Acta Cryst. (1964). **17**, 21

Errors Arising from the Photographic Recording of X-ray Intensities

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(*Received* 5 *February* 1963 *and in revised form* 10 *April* 1963)

Photometric measurements on simulated and actual integrating Weissenberg films show that over the normal range of optical densities the error due to the film is less than 1% of the greatest intensity measured on a film, provided this is arranged to give a density of about 1·0. The effects of development techniques and spot size, the dependence of errors on density and the consistency between different observers were investigated.

Introduction

This investigation was carried out as part of a program for achieving the highest possible accuracy in the photographic measurement of X-ray diffraction intensities (Jeffery & Rose, 1964; Jeffery & Whitaker, 1963; Jeffery, 1963). The maximum accuracy is limited in the first place by the errors inherent in the recording method and this was investigated by means of photometer measurements on simulated integrating Weissenberg photographs, and on actual diffraction photographs. The results show that errors due to photographic recording can be reduced well below 1% for exposures giving an optical density of about 1·0. This is considerably less than has commonly been estimated and it seems clear that much of the error attributed to photographic recording is due partly to the crystal and partly to inadequate methods of measurement.

Photometer measurements

All measurements of optical density were made on the photometer described by Jeffery (1963) (or an earlier version) after steady conditions had been reached. Photometer errors are quoted from that paper. φ is used for photometer scale readings, φ_S for the spot, φ_B for the background.

Simulated diffraction photographs

Ilford Industrial G films were set up normal to the beam 3 m from a micro-focus X-ray tube. In front of the film was placed a drilled copper mask. The pattern of holes is shown in Fig. 1. The lines of holes running the length and breadth of the mask were used to check the uniformity of the beam. A series of exposures was made to provide films in a range of densities and for the assessment of alternative development techniques. This procedure assumes that the effect of a uniform beam containing the whole X-ray spectrum will be similar to that of a uniform monochromatic beam. This assumption is justified later by a comparison with results from actual diffraction photographs produced by Cu $K\alpha$ radiation.

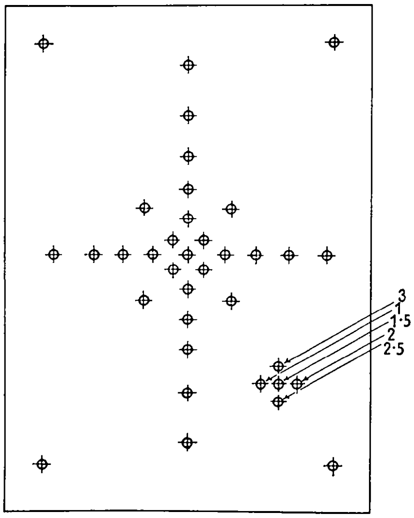

Fig. 1. Diagram (approx. one-third actual size) showing the pattern of holes on the mask used for producing simulated diffraction photographs. All holes are 1·5 mm in diameter except those whose diameters (mm) are marked.

Development techniques

Tank development is employed, using filtered solutions in a thermostatic bath, with paddle agitation of the developer every 15 seconds. The film holder and paddle is shown in Fig. 2.

As a final check on this arrangement two of the exposed films were processed, one by the standard technique and the other by simple immersion without agitation or temperature control in solutions which had been in general use for some time. The densities of the central five spots above background were measured three times on each film. The average densities of the two films were both about 0·3. The use of the old developer increased the background fog from 0·142 to 0·165 and the standard deviation of the

