large variations from one reflexion to another of the same θ.

Finally it cannot be too strongly emphasized that only the measurement of symmetry-related reflexions can give a full indication of absorption errors. Measurement of the same reflexion about two different axes only presents partially different aspects of the crystal to the X-rays (related by rotation about the plane normal) and, in general, these aspects are unlikely to be as different as those corresponding to different reflexions.

In this paper the 'coefficient of variation' (percentage standard deviation from the mean) of the intensity measurements on a set of symmetry-related reflexions is taken as the measure of the error in intensity.

2. Method of presentation

Section 3 examines the sources of errors, other than crystal errors, in measuring intensities and estimates their magnitude. § 4 discusses crystal errors. Because of the tendency to discount absorption errors it was felt desirable to present some calculations of absorption correction factors for cases which can be easily checked, as a basis for comparison with the subsequent experimental results on the measurement of the intensities of symmetry-related reflexions for a number of crystals ground to an approximately spherical shape. For the latter case a semi-empirical relationship is developed between the measured deviations from a true sphere and the variation of intensity due to absorption errors. In § 5 the calculation of total errors is dealt with and in § 6 the relation of § 4 is applied to some typical cases, and examples from the literature are discussed. Some deductions are drawn concerning the methods of minimizing absorption errors, and the relative merits of copper and molybdenum radiation and counter and photographic recording are examined.

3. Sources of error in measuring intensities other than crystal errors

(*a*) *Recording and measuring errors*

All recording of X-ray reflexions in this investigation has been done by the use of an integrating Weissenberg camera (Wiebenga & Smits, 1950). With care the instrumental errors involved can be reduced well below the photographic recording errors (Jeffery & Whitaker, 1963). These latter errors have been investigated (Rose & Jeffery, 1964), and under carefully controlled conditions are constant over the range of optical densities used at 0·006. Since the highest density normally measured is about 1·2, this means that photographic recording errors are approximately 0·5% of the highest intensity measured.

The optical densities of the central plateau of the integrated reflexions have been measured with a simple photometer (Jeffery, 1963) which, handled with care, will measure these uniform regions with an error of less than 0·5% for densities between 0·1 and 1·4. Below densities of 0·05 reflexions are best measured against a standard scale.

However, although a uniform optical density can be measured with negligible error, this is not the case for a region of variable density and such errors are discussed in the next section.

(*b*) *Errors due to the background*

Rose (1964) has discussed in detail the considerations involved in estimating these errors. The density of the background must be subtracted from that measured at the centre of the spot. If the background is uniform it can be measured at any convenient position, but where it is varying at a significant rate it is necessary to make two measurements of background symmetrically on either side of the $K\alpha$ reflexion and to take the mean. Difficulties arise, however, when a reflexion stands on a pronounced 'Laue streak'.

Rose (1964) has shown that even for copper radiation, errors of 30% in intensity measurement can arise, in extreme cases, from taking a mean value of the background. For molybdenum radiation the position is worse because the Laue streaks are far more intense and affect more reflexions. Also the absorption edges for silver and bromine on either side of Mo $K\alpha$ introduce further irregularities and the β filter has more effect on the Laue streak than is the case for copper radiation.

For copper radiation instances of large errors are fortunately rare and only occur with low-angle reflexions, where the geometrical factor reduces the absolute error.

4. Crystal errors

4·1. *Absorption errors*

In all but the most transparent crystals absorption modifies the reflected intensity by an amount which depends on the crystal shape and Bragg angle. The magnitude of this effect can be calculated for simple shapes and in 4·1(*a*) the results of calculations of the absorption correction factor, A^*, for a square prism are given. ΔA^*, the difference between the factors for the two cases considered, gives an indication of the error involved in ignoring such corrections, as a basis for comparison with the measured errors of 4·1(*b*).

(*a*) *Calculation of the absorption correction factors, A^*, for two reflexions from a square prism of side a* cm *for various values of μa.*

Fig. 2 gives the directions of the incident and reflected beams for the two cases considered. The crys-

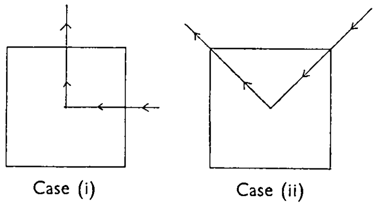

Fig. 2. The directions of incident and reflected beams in relation to the square prism for which the absorption correction factors of Table 1 were calculated.

