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X-ray Photography as a Means of Accurate Intensity Measurement

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The methods normally used for photographic intensity measurement are briefly reviewed and the evidence given for the accuracy claimed ($\sim$1% error) for the method of choice – photometry of integrating Weissenberg photographs taken with Cu $K\alpha$ radiation. Examples are given of the use of the method in critical cases and the advantages and requirements of the photographic method are stated.

Introduction

The methods normally used for intensity measurement by photographic means may be classified as:

(1) Eye estimation against a standard scale, preferably made from a reflexion of the crystal concerned, and followed by spot area correction. The best accuracy that can be expected is not much better than 10%.

(2) Flying spot photometry of a normal (non-integrated) reflexion. This may be necessary if minimum exposure times are required for any reason, but apparatus is complicated and expensive and the accuracy only about 3–4%. The contouring photometer may serve the same purpose for a few reflexions, but is mainly useful for following changes taking place in the specimen.

(3) The photometry of integrated reflexions produced by an integrating Weissenberg or precession camera. This involves increasing the exposure time by a factor of 2 or 3, but spots with a uniform central area, whose optical density is proportional to the integrated reflexion, can be measured with a simple photometer of moderate cost (Jeffery, 1963). Such an instrument gives an accuracy of better than 1% in measurement of optical density over the required range. It is this third method that we have investigated, specifically for the case of an integrating Weissenberg camera using Cu $K\alpha$ radiation.

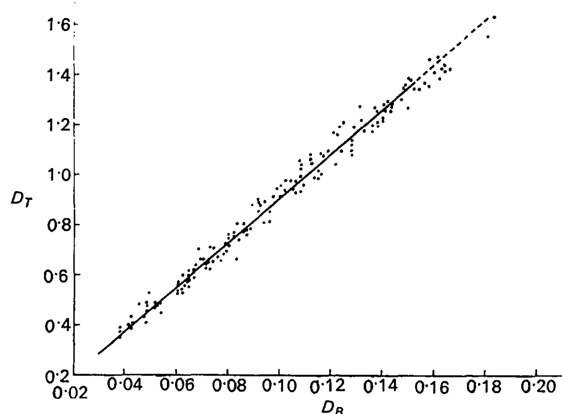

Fig. 1. D_T (density on top film) *vs.* D_B (density on bottom film). This is a typical example from a large number of plots all of which show linearity beyond $D_T = 1{\cdot}0$.

Accuracy attainable

The work of evaluating the accuracy of photographic measurements was started by Dr Rose, then a part-time student at Birkbeck College, before the first investigation of X-ray films undertaken for the I.U.Cr. (1956). Only Ilford Industrial G and B films were investigated, but in more detail than could be done by the wider investigation. Rose employed a mask with holes of various sizes and distributions to produce simulated integrated diffraction photographs, using the direct beam at a considerable distance from a fine focus tube. He investigated the effect of development techniques; spot size; edge effects; the dependence of errors on density; background errors; errors on the second (Industrial B) film of a pack. His results showed a constant error in optical density of 0·005, independent of any of the factors listed above. Since an optical density of about 1·0 is the maximum that can be used, the error here would be $\frac{1}{2}$%, rising to 1% at density 0·5 and 10% for very weak reflexions at density 0·05.

However, comparison of two integrated diffraction photographs from the same crystal, with nearly identical exposures, showed that the top film errors could best be considered as due to a constant error of 0·006 plus an independent error of 0·3% of the spot density. The second film had a constant error of 0·008 plus 1·5% of the density. Subsequent work by various people has verified this increased error on the second film and Rose (1965), in an appendix to his thesis, showed that the two results could be reconciled by taking account of the effect of white radiation (with much lower absorption) on the masked films. Most of the results on masked films are valid, but the result on the size of the errors only gives a lower limit and does not show the dependence on density which actually occurs with Cu $K\alpha$ radiation. Since the results for Cu $K\alpha$ depend on one pair of diffraction photographs (although there is implicit confirmation from later results on total errors, *i.e.* including absorption errors) it would be useful to have them checked by an investigation of masked films using fluorescent radiation. The second I.U.Cr. investigation on films (Morimoto & Uyeda, 1963) included 'homogeneity' but no detailed results were given. Such an investigation should show a decrease of dependence on density for Mo$K\alpha$ compared with Cu $K\alpha$.

