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Microdensitometry Applied to X-ray Photographs

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A theoretical examination is made of the limitations on microdensitometry of X-ray diffraction photographs by optical means. It is shown that only small ranges of density can be included in the field of view of the microscope at any instant if a satisfactory overall accuracy is to be achieved. A consequence of this is that powder lines and diffraction spots on Weissenberg photographs should be larger than usual. Methods are given for estimating the errors in any given set of experimental conditions. The geometrical conditions which must be satisfied in scanning a diffraction spot along a zigzag path are investigated.

1. Introduction

The study of X-ray films is somewhat easier than the study of films darkened by exposure to light. When X-rays blacken a film there is a simple linear relation between the quantity D, called the density, and the total number of X-ray quanta which have produced the density. The total number of quanta incident on the film is proportional to the product of the intensity of the X-ray beam and the time during which it falls on the film. The product is thus proportional to D. Now D is defined in the following way. We suppose a light beam of intensity I_0 to be incident on a darkened film and the intensity of the transmitted beam to be I. Then D is given by the equation

$$D = \log_{10}(I_0/I)\,. \tag{1}$$

Thus the X-ray intensity is related in a logarithmic way to the intensity of the light transmitted through the film. If we plot I against D (Fig. 1) then we obtain a curve AB as shown between the D-values 0–1. If the I-value be multiplied by 10 we obtain the same curve, CD, between D-values 1–2 and, if we multiply I_D by 100, again the same curve EF between D-values 2–3. The curvature of AB, CD, EF makes it impossible to carry out accurate measurements of D when the blackening of the illuminated area is not uniform all over. X-ray films have relatively large grains of silver which are clearly visible with a pocket lens. For this reason it is not worth while to examine an area less than 0·1 × 0·1 mm. (The result of examining a smaller area is that the number of grains in the field of view varies considerably even over an area which has been uniformly exposed to X-rays. In other words, what is gained in resolution, in narrowing down the area examined, is lost in reproducibility.) To illustrate the point under discussion we shall suppose the illuminated area varies uniformly in density from one side to the other. We shall determine the inaccuracy which the formula (1) indicates will be present, irrespective of the accuracy of the measuring instrument. If AB were a straight line the average intensity of the light passing through the illuminated area would be linearly related to the average density. Because AB is curved this is not the case. If the density variation across the field of view is small then the average intensity of the transmitted light will be nearly given by the average density. For a large variation of density much inaccuracy is introduced by making this assumption. Let us now see how the inaccuracy rises with increase in the ranges of density included in the field of view. It is shown in the Appendix that if the density varies uniformly across a rectangular field of view from D_1 on one side to D_2 on the other, that the average density, D', calculated from the amount of light passing through the film, is given by

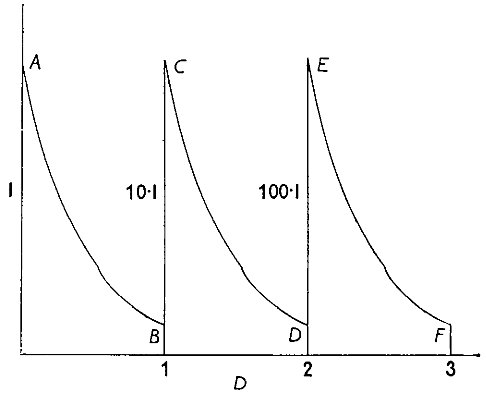

Fig. 1. Diagram showing the logarithmic variation of the intensity, I, of the light transmitted through a film as a function of the darkening D.

$$D' = \log_{10}\left[\frac{D_2-D_1}{0\cdot4343}\,\frac{1}{\text{antilog}\,(-D_1)-\text{antilog}\,(-D_2)}\right]. \tag{2}$$

The true average density is clearly $(D_1+D_2)/2$. By the use of formula (2) the data given in Table 1 have been calculated.

Table 1. *Percentage error caused by a uniformly varying density in the field of view*

Range of density in the field of view	Percentage error in the determination of the average density
0·0 – 0·1	1·6
0·0 – 0·2	3·1
0·0 – 0·5	9·2
0·0 – 1·0	18
0·0 – 2·0	33
0·0 – 3·0	44

The observed density is always too small because the effect of the light parts of the film outweighs the contribution of the dark parts.

If the light side of the area seen in the microscope is of density greater than 0·0 all these percentage errors are reduced. From the logarithmic form of the variation of I with D the difference between the observed average density and the true value will always be the same for a given range of density. Thus between densities 1·0 and 1·5 the absolute error is the same as between 0·0 and 0·5. *The percentage error is therefore inversely proportional to the true average density.*

It is usual to aim at an overall accuracy of 5% in microdensitometer measurements. A higher accuracy than this is difficult to achieve because of variations in the sensitivity of the photographic film and in the development processes. If an accuracy of 5% is to be attained, errors due to the cause we have been discussing must be kept down to about 1%. The range of density which is consistent with this requirement is given in Table 2.