Table 1. *Values of the absorption correction factor, A^*, for two cases of reflexion ($2\theta = 90°$) from a square prism of side a* cm *for various values of μa*

The equivalent values of μr for a cylinder are taken from the A^* tables

μa	3·2		1·6		0·8		0·4		0·2		0·1	
	A^*	μr	A^*	μr	A^*	μr	A^*	μr	A^*	μr	A^*	ur
Case (i)	7·7	1·66	3·51	0·866	2·00	0·438	1·44	0·221	1·204	0·1114	1·098	0·0545
Case (ii)	11·2	2·19	4·03	0·984	2·11	0·476	1·47	0·236	1·217	0·1178	1·104	0·0580
Diff. %	37	27·5	13·8	12·8	5·4	8·4	2·4	6·6	1·1	5·6	0·5	6·2
Δr	0·0166		0·0078		0·0048		0·0038		0·0032		0·0035	
$\hat{r}$	0·060		0·058		0·057		0·057		0·057		0·056	

tal is assumed to be bathed in a uniform incident beam and the absorption correction factors, A^*, were calculated by the method of Albrecht (1939). The results are given in Table 1. The value of the equivalent μr is taken from the A^* table for cylindrical crystals, p. 295 of the *International Tables for X-ray Crystallography* (1959). The differences are given as percentages of the average A^* or μr.

If we assume a constant value of $a=0{\cdot}1$ cm, then μ for the various columns is easily found. Dividing $\Delta\mu r$ and μr in each case by the corresponding μ gives Δr and r. These values are given in Table 1 and for the lower values of μ remain remarkably constant. This means that at least up to $\mu r=0{\cdot}5$ the equivalent perfect cylinders for the two cases remain the same size and the variation in ΔA^* (or the error, if corrections are not applied) is due entirely to the variation in μ. From $\mu r=1$ upwards the differences between the radii of the two equivalent cylinders increases rapidly with μ, but the average rises only very slowly.

The experimental results for approximately spherical crystals (4·1(*b*) and Fig. 3) indicate that the variation of equivalent perfect spheres for different aspects of an imperfect sphere is constant to much higher values of μr, presumably because the departure from circularity of each section is much less than for a square.

The percentage difference in A^* can be taken as a measure of the error incurred by ignoring absorption corrections for a square prism, but the figures quoted make no allowance for errors arising from the terminations of the prism and apply only to the two extreme cases for one Bragg angle, $\theta=45°$. It is difficult to assess the errors for all values of θ and all aspects of the crystal. However, the experimental results for spheres suggest that, for μa small one underestimates, and for $\mu a>1$ overestimates the errors, by using the percentage difference in A^* in lieu of the coefficient of variation of intensity.

(*b*) *The measured intensity errors for approximately spherical crystals and their relation to imperfection of crystal shape.*

The absorption correction factors for spheres and cylinders are tabulated, but actual crystals, even when specially prepared, depart from these exact geometrical shapes and thus make exact correction for absorption impossible. At each reflecting position the true absorption factor for an approximately spherical crystal will differ slightly from the absorption factor for a perfectly spherical specimen with the same volume. For each reflexion there will be a corresponding perfect sphere, the radius of which varies from reflexion to reflexion. For a set of crystallographically equivalent reflexions the standard deviation of the corresponding radii, $\sigma(R)$, is an indirect but convenient measure of the imperfection of the crystal shape. This model may be used to estimate the absorption errors arising from measured departures from a truly spherical crystal specimen. The necessary relations are developed in the next paragraph.