The other result partially vitiated by use of radiation from the X-ray tube concerned the extent of linearity of density *versus* X-ray intensity. Rose used a stepped rotating disc and corresponding line of holes in a mask to produce simulated diffraction spots of varying exposures. He found that linearity did not extend beyond a density of 0·8. However, when the reflexions on a double film pack from diffraction photographs are compared, the limit of linearity goes up. Rose could not get fully reproducible results, but the lowest linear range for Cu $K\alpha$ was 0·9 and it went up to 1·4. Subsequent work has shown that linearity normally extends up to density 1·2.

Since the film-to-film ratio for a double film pack has to be obtained in each case, it is best to plot the densities of spots measurable on both films against one another, and obtain the ratio fron the slope of the straight portion of the graph and the extent of linearity at the same time (Fig. 1).

One can roughly summarize the results on photographic measurement of intensity by saying that the errors can be reduced to the order of 1% by arranging to obtain an optical density of around 1·0, but that for normal purposes with a two-film pack the errors in a range of intensities from 1 to 1000 are as given in Table 1. Very weak reflexions 1–5 on this scale will normally be measured to, at worst, 10% by eye estimation of a non-integrated Weissenberg photograph taken before the integrated one, which also allows a check on spot size for integration.

In most cases these errors are less than those arising from crystal shape and texture, but there is one exception which can provide an important limitation. The white radiation streak through low angle reflexions derives to a considerable extent from higher order reflexions than the one being measured and therefore the background density must be measured in the streak on either side of the reflexion. If the background is varying linearly, little additional error is caused, but this is by no means always the case. Rose (1965) investigated this in detail and found one case of a medium intensity, low order reflexion, on a Laue streak deriving from strong higher orders, where the slope of the background was changing so rapidly in the neighbourhood of the reflexion that an error of 30% was caused by taking it to be linear. It is one of the real advantages of proportional counters and discrimination that such problems can be effectively dealt with. However, only a few reflexions are usually affected with Cu radiation although the problem is more serious with Mo. Such reflexions must be given a lower weight in least-squares procedures.

That the estimate given here of the accuracy attainable is not unduly optimistic and may, in fact, be an

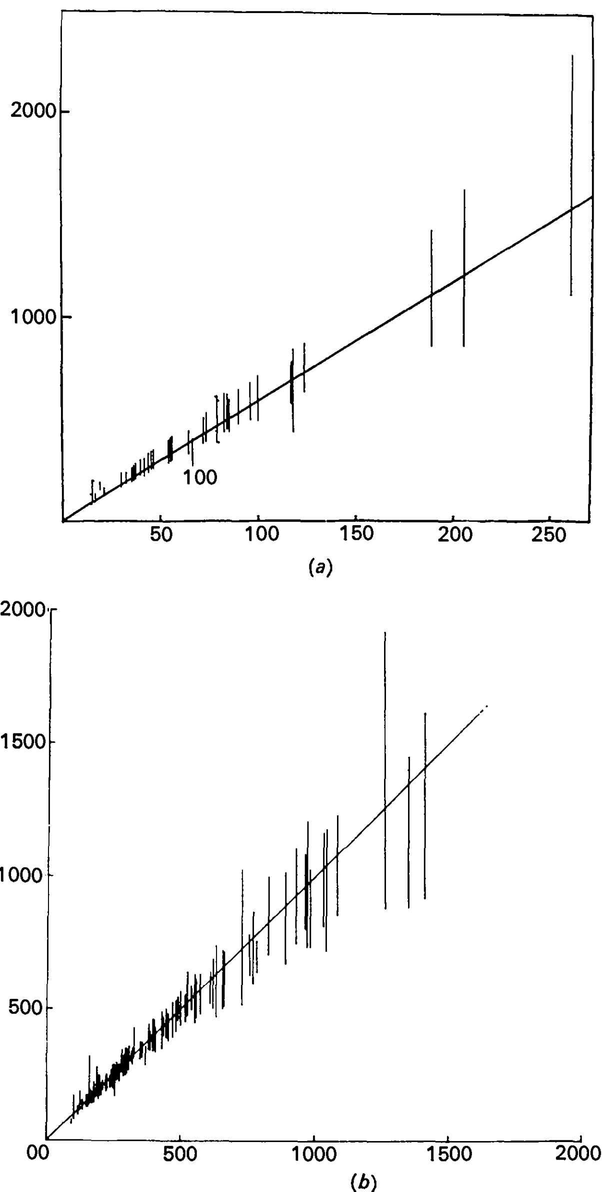

Fig. 2. Photographic results for the I.U.Cr. intensity project crystal (the points along the line) compared with the spread of the reported diffractometer results (the vertical lines). (*a*) for *hk*0 (unscaled), and (*b*) for *hk*1 and *hk*2 (scaled).