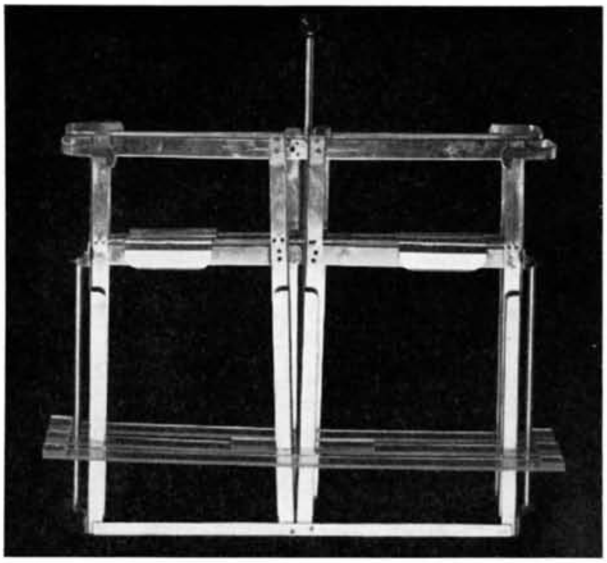

Fig. 2. Photograph of the frame and paddle used to produce controlled agitation during development. The frame is formed from two adapted Kodak No. 16 double film channel hangers joined together to give a 4-film rack. The 3-strip Perspex paddle with 9 mm gaps for the films can be raised by the central rod.

spot density from 0·0064 to 0·0102. Most of the latter increase is probably due to the lack of proper agitation. It was concluded that the standard technique adopted could not usefully be improved upon and that development conditions, although important, were not critical.

The rest of the masked films were processed by the standard technique.

Effect of spot size

Photometer deflections for the group of spots of different sizes were measured five times on one film. The average deflection varied from 14·06 to 14·40 cm, but the variation was not a function of size. Since the light beam in the photometer has a diameter of 0·5 mm these observations suggest that there are no edge effects in the spots. A check of this was made by measuring different parts of a typical spot 1·5 mm in diameter. The average of 15 galvanometer deflections distributed over the spot was 24·83 cm and the average of three taken at the centre was 24·87 cm.

The dependence of errors on average density

Since $D = \log (\varphi_0/\varphi_S)$ where φ_0 is the constant reading without any film, it follows that the standard deviation, $S(D)$ of the density variation over one film is given by:

$$S(D) = S(\varphi_S)/\varphi_S\ .$$

The values of $S(D)$ were obtained from 106 measurements on 10 films and adjusted for photometer errors. The average densities of the 10 films ranged from 0·08 to 1·10 and the adjusted values of $S(D)$ from 0·0032 to 0·0106. $S(D)$ is not a function of the density and the best value obtained by pooling all the results is 0·0051.

This value has been used as applicable to all of the Ilford Industrial G film measured.

Uniformity of the background

Sets of 30 observations of φ_B were made in the background on each of three films. The average standard deviation of background density calculated from these observations was 0·0033 and did not vary significantly between films.

Standard deviation of the density of an integrating Weissenberg reflexion

In observations of the optical density of a diffraction spot, variations of spot density and background density will combine to produce the observed variations. The standard deviation will be

$$\begin{aligned} S(D) &= (3{\cdot}3^2 + 5{\cdot}1^2)^{\frac{1}{2}} \times 10^{-3} \\ &= 6{\cdot}1 \times 10^{-3} \end{aligned}$$

Comparison of measurements on diffraction photographs

Provided other instrumental errors are negligible, the differences between the same reflexions on two integrating Weissenberg films taken under identical conditions should be equivalent to this standard deviation of $6{\cdot}1 \times 10^{-3}$. This test was accompanied by a test of the uniformity of the nickel filter used on the layer line screen. The original pair of photographs, both taken without a filter, could not be used and the authors are indebted to Mr A. Whitaker for providing data from two similar pairs of photographs taken with a lithium fluoride crystal. The exposures for the two pairs were adjusted to give a wide range of densities and all the densities measured on one film of a pair were plotted against those of the other. The slope of the best straight line from the origin was used to multiply the second set of intensities to make them comparable with the first. The differences between corresponding spots were averaged over symmetry-related sets (7 or 8 in a set) and divided by 1·128 to give the standard deviation. Adjustments were made for photometer errors to give the standard deviation for all other instrumental errors (Table 1). A double film pack was used. The first group of results in Table 1 is for the top films (Ilford Industrial G) and the second set for the bottom films (Industrial B). The figures are very scattered but there is a tendency, probably real, for the standard deviation to rise with density, and the standard deviation can be expressed

Table 1. *Standard deviations due to instrumental errors other than photometer errors*