The observed integrated intensity, I, is inversely proportional to the absorption correction factor, A^*, and so,

$$\sigma(I)/I=\sigma(A^*)/A^* \,.$$

Since A^* is a function of R

$$\sigma(A^*) = \left(\frac{\partial A^*}{\partial R}\right)\cdot\sigma(R)$$

These expressions lead directly to

$$\frac{\sigma(I)}{I} = \frac{R}{A^*}\left(\frac{\partial A^*}{\partial R}\right)\cdot\frac{\sigma(R)}{R}$$

or

$$\nu(I) = \frac{R}{A^*}\left(\frac{\partial A^*}{\partial R}\right)\cdot\nu(R) \tag{1}$$

where $\nu(I)$ and $\nu(R)$ are the coefficients of variation of I and R respectively. The factor which converts $\nu(R)$ to $\nu(I)$ has been evaluated from the standard tables for A^* and it remains to relate $\nu(R)$ to the shape of the crystal specimen.

Measurements of crystal shape can be made by taking photomicrographs and from these the average crystal radius, $\hat{r}$, and an estimate of $\sigma(r)$, the standard deviation of the crystal radii, can be obtained. For an approximately spherical crystal, $\hat{R}\simeq\hat{r}$. The value of $\nu(I)$ can be obtained from a diffraction photograph by measuring the densities of spots in symmetry-related sets. After adjustment for film errors, the root mean square deviation of the densities in a set is an estimate of $\sigma(D)$ and $\nu(I)=100\sigma(D)/D$, where D is the average density of the related set. From equation (1) the value of $\nu(R)$ and thus $\sigma(R)$ can now be calculated for comparison with $\sigma(r)$.

This comparison has been made for seven specimens and the results are plotted in Fig. 3. Although many more results will be required to check the relationship it appears that the model of an imperfect sphere is a satisfactory one and that $\nu(r)$, the measured variation is approximately linearly related to $\nu(R)$, the variation derived from the model, *i.e.*

$$\sigma(R)/\sigma(r)=\nu(R)/\nu(r)=\alpha \,,$$

where α is about 2·8. For individual crystals α varies from 1·5 to 3·2 and the slope of 2·8 is likely to change as more results are obtained. The relation may turn out to be non-linear, but a linear approximation is likely to be sufficient for most purposes.

Thus the contribution of absorption to the coefficient of variation of the integrated intensities of reflexions from an imperfectly spherical crystal is

$$\nu(I) = \frac{\alpha R}{A^*}\left(\frac{\partial A^*}{\partial R}\right)\cdot\nu(r) \tag{2}$$

As it stands, the factor, β, relating $\nu(I)$ to $\nu(r)$ is a function of μ and R, but, by a simple transformation,

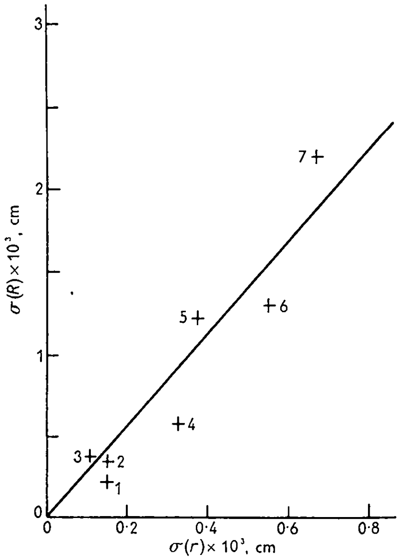

Fig. 3. Plot of $\sigma(r)$, the standard deviation of the measured crystal radius, against $\sigma(R)$ the standard deviation derived from the variations in density among sets of symmetry-related reflexions, with a sphere of variable radius used as a model.

Key

	μ	Radius
1. Paramelaconite No. 2	270 cm^{-1}	$9{\cdot}4\times10^{-3}$ cm
2. Whitlockite	274	11·2
3. Lithium fluoride	33·8	8·21
4. Co[Hg(CNS)$_4$] No. 2	480	10·2
5. Co[Hg(CNS)$_4$] No. 1	480	16·6
6. Benzil No. 4	12·9	16·7
7. Benzil No. 1	12·9	25·0