Table 1. *Summary of film errors in measuring* X-*ray intensities photographically*

A second exposure of 1/10 duration gives smaller errors than a 2 film pack.

Intensity	1–5	5	60	120	120	1000
Error	10%	10%	1%	½%	5% (2%)	2% (1%)
Method	Top film Eye estimation	Top film Photometry			Bottom film (Second exposure) Photometry	

underestimate can best be illustrated by some examples of the results of using the method, *e.g.* some results on D–tartaric acid crystals obtained by Dr R. Baker (Fig. 2). Very few of our results are outside the range of the diffractometer results of the I.U.Cr. single crystal intensity project and none significantly.

In the structure determination of $Co(SCN)_4Hg$ (Jeffery & Rose, 1968) where the relative scattering power of C and N is about the same as that of H in an organic structure, it was nevertheless possible not only to distinguish between C and N, but, by measurement on the three main Fourier sections through the centres, to plot a radial distribution function which appears to show electron transfer from N to C.

It was also possible to distinguish between *a* and *b* in a crystal with Laue symmetry $4/m$ by using anomalous dispersion. All eight {224} reflexions of Table 2 should have equal intensities. However, the point group is $\bar{4}$ and anomalous dispersion can produce differences in the four pairs. The observed ratio of 1·32 compares with the calculated value of 1·40.

Table 2. *The measured values of the eight symmetry equivalent* {224} *reflexions, showing the effect of anomalous dispersion*

hkl	Density	Ratio
224	0·373	1·44
$2\bar{2}4$	0·259	
$2\bar{2}\bar{4}$	0·362	1·25
$22\bar{4}$	0·304	
$\bar{2}\bar{2}4$	0·334	1·27
$\bar{2}24$	0·264	
$\bar{2}2\bar{4}$	0·367	1·30
$\bar{2}\bar{2}\bar{4}$	0·283	
Overall average		1·32 ± 8

In the structure determination of struvite, $MgNH_4PO_4.6H_2O$, by Whitaker (1965) the H atoms show clearly on the difference Fourier (Fig. 3) and the R factor was 2·8%. This compares with an expected 1·3% calculated from comparison of symmetry-related reflexions. For the first time, direct evidence of a rotating NH_4 group was obtained using X-rays. Fig. 4 shows

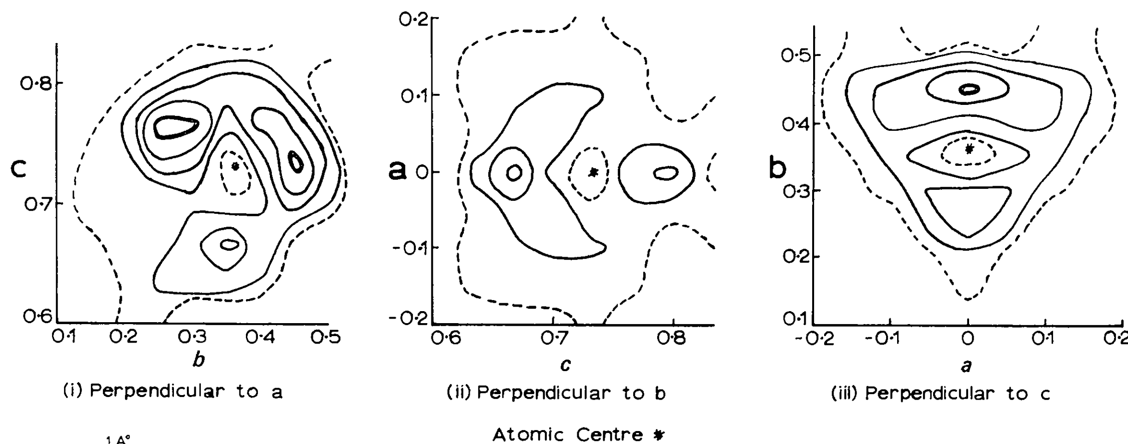

Fig. 3. Difference Fourier sections through the centre of the N atom of the NH_4 group. N scattering factor used in the structure factor calculations.

