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Photographic intensity scales for use with three-dimensional data. By H. J. GRENVILLE-WELLS,[*]

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Measurements of the intensities of X-ray diffraction maxima on higher layer lines, whether on oscillation or Weissenberg photographs, must be corrected for a number of effects. The Lorentz and polarization corrections have now been combined with the Cox–Shaw factor (Cox & Shaw, 1930) in a single chart (Cochran, 1948; Kaan & Cole, 1949) and will not be considered here. This note, which deals specifically with oscillation photographs, is concerned with two aspects of the obliquity correction, which has been discussed by Bullen (1953), Qurashi (1953) and Whittaker (1953). First, oblique incidence alters the shape of the spot and increases its area, thus decreasing the blackening of the spot as ν_n, the inclination of the diffracted beam to the equatorial layer, increases. Secondly, when a film-pack (Robertson, 1943) is used, oblique incidence increases the ratio of the intensities in higher layers recorded on successive films because the path length in the films traversed by the diffracted beams increases as ν_n increases.

If I_0 and I are the intensities of the incident and transmitted beams respectively, μ is the effective absorption coefficient and t the thickness of the film, then the film factor for the nth layer is given by

$$R_n = (I_0/I)_n = \exp(\mu t \sec \nu_n), \qquad (1)$$

so that

$$R_0 = (I_0/I)_0 = \exp(\mu t) \qquad (2)$$

and

$$\log_e(R_n/R_0) = \mu t [\sec \nu_n - 1]. \qquad (3)$$

(For the double-coated X-ray film now in general use, $\mu t \approx 1$, so that for the nth layer line $R_n \approx \exp(\sec \nu_n)$, and $R_n/R_0 \approx 2\cdot7$ for $\nu_n = 60°$, which shows how rapidly the intensity falls off on the highest layers of successive films in a film pack.)

Corrections of this type, though tedious, can be applied numerically. It is, however, a matter of common experience that large errors are liable to arise in the visual estimation of intensities when spots of unequal size and shape are to be compared; the greatest difficulty which in practice attends the measurement of oscillation photographs is the change in size and shape of the spots on higher layers due to oblique incidence.

It is customary to estimate the intensities with a scale prepared by choosing a suitable reflexion on the zero layer and recording a series of increasing exposures of this reflexion on the same film, and then assuming that the reciprocity law holds. This method suggests a very simple experimental technique for dealing with both the problems introduced by oblique incidence.

Suppose an intensity scale is made with a pack of three films, S_1, S_2 and S_3, and an oscillation photograph of the

crystal is recorded on a pack of three similar films, C_1, C_2 and C_3. Then (writing S_1 for the intensity of the reflexion hkl on the film S_1) we have, for any reflexion on the zero layer,

$$(C_1/S_1)_0 = (C_2/S_2)_0 = (C_3/S_3)_0.$$

However, if this zero-layer intensity scale is used to measure intensities on higher layer lines,

$$(C_1)_n/(S_1)_0 > (C_2)_n/(S_2)_0 > (C_3)_n/(S_3)_0,$$

and numerical corrections must be applied.

If, however, the complete upper half on an oscillation photograph having a few reflexions on each layer be used to prepare an intensity scale film-pack—as has been done in Fig. 1 by using only one of the two screens on a Weissenberg camera—then scales consisting of spots of the correct sizes and shapes are available for every layer, so that visual comparison is very much easier. Further, since

$$(C_1/S_1)_n = (C_2/S_2)_n = (C_3/S_3)_n, \qquad (4)$$

the need for numerical corrections to compensate for the increased film factor for higher layers is eliminated.

Although equation (4) shows that the values of R_n are not in fact required when this technique is employed, they can be obtained experimentally from such a multi-layer scale, since $R_n = (S_1/S_2)_n = (S_2/S_3)_n$. Some values are given below to indicate the magnitude of the obliquity effect and the accuracy obtained. The observations should satisfy equations (1), (2) and (3); thus if $\log_e R_n$ is plotted against $\sec \nu_n$, a straight line should be obtained whose slope is equal to μt, and thus gives R_0, the customary film factor for X-rays incident normally upon a film-pack. For Ilford 'Industrial G' film the results shown in Table 1 were obtained from the set of scales to which Fig. 1 belongs.