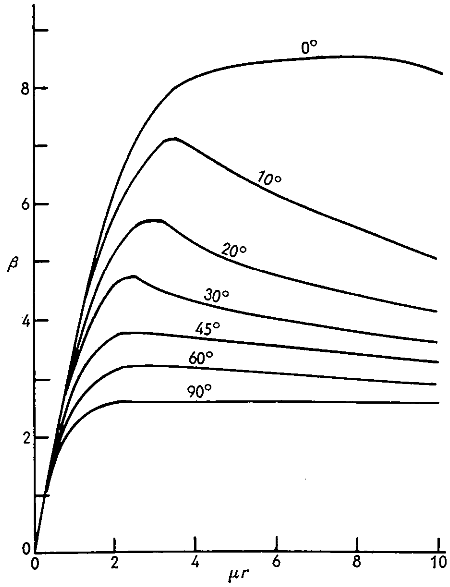

Fig. 4. Graph of $\beta = \nu(I)/\nu(r)$ against μr for various values of θ.

$$\beta = \frac{\alpha R}{A^*}\cdot\mu\cdot\left(\frac{\partial A^*}{\partial \mu R}\right)$$

(where μ is the linear absorption coefficient) and is thus a function of μR ($\simeq \mu r$) and can be plotted against it (Fig. 4).

The plot shows that for many organic crystals where μr is less than 0·4, absorption errors can be estimated from the much simpler relation,

$$\nu(I) = 380\mu . \sigma(r)\ . \tag{3}$$

This rule breaks down for larger μr; $\nu(I)$ then becomes dependent on Bragg angle and r.

4·2. *Extinction, disorder, thermal (or phonon) scattering, anomalous scattering and double reflexion*

Some of the scatter of the points in Fig. 3 may be due to variation of extinction effects with direction in the crystal, but comparison between spheres made from the same batch of crystals indicates that most of it is probably due to non-random shape variations. Whether extinction ever makes a significant contribution to $\nu(I)$ or not, its main effect is to produce systematic errors in the F values calculated from the intensities, and only the investigation of a number of crystals, or measurements on powders too fine to give extinction effects, or the direct measurement of extinction using polarized X-rays (Chandrasekhar, 1960) can eliminate or correct for these effects which may, in the case of a well ordered crystal, be the major obstacle to the production of a set of F values free from systematic errors.

Where a crystal shows significant disorder effects, accurate intensity measurements may allow deductions to be made about the type and extent of the disorder, but such crystals are unsuitable for accurate structure determinations since the corrections for disorder cannot be accurately obtained.

Thermal diffuse scattering (or phonon scattering) produces a background in the immediate neighbourhood of reflexions which cannot be effectively separated from the reflexion except by calculation which, at present, can only be carried out for simple cubic crystals. Nilsson (1957) gives a figure of 30% for the error in the integrated Bragg reflexion which may arise at high angles from this cause. The overall effect for potassium chloride and sodium chloride is to reduce the true temperature factor, and if this is at least approximately true in general the errors in bond lengths or integrated electron density from this source should be small. The errors in the temperature factor will, of course, be large and the electron density distribution will correspond to a lower temperature than that actually obtaining.

For crystals lacking a centre of symmetry, anomalous scattering may cause differences which could increase the variation in sets of reflexions related by Laue symmetry. This is unlikely to cause much increase in the variation unless the specimen contains atoms whose absorption edges are very near the incident X-ray wavelength. Statistical analysis of our results has shown no sign of such an effect.

Finally, if the symmetry-related reflexions contained a second reflexion, the inevitable slight missetting of the crystal would cause variable contributions from this second reflexion and give rise to an increase in $\nu(I)$. The comparatively small unit cells of the crystals used in this investigation make it unlikely that this effect has been present, but it cannot be completely ruled out.

5.1. *Estimation of total error*

To obtain an estimate of the errors in intensity (neglecting the errors discussed in 4·2) it is first necessary to measure the coefficient of variation of crystal radius and thus obtain $\nu(I)$ as detailed below. For each density $\sigma(D)=D.\nu(I)/100$ is easily obtained and combined with the film error.

To obtain the coefficient of variation of the radius the crystal should be photographed from at least three and preferably five directions at a magnification of a few hundred times. The directions should be typical of the whole crystal but need bear no special relation to the axes. (Normally the crystal will be rotated about an axis through 30° between exposures and the axis should make an angle of about 45° with the microscope axis if weighting of the measurements is to be avoided.) On each photograph a point corresponding to the crystal centre is chosen by finding the centre of the circle which is the best fit to the profile of the crystal. The crystal centre so obtained will not necessarily be the same in each photograph but if the crystal is essentially spherical the discrepancy is not important. Measurements of crystal radii can now be made and $\nu(r)$ calculated. To obtain a reliable result about 50 radii should be measured.