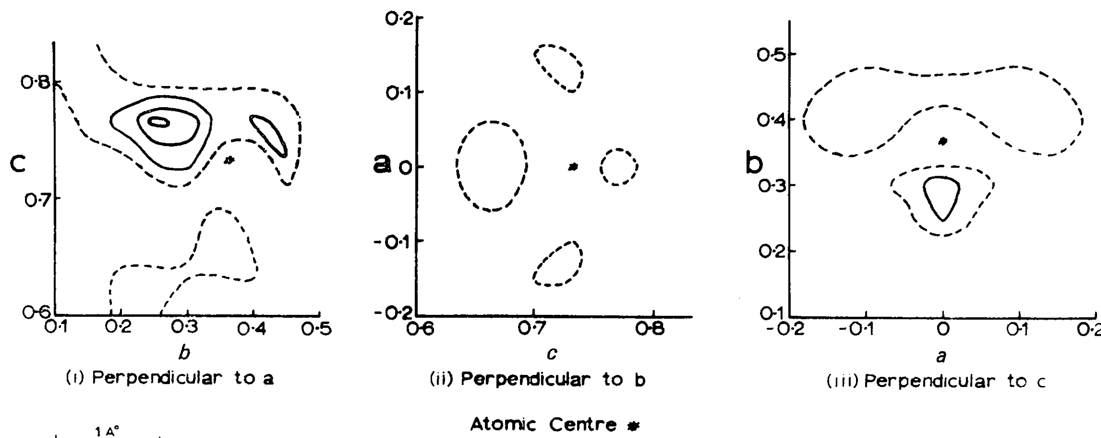

Fig. 4. As for Fig. 3, but using a spherically disordered NH_4 scattering factor.

three sections of the difference map through the N atom using the N scattering factor in the S.F. calculations, while Fig. 5 shows the corresponding sections using a spherically disordered NH_4 scattering factor. The remaining peak of any significance is in the direction of the single H-bond and probably indicates rotation about this bond rather than complete spherical disorder. Neutron diffraction is being used to check this conclusion.

Integrating photographic methods have been used by P. Clewer for measuring extinction with plane polarized X-rays, using the arrangement of Chandrasekhar & Phillips (1961) modified for use with an integrating Weissenberg camera. Fig. 5 shows photographs on the same film of the 220 and 422 reflexions of LiF with the plane of polarization (*a*) $\perp$, (*b*) // and again (*c*) $\perp$ to the reflexion plane, the third photograph providing a check on the stability. Table 3 shows the effects to be expected for various amounts of extinction and it is clear that small differences in the ratio of intensity for $\perp$ and // polarization have to be measured. Table 4 gives the results for this crystal of LiF. To reduce exposures, a rotating anode tube is to be incorporated in the apparatus before further measurements are attempted. It is hoped to make the method into a routine measurement of extinction.

Table 3. *Calculated effect for different amounts of extinction in* LiF

	$I_{\parallel}/I_{\perp}$	
%Extinction	220	422
0	0·172	0·570
5	0·180	0·582
10	0·188	0·597
15	0·197	0·613
20	0·208	0·631
25	0·220	0·651

Table 4. *Observed effect of extinction in* LiF

	$I_{\parallel}/I_{\perp}$	%Extinction
220	0·214	22·5
422	0·160	14·5

The same apparatus, giving a monochromatic beam with only a small amount of higher orders, has been used to measure absolute integrated reflexions photographically. Fig 6 shows the integrated direct beam through a Pt pinhole, followed by an integrated photograph of the 220 and 422 reflexions of LiF. This was repeated twice with the LiF crystal rotated 120° about [111] each time. Crystal and pinhole were interchanged 5 times. Table 5 shows the results - a variation in the direct beam density (D_0) of less than 1%. The formula for the integrated reflexion reduces to

$$\varrho = \frac{\pi a}{9} \cdot \frac{D}{D_0} \cdot \frac{L}{30} \cdot \frac{N_0}{N}$$

where a = area of pinhole, cm²; D = optical density of reflexion; D_0 = optical density of direct beam; $L/30$ = length of one integrating step (longitudinal) in cm; N_0 = number of integrations of direct beam; N = number of integrations of reflexion.