Average density	No. of pairs	Mean difference	Standard* deviation
0·05	8	0·003	0·0027
0·31	8	0·011	0·0095
0·36	8	0·007	0·0060
0·90	8	0·009	0·0076
1·38	8	0·020	0·0162
0·05	8	0·003	0·0027
0·26	8	0·006	0·0053
0·53	8	0·019	0·0168
0·78	7	0·014	0·0120
1·19	8	0·022	0·0188

* See Table 2.

as $S(D)=[0{\cdot}006^2+(0{\cdot}01D)^2]^{\frac{1}{2}}$ for the top films and $S(D)=[0{\cdot}006^2+(0{\cdot}02D)^2]^{\frac{1}{2}}$ for the bottom films. The first error proportional to D was subsequently shown to be due mainly to the inadequate size of the uniform centres of the integrated spots, so that differences in positioning the spots on the photometer produced errors which would not arise with sufficiently large integrating limits (see next section). If the additional independent error in the bottom films is due to the lack of uniformity in the absorption in the top film, this gives an error of about $0{\cdot}017D$ from this cause.

The test combined with a check on the nickel filter was made with a benzil crystal (No. 4) (Jeffery & Rose, 1964). One photograph was taken with the filter in place, one without. Since, in order to keep a constant background error, measurements were made in this, as in the previous case, to one side of the Laue streak, it was necessary to obtain the correlation factor for each group of symmetry-related reflexions independently. The results were otherwise treated exactly as for the previous case and are given in Table 2. Again, with considerable scatter, the results are consistent with a standard deviation of 0·006 due to the film, and an independent error due to the filter with a standard deviation of $0{\cdot}028D$. This latter error would correspond to a standard deviation in thickness of the nickel filter of $0{\cdot}7\ \mu$ (a relative variation of 3%). It would therefore seem desirable, where filtration is necessary, to put the filter in the primary beam and not round the layer line screen. The consequent increase in background radiation on the film should not normally produce errors of more than a fraction of 1%. Although it cannot be taken as completely established that the increased variation with higher densities is due to the filter, it is significant that the variation found by Lonsdale (1948) using a counter technique, is of the same order.

Table 2. *Check on error due to filter*

Average density	Number of pairs	Mean difference	Standard deviation*
0·05	13	0·005	0·0044
0·10	14	0·006	0·0053
0·20	7	0·012	0·0106
0·60	6	0·009	0·0082
1·4	7	0·037	0·031
1·6	7	0·061	0·049

* Standard deviation of repeated measurements after allowing for photometer errors.

Reproducibility of measurements on integrating Weissenberg film

Known contributions to variation arise from the background, the spot and the photometer. The background standard deviation is 0·0033 and that of the spot will probably be little greater because repeated measurements are made in almost exactly the same place. If we assume the two to be equal the combined standard deviation will be $0{\cdot}0033\sqrt{2}=0{\cdot}0047$. This constant value must be combined with a photometer error which varies with the density.

One set of 8 symmetry-related reflexions from a hexamine crystal was measured by three observers and five sets of 7 or 8 were measured by two observers. The average standard deviation calculated from the difference between pairs or the greatest difference among triplets, and after allowing for the photometer error, is 0·0027 for the three observers and 0·0042 for the two observers, compared with the expected value of 0·0047. Thus repeated measurements by different observers are consistent with the film and photometer errors previously derived.

Proportionality of blackening and exposure

A direct check on the linearity of Industrial G film was made with a rotating sectored disc. All the films gave plots of density *versus* exposure which showed small departures from linearity at densities well below 1·0, whereas graphs obtained by plotting D_1 *versus* D_2 for double film pack integrating Weissenberg photographs (Jeffery & Rose, 1964) show a linear relationship to well above density 1·0. Since in the latter case the effect is due to monochromatic radiation it seems probable that the rotating sector is showing up a slight failure of the reciprocity law over the wide range of wavelengths involved, rather than a lack of proportionality between blackening and exposure for Cu $K\alpha$ radiation.