The method assumes that deviations from spherical shape are random. In particular, if there is any tendency for the shape to approximate to an ellipsoid of revolution about the rotation axis, $\nu(r)$ will be overestimated. If sufficient sets of symmetry-related reflexions are available in the data, they should be used to check, and if necessary correct, the value of $\nu(r)$ obtained from the photomicrographs. The value of μr is calculated and used with Fig. 4 or equation (3) to determine $\nu(I)$. If μr is greater than 0·4 it will be necessary to work with several values of β corresponding to ranges of Bragg angle. Three values, for 8° to 15°, 15° to 30° and over 30° are generally convenient for desk calculation.

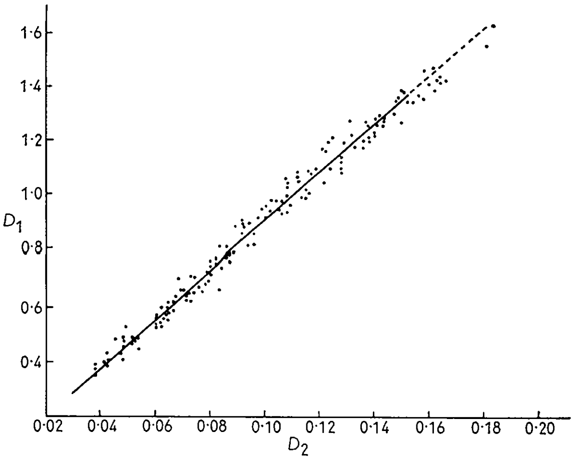

Fig. 5. Plot, for the $hk0$ reflexions of $Co[Hg(CNS)_4]$, of D_1, the density of a reflexion on the top film against D_2 for the second film. The linear relationship begins to break down for $D \sim 1{\cdot}4$. Top film: Ilford Industrial G; bottom film: Ilford Industrial B.

When two films are used it is necessary to determine the ratio, k, of the densities D_1 and D_2, of the same reflexions on the top and second films and then to convert the densities on the second film to their top-film equivalents by the relation, $d_1=kD_2$. This process, by itself, introduces little error if there is a fair number, N, of measurable reflexions common to both films from which k can be determined (Fig. 5). The error can be estimated as follows. If $k=D_1/D_2$ then

$$\frac{\sigma(k)}{k} = \left[\left(\frac{\sigma(D_1)}{D_1}\right)^2 + \left(\frac{\sigma(D_2)}{D_2}\right)^2\right]^{\frac{1}{2}}$$
$$= \sqrt{2}\,.\,\sigma(D)/D$$

in the range of densities where $\sigma(D_1)/D_1=\sigma(D_2)/D_2=\sigma(D)/D$.

Thus the standard error of k is

$$\alpha(k)=\sqrt{2}\,.\,k\,.\,\sigma(D)/D\,.\,\sqrt{N}\ .$$

If d_1 is the equivalent density on the top film to the density D_2 of a reflexion on the second,

$$d_1=kD_2$$

and

$$\frac{\alpha(d_1)}{d_1} = \left[\left(\frac{\alpha(k)}{k}\right)^2 + \left(\frac{\alpha(D_2)}{D_2}\right)^2\right]^{\frac{1}{2}}.$$

The standard error of a single observation is the standard deviation of the population from which it is drawn

$$\therefore \frac{\alpha(d_1)}{d_1} = \frac{\sigma(d_1)}{d_1}\,;\ \frac{\alpha(D_2)}{D_2} = \frac{\sigma(D_2)}{D_2} = \frac{\sigma(D)}{D}\ .$$

Thus by substitution

$$\frac{\sigma(d_1)}{d_1} = \frac{\sigma(D)}{D}\left[\frac{2}{N}+1\right]^{\frac{1}{2}}.$$

Since N is normally a considerable fraction of the total number of reflexions observed, the additional error introduced by transferring densities from the second film to the first is small.