Table 6 gives the comparison with calculated values.

Table 5. *Density measurements on Fig.* 6

	D_{220}		D_{422}		
	T	B	T	B	D_0
1	0·639	0·597	0·190	0·199	0·872
2	0·558	0·622	0·210	0·214	0·874
3	0·557	0·588	0·203	0·185	0·883

	σ
$D_{220} = 0·593 \pm 30$, $D_{422} = 0·200 \pm 10$	5%
$D_0 = 0·876 \pm 5$	1%

Table 6. *Comparison of observed and calculated integrated reflexions*

	Calculated		Observed	
	(*a*)	(*b*)	(*c*)	(*d*)
220	6·26	5·16	4·38	5·62
422	2·54	1·42	1·40	1·64

(*a*) Temperature factor $(B)=0$. (*b*) Temperature factor as given in *International Tables*, $B_{Li}=1·10$, $B_F=0·67$. (*c*) Intensities as measured. (*d*) Intensities corrected for extinction.

Self checking properties

An integrating Weissenberg camera should not be regarded as just a poor man's 4-circle diffractometer. It is true that it is only possible with considerable difficulty to get the crystal in the reflecting position and then rotate it about the normal to the reflecting planes to pick up multiple reflexions and the varying effect of absorption. But even if one has the expensive, facilities for doing this easily, trouble has still to be taken to ensure correct setting and also that the machine is functioning properly, a situation which does not occur to anything like the same extent with photographic recording. There, the crystal must be centred in a uniform beam of X-rays (this is fairly easily done with a camera, but involves the assumption that if the total radiation stopped by the film is uniform, the characteristic radiation, which for Cu will be a sizeable fraction of it, will not be far off). Whitaker (1968) has described the gadget we use for photographing the beam (*a*) at, or very near, the crystal position and (*b*) to give a radiograph of the crystal.

An initial check is required that your axes intersect at right angles, but almost any malfunctioning of the apparatus shows up on the photograph. Fig. 7 shows the effect on an integrated spot of the sticking of a cam follower rod, while Fig. 8 shows the integrated direct beam through a Pt pinhole, which should, of course, be uniform if the camera translation is working proper-

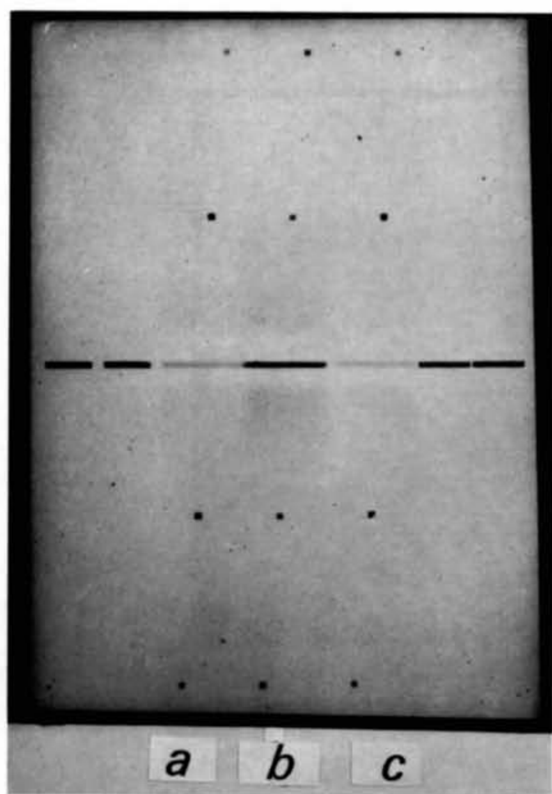

Fig. 5. Integrating Weissenberg photographs of LiF about [111] taken with plane polarized X-rays.