Table 1

n	ν_n	$\sec \nu_n$	R_n (obs.)	R_n (calc.) $\mu t = 1\cdot20$	R_n (calc.) $\mu t = 1\cdot15$
0	0	1·00	3·33	3·20	3·05
1	6·6	1·01	3·33	3·35	3·18
2	13·8	1·03	3·33	3·44	3·27
3	20·8	1·07	3·64	3·61	3·42
4	28·4	1·14	4·00	3·92	3·69
5	35·1	1·22	~4·00	4·34	4·08
6	45·8	1·43	5·00	5·60	5·21
7	57·0	1·84	7·50	9·06	8·25

This gives a value of $R_0 > 3$, a rather high figure which has, nevertheless, been found on several occasions for this film. It can be seen from the values of R_n(calc.) shown in the table that there is an apparent departure
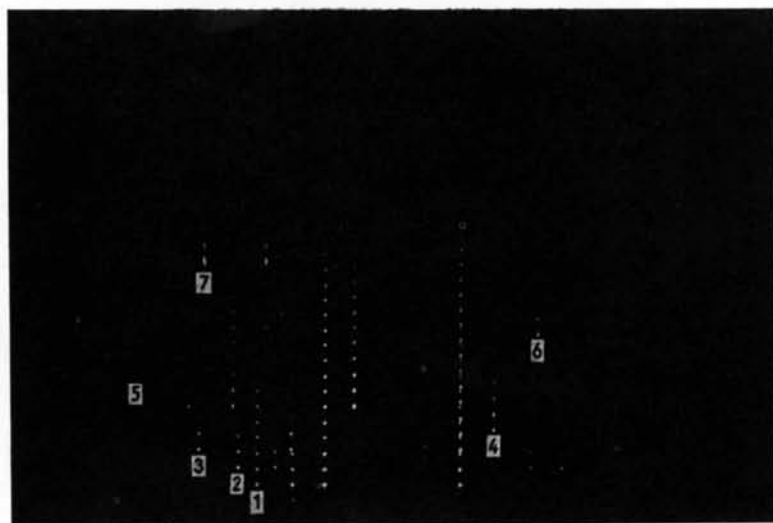
Fig. 1. The strongest film (S_1) of a pack of intensity scales made with a crystal of i-erythritol. Cu $K\alpha$ radiation; [100] vertical; $10°$ oscillation. The numbers indicate a typical scale for each layer line.

from the linear relationship of equation (3), but this example does not involve enough data for this departure to be regarded as significant.

This technique cannot, of course, permit any special solution of the problem of placing intensities on different layer lines on a single scale, though it does provide intensity scales with a larger variety of spot shapes and sizes from which such scaling may be done experimentally with the help of photographs obtained for rotation about different axes. It also provides more consistent data within any one layer, which would be useful if scaling were to be done separately for each layer with the help of a set of calculated structure factors, whether at a late stage in the analysis to improve the final accuracy (Wheatley, 1954), or at the outset on the basis of a

'possible structure' (Grenville-Wells, to be published). As such a scale takes no longer to prepare than the usual zero-layer intensity scale, there is much to gain and nothing to lose by employing it.
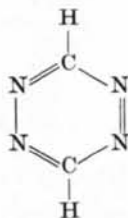
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X-ray study of s-tetrazine.

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Tetrazine is a deeply red coloured substance which melts at $99°$ C. and sublimes easily. It was first prepared by Hantzsch & Lehmann (1900), who proposed a formula which was later shown to be incorrect (Curtius, Darapsky & Müller, 1906) and replaced by the formula:

constitution of tetrazine and benzene, since, theoretically, replacement of four CH groups of the benzene molecule by four isoelectronic nitrogens gives tetrazine.

In view of the above relationship and of the peculiar physicochemical properties of s-tetrazine, an X-ray study was undertaken in order to elucidate its crystal and molecular structure. The diffraction intensities were recorded both with a Weissenberg and with a precession camera equipped with a device (Kaufman & Fankuchen, 1949) for cooling the crystal in a stream of cold air to about $-20°$ C. during the exposure.

The unit cell has the dimensions:

$$a = 5 \cdot 23 \pm 0 \cdot 01, \ b = 5 \cdot 79 \pm 0 \cdot 01, \ c = 6 \cdot 63 \pm 0 \cdot 01 \ \text{Å};$$
$$\beta = 115 \cdot 30' \pm 15'$$

A close similarity therefore exists between the chemical and contains two molecules.