Difficulty will be experienced with high angle reflexions which partially resolve the $K\alpha$ doublet. The additional error here can only be roughly estimated from experience in the photometry of such spots. Fortunately, for both this special case and the case of low-angle reflexions on strong Laue streaks, the geometrical correction factors are small and the absolute errors are thereby reduced.

5.2. *Computation of expected errors*

The calculation of expected errors as outlined above is easily adapted to electronic computing. A simple Autocode program for the Ferranti Mercury Computer forms errors by computing the expression:

$$\sigma(D) = \surd(a^2 + (bD)^2 + (cD)^2)$$

where a is a constant (normally taken as 0·006) and b is a factor which is zero for most reflexions but, for the difficult cases mentioned above, is an estimate of the additional error and is put in with the corresponding intensity data. So far values of b have been taken in the range 0·03–0·07, including 0·04 for values of $D > 1{\cdot}0$ which allows for an error in the factor, k, used in determining D-values from the second film. The high value of 0·07 applies to reflexions on the second film which also lie on a strong Laue streak or have partial $\alpha_1\alpha_2$ separation. The values have been deliberately estimated on the high side since the errors are ultimately used to form weights for a least-squares program. c is the main factor and is derived from a curve, plotted from the data of Fig. 4, of $\sigma(D)/D$ *versus* d^*. The ordinates of this curve are fed in as part of the data and the program forms $\sigma(D)$ and multiplies both this and the value of D by Lp and A^* correction factors. $\surd W = \text{Const}/\sigma(D')$ is then formed for use in least-squares correlation of layers. In a subsequent program for producing a correlated and averaged set of intensities, $\surd W' = k\surd(\Sigma W \times D')$ is formed, where W' is the weight for the corresponding F value, and $\surd W'$ is expressed as an integer in the range 1–31, ready for use in Rollett's (1961) S.F.L.S. program (World List 4036).

6.1. *Calculated errors in typical cases*

Fig. 6 shows examples of $\nu(I)$ calculated for several typical cases for crystal errors only. The radius of the sphere is taken as 0·15 mm in all cases, and $\nu(r)$ has the value of 2·5%, corresponding to the average variation of the spheres used in this investigation. (The variation for the sphere of lithium fluoride, which is the best so far produced, is 1·36%). Table 2 gives values of μ for various typical cases.

Table 2. *Values of* μ *for* Mo $K\alpha$ *and* Cu $K\alpha$ *together with an indication of the kinds of material having such absorption coefficients*

μ		
Mo $K\alpha$	Cu $K\alpha$	Substance
1·5	10	Molecular organic compounds, no atom heavier than O.
4	30	Na salts of organic acids, *etc.*; inorganic crystals composed of atoms of low atomic number and containing large amounts of water of crystallization
12 80	100	Organic bromides, *etc.*; inorganic crystals composed of light elements or heavier elements with water of crystallization
35 200	300	Organic crystals containing fairly heavy atoms; inorganic crystals composed of elements in the intermediate range
200	500	Crystals containing very heavy elements

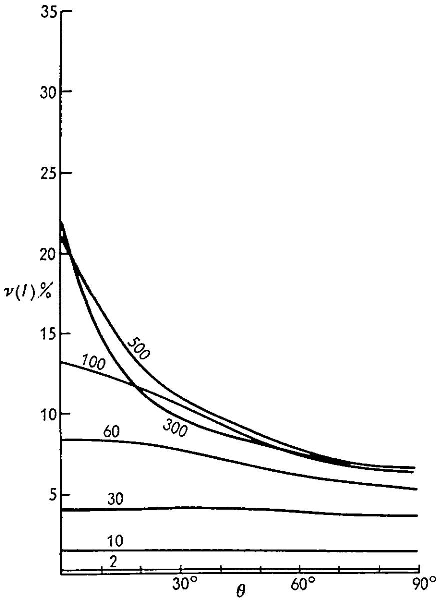

Fig. 6. Graphs showing values of $\nu(I)$ against θ for various values of μ (marked on the curves) and spheres of radius 0·15 mm. The value of $\nu(r)$ is taken as 2·5% corresponding to the average of the spheres used.