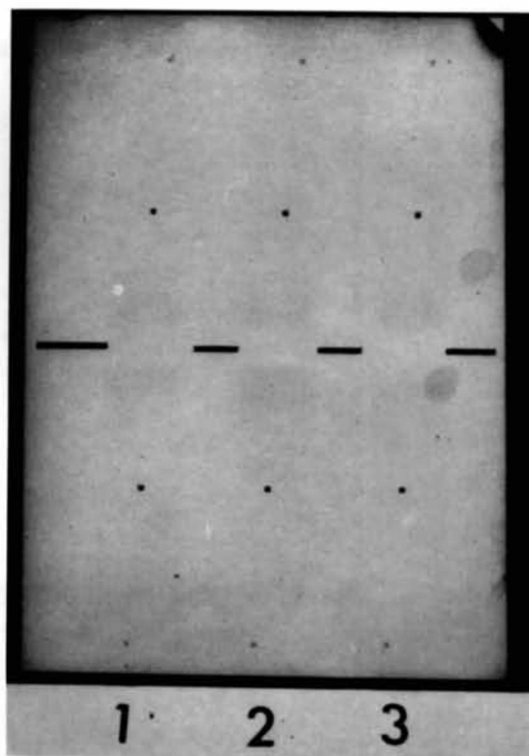

Fig. 6. Photographs of LiF combined with measurements of the direct beam to determine absolute intensities.

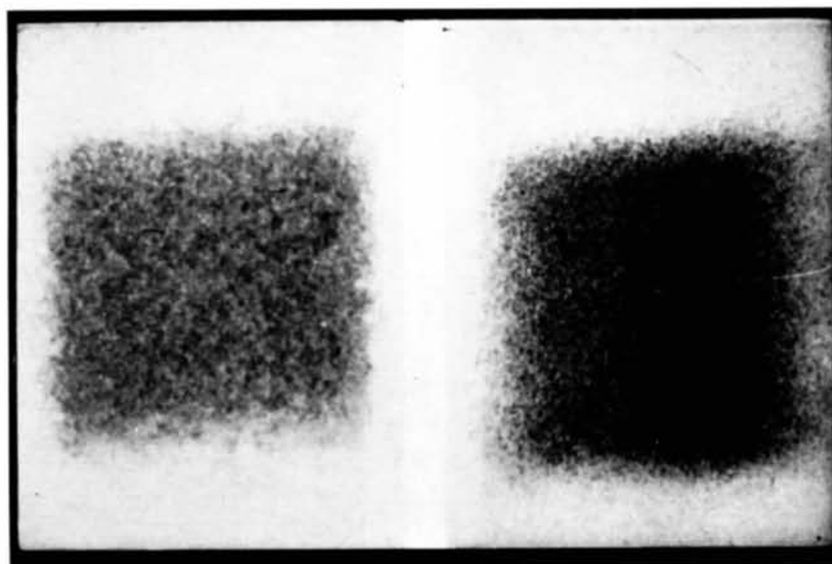

Fig. 7. Two enlargements of integrating Weissenberg reflexions, one showing the effect due to a sticking cam-follower rod.

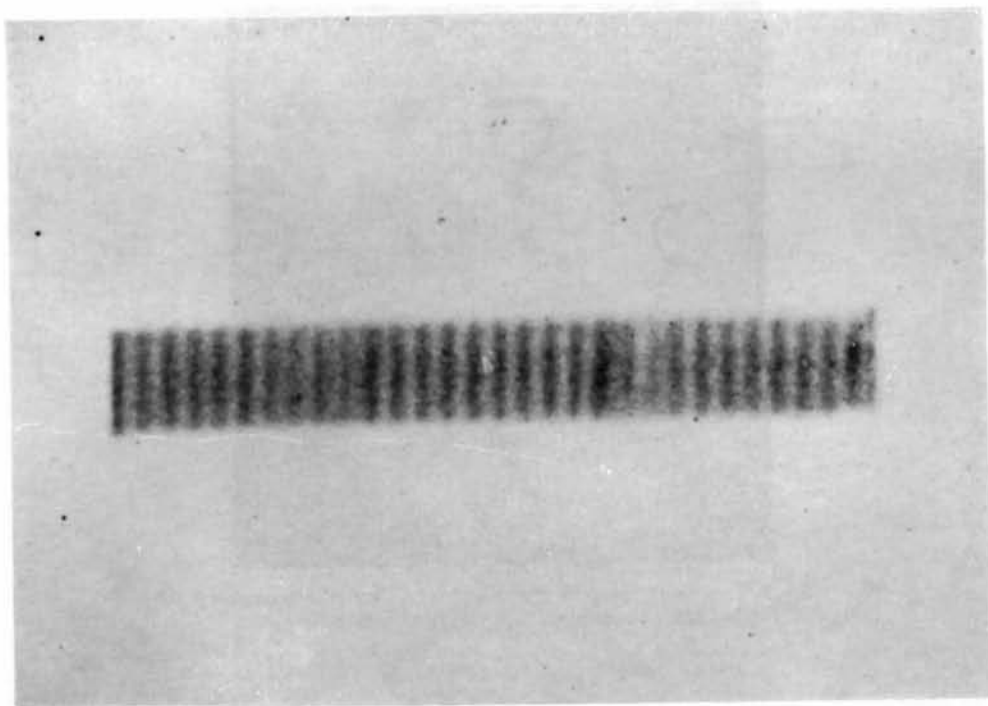

Fig. 8. Direct beam streak, showing non-uniform traverse of the cassette.