Conclusion

From measurements on simulated diffraction photographs, checked in various ways by measurements on integrating Weissenberg photographs, it is concluded that with careful development and photometric techniques the error in intensity due to photographic recording is about 0·5% of the greatest intensity measured on the top film (*i.e.* a spot of density slightly greater than 1·0). For reflexions too intense to be measured on the top film the error will, of course, be multiplied by the factor of about 8, relating densities on the top to those on the second film, but the intensities will be multiplied by the same factor, so that for this group the error will also be about 0·5% of the greatest intensity measured, corresponding to a nominal density of about 8·0. The lack of uniformity of absorption in the top film will increase this error to about 1·5%.

The contribution to the error from the photometer is negligible over most of the range of density measurement, although, since it is difficult to separate out the two contributions, it is possible that the film error is slightly smaller and the photometer error larger than has been estimated. The main finding, however, is that the total error is small.

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Acta Cryst. (1964). **17**, 24

The Crystal Structure of Nickel β-Alanine Dihydrate*

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(*Received* 22 *October* 1962 *and in revised form* 18 *March* 1963)

Nickel β-alanine dihydrate, $Ni(NH_2CH_2CH_2COO)_2.2H_2O$, crystallized from aqueous solution, is triclinic, space group $P\bar{1}$ with one molecule per unit cell of dimensions

$$a=8{\cdot}48,\ b=6{\cdot}77,\ c=4{\cdot}93\ \text{Å};\ \alpha=103{\cdot}0^\circ,\ \beta=95{\cdot}2^\circ,\ \gamma=102{\cdot}3^\circ.$$

The two nitrogen atoms, the two carboxylic oxygen atoms (one from each β-alanine molecule) and the two water oxygen atoms form a slightly distorted octahedron around the nickel atom. The nickel β-alanine dihydrate units are held together by hydrogen bonds in a stable layer structure parallel to (100). The neighbouring layers are linked with each other by van der Waals bonds.

Introduction

In a study of β-alanine in this laboratory, a suitable trial structure could not be postulated because of the lack of knowledge of molecular geometry. The present structure analysis of nickel β-alanine dihydrate was undertaken in order to determine the structure of the β-alanine residue, and also because it was of interest to compare its crystal and molecular structure with those of other similar metal complexes. The crystal structure of copper β-alanine hexahydrate has recently been determined (Tomita, 1961).

Experimental

The crystals of nickel β-alanine dihydrate were obtained from aqueous solution. They are triclinic and grow as needles elongated along the short c axis. The crystal and physical data obtained are as follows:

$$a=8{\cdot}48,\ b=6{\cdot}77,\ c=4{\cdot}93\ \text{Å};$$
$$\alpha=103{\cdot}0^\circ,\ \beta=95{\cdot}2^\circ,\ \gamma=102{\cdot}3^\circ.$$

Space group, $P\bar{1}$.

Preliminary values of axial lengths were obtained by means of rotation photographs, and more accurate values were determined from high-angle axial reflexions in Weissenberg photographs, from which the angles α, β and γ were also obtained.

The observed density at 25 °C, measured by the flotation method, is 1·720 g.cm^{-3}, and the calculated density for one molecule of $Ni(NH_2CH_2CH_2COO)_2.2H_2O$ per unit cell is 1·689 g.cm^{-3}.

The linear absorption coefficient μ for Cu $K\alpha$ radiation is 30·1 cm^{-1}. Reflexions of the type $hk0$, $h0l$ and $0kl$ were obtained from zero layer Weissenberg photographs, using Cu $K\alpha$ radiation and the multiple film technique. Of the 144 possible reflexions in the $hk0$ zone, 107 were observed, while in the $h0l$ and $0kl$ zones, 73 and 68 reflexions were observed out of a possible 100 and 87 respectively. The specimens used were between about 0·1 mm and 0·25 mm thick along different directions, normal to the oscillation axes. Intensities were measured visually and corrected for the Lp factor in the usual way. No absorption correction was applied.

Preliminary values of the scale factors and the temperature factors, obtained by Wilson's method (1942) were improved during the later stages of

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* Communication No. 538 from the National Chemical Laboratory, Poona-8, India.