6·2. *Relation of* $\nu(I)$ *to* μ *and crystal shape and size*

For crystals of a given perfection of shape the absorption errors increase initially as substances of higher linear absorption coefficient are examined, (linearly up to $\mu r = 0{\cdot}4$). When, however, a value of μr of about 2 is reached there is little further increase in the errors. It is always an improvement to reduce $\sigma(r)$, if r is constant, but Fig. 4 shows that it is not advantageous to reduce r, even if $\sigma(r)$ can be reduced in the same ratio ($\nu(r)$ constant), unless μr can be made less than about 2. If μr is less than 0·4, $\nu(I)$ becomes independent of r, and, for a given substance, depends only on $\sigma(r)$.

6·3. *Examples from the literature*

In the very careful work of Drenth & Wiebenga (1955) the intensity 'error' of 5·8% was probably at least half due to absorption (although the value of μ was only 5 cm^{-1}) since the crystal of $C_{20}H_{18}$ was in the form of a rhomb, approximately 0·03 cm across, and $\sigma(r)$ for such a shape will clearly be several times as great as the 1×10^{-3} cm for a rather poor sphere of the same size. If it is only twice as great $\nu(I) \sim 4\%$.

Swallow & Truter (1960), in the very accurate structure determination of $(PtO_2C_{12}H_{24})_2$, used an equant crystal of 0·1 mm side. Since μ was nearly 200 cm^{-1}, this gives $\mu a = 2$. From Table 1 the difference in A^* for the two reflexions of Fig. 2 for such a crystal would be nearly 20% and it is probable that the variation in intensity produced by absorption in this crystal was at least 10%. In other words, at least two-thirds of the R value of 7·6% was probably due to absorption errors.

6·4. *Copper and molybdenum radiation with photographic and counter recording*

Even for spheres of $\mu = 10$, $v(I)$ for an average sphere would be 1·4%, and with the best sphere so far produced, 0·4%, without taking into account recording errors. For film these latter errors give $\sigma(D) = 0{\cdot}006$ and in the average case (which is likely to be difficult to achieve with soft organic crystals) crystal errors are greater than this for $D > 0{\cdot}5$. Thus the increase of recording accuracy possible with counters would in most cases only be justified if a considerable number of weak reflexions were to be measured. This would be the case if it were desired to measure beyond the limiting sphere for Cu $K\alpha$ radiation, by using molybdenum radiation. Here the necessity of discrimination to deal with the background problem, together with the much greater efficiency of scintillation counters for short wavelength radiation, provide cogent reasons for the use of such counters. The use of molybdenum radiation also reduces crystal errors — often considerably — but only to a very limited extent when elements from nickel to yttrium or holmium to uranium are responsible for most of the absorption. The higher values of μ in the Mo $K\alpha$ column of Table 2 correspond to such cases. Even when absorption is reduced considerably by the use of Mo $K\alpha$ radiation, crystal errors will often be comparable to, or greater than, recording errors for the strong reflexions, even with organic crystals.

Where molybdenum radiation is used to reduce θ values, as in the case of retigraphs, the desirability of discrimination is a strong argument for the use of counters. However, apart from its much greater simplicity, the general survey and self-checking properties of photographic recording are very desirable where many hundreds of reflexions have to be measured, and the arguments for the use of counters need to be very strong to justify sacrificing these properties.

If photographic recording is employed, Cu $K\alpha$ radiation has many advantages — shorter exposure times, reflexions more widely spaced, far less background of Laue streaks, less liability to produce simultaneous reflexions — and where absorption is not greatly reduced by the use of Mo $K\alpha$ radiation it will normally be the radiation of choice. For large unit cells, where integrated reflexions with Mo $K\alpha$ radiation would merge into one another, it will also be required. However, for smaller unit cells, and where absorption is considerably reduced by the use of Mo $K\alpha$ radiation, it may be that the reduction of absorption errors will more than compensate for the increase in background errors, although the margin of advantage is not likely to be large, especially as a number of difficulties connected with the reduction in size of the reciprocal lattice have to be taken into account (Jeffery & Whitaker, 1964). It will be necessary to compare experimentally the results obtained using the two radiations on a suitable crystal. Since background errors may well be largely systematic, comparison must be made with intensities calculated from the crystal structure, and extinction will also have to be taken into account.

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