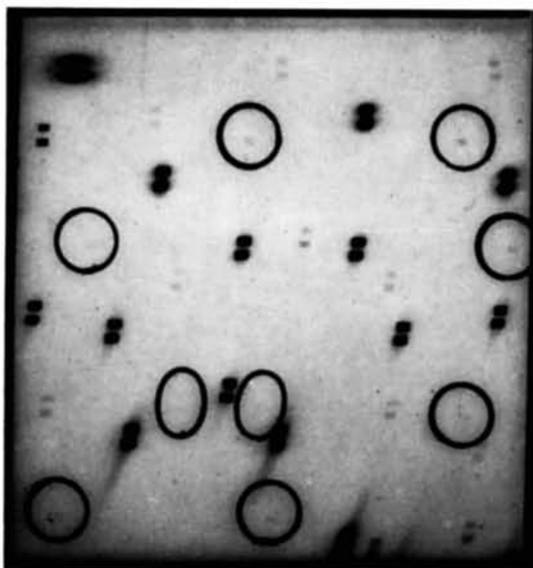

Fig. 9. Two nearly superimposed bottom halves of Weissenberg second layer photographs, showing double diffraction.

ly. The pitch is the same as that of the lead screw and the fault was traced finally to a corroded bearing.

Systematic double diffraction can be detected by registering the axial reflexion on the centre line of the film. Fig. 9, obtained by Dr R. Baker, shows two nearly superimposed bottom halves of Weissenberg second layer photographs from a crystal with one set of very strong and one of very weak reflexions. The streak at the top is the axial reflexion. The camera angle, μ, was misset by half a degree and the second photograph taken. The streak has almost disappeared and so have all the ringed reflexions. The single reflexion in each ring is entirely due to double diffraction.

The great advantage of the photographic method is that it has millions of reliable photon detectors arranged all round the crystal recording everything that is going on, as against the single (or perhaps triple) detectors of a diffractometer. On its own or in cooperation with the diffractometer method it has a large part to play in many fields, in the future as in the past.

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DISCUSSION

POST: How did you arrive at your figures of $\frac{1}{2}$–1%? Is this precision or accuracy?

JEFFERY: These figures refer to the ability with which photographic film can record X-ray spots and were obtained by measuring artificially made identical spots recorded at different points on one film.

POST: Did you ever compare your photographic results with counter data from the same crystal, taking a comparable time for the measurements?

JEFFERY: We have made comparisons of photographic and linear diffractometer data and got very similar comparisons of symmetry-related reflexions and very similar final R-factors. In general you can get better results with a diffractometer if you have a specimen which justifies this accuracy.

ALEXANDER: Do you favour one-dimensional or two-dimensional integration on your film?

JEFFERY: We always have two-dimensional integration except for the direct beam experiments.

WOOSTER: You can get your integration on the microdensitometer without increasing your exposure time.

JEFFERY: I am not sure that microdensitometer integration is as accurate as camera integration.

RIVA DI SANSEVERINO: Have you any experimental data to justify your figures of 10% for eye estimation and 5% for flying spot measurements?

JEFFERY: The figure of 10% is a general conclusion from the literature. I refer the question of flying spot microdensitometers to Dr Milledge.

MILLEDGE: We conclude that we get 3–4% accuracy in our structure factor measurements from the fact that we get routine refinements of structures to R-factors of about 5%.

JEFFERY: The accuracy of measurement with a flying spot must depend greatly on the diffraction spot size.

MILLEDGE: With our iso-densitracer we have, very surprisingly, found a linear relationship between exposure and density up to $OD=3{\cdot}0$ (*cf.* the paper by Milledge in these Proceedings. *Acta Cryst.* A**25**, 173).

JEFFERY: This needs sorting out: we only get a linearity up to $OD=1{\cdot}4$.