Table 2. *Range of density as a function of mean density which gives a fixed error*

Range of included density	Mean density for which the error is	
	1 %	2 %
0·1	0·09	
0·2	0·31	0·155
0·3	0·85	0·43
0·4	1·46	0·73
0·5	2·3	1·15
1·0	9·0	4·5

2. The integrated intensity of a line

In measuring the integrated intensity of a line it is usual to make the film pass at a uniform speed under the scanning light spot and to record at each instant the density of the film. As already stated, it is not in general useful to employ a light beam which produces on the film an illuminated area narrower than 0·1 mm. (The length of the illuminated area is determined by the angular divergence permitted to the rays entering the objective, by the optical stops along the train of lenses and by prisms leading to the photocell.) In all that follows the aperture will be assumed to be 0·1 mm wide. At each setting of the line under the objective the microdensitometer registers an apparent optical density D' and the integral $\int D'dx$ over the line is the measured integrated density. The true integrated density is $\int Ddx$ and this differs from $\int D'dx$ by an amount which depends on the maximum density and on the width of the line. X-ray powder lines differ in profile, even on a given film, and to obtain some idea of the importance of this influence two profiles have been assumed. The first is rectangular and the second is in the form of an isosceles triangle. The background density has been taken as zero throughout. The effect of different widths of line has been studied by taking three profiles of width 0·5, 1·0 and 2·0 mm respectively. The curve showing the variation of apparent density with distance across the line has been plotted and the area under this curve taken as proportional to the integrated density. Table 3 gives the results of these calculations.

Table 3. *Errors in integrated density determined by scanning across a powder line of maximum density* 2·0, *with an aperture* 0·1 *mm wide*

	% Error in integrated density	
Width of line	Rectangular profile	Triangular profile
0·5 mm	11·0	4·2
1·0	5·5	1·9
2·0	2·8	0·34

It will be seen that this error, even in the favourable case of a triangular profile, is nearly 2% for a line of width 1 mm and increases as the width is decreased. If the maximum density is increased the line-width must be proportionately increased in order to keep the percentage error the same. Thus for lines of width 0·5 mm the maximum density should not exceed about 0·6 whereas if the maximum density is 4·0 the line width should not be less than 3·0 mm.

3. The integrated intensity of a spot

A measure of the integrated intensity of a spot may be obtained by moving the film under the scanning light beam at a uniform velocity in such a way that all parts of the spot are sampled. (Wooster & Fasham, 1958). The path of the light beam across the spot may be zigzag or it may be along parallel equidistant lines or it could be arranged to be spiral in form. It will make no significant difference to the measured values of the integrated density which of the possible kinds of scanning is adopted provided that the same type of scan is used for all the spots to be compared. The limiting case is that in which every point within the spot is given an equal chance of contributing to the integrated density. This integrated value I_A may be expressed as

$$I_A = \iint D_{xy}\,dx\,dy \tag{3}$$

where D_{xy} is the density at a point having coordinates $x\,y$, and the double integration is performed over the whole area covered by the spot. The size of the illuminated area on the film will be assumed to be $0{\cdot}1 \times 0{\cdot}1$ mm for a square spot and a circle of diameter 0·1 mm for a round spot. A drawing is made giving a projection of the density contours within the spot. These contours are chosen with an interval of 0·1 in density. From Table 1 it may be seen that over the range 0–0·1 in density the error in assuming that the intensity of the transmitted light is proportional to the mean density is 1·6%. Over the range 0·1–0·2 the error is 0·5% and this error diminishes as the mean density increases. The contribution to the integrated density of the 0–0·1 range is always small and the mean error due to using the contours with intervals of 0·1 is less than 1%. If within the illuminated area the density contours at any instant are of areas $a_1, a_2 \cdots a_n$ and the corresponding mean densities are $D_1, D_2 \cdots D_n$, then the intensity of light I_n transmitted through the region of density D_n is

$$I_n = Fa_n 10^{-D_n}$$

where F is the amount of light incident per unit area. The amount of light transmitted through the whole spot is given by

$$\Sigma I_n dn = F\Sigma a_n \operatorname{antilog}(-D_n)\,.$$

The amount of light incident on the illuminated area is FA where A is the area illuminated. Thus the apparent density D'_{xy} is given by

$$D'_{xy} = \log_{10}\left[\frac{FA}{F\Sigma a_n \operatorname{antilog}(-D_n)}\right]. \qquad (4)$$

The integrated density measured over the whole spot is denoted by I'_A where

$$I'_A = \iint D'_{xy}\,dx\,dy\,. \qquad (5)$$

The object of our present study is to find the percentage difference between I'_A and I_A.

3.1. *A spot having a density distribution corresponding to a square prism*

The first density distribution assumed is that of a square prism, having a background of density 0·0 and a uniform density of 2·0 over the area of the spot. Three sizes of spot are considered of side 0·5, 1·0 and 2·0 mm respectively. The illuminated area is assumed to be a square $0{\cdot}1 \times 0{\cdot}1$ mm having its sides parallel to the sides of the spot examined. By the use of equation (2) contours for values of D'_{xy} equal to 0·0, 0·1, *etc.* were drawn in and the areas between each pair of contours determined. The product of the area between two consecutive contours and the mean value of the density over this area was evaluated and the sum of all such products for neighbouring pairs of products was taken as I'_A. The difference between I_A and I'_A is given in Table 4.

Table 4. *The percentage error in the measured integrated density for a square spot of uniform density* 2·0

Length of side of spot	% Error in I_A
0·5 mm	20·4
1·0	10·8
2·0	5·5

3.2. *A circular spot having a Gaussian distribution of density*

A spot of uniform density which descends sharply to zero at the edges is not met with in practice and to approach more nearly to actual distributions it is assumed that the spot has a radial distribution corresponding to an error curve, *i.e.* the intensity at a distance x from the centre is given by $G \exp(-ax^2)$ where G is 2·0 and corresponds to a peak density of 2·0 at the centre of the spot and a is a constant defining the diameter of the spot. To cover the range of sizes encountered on usual Weissenberg and other photographs we assume that the diameter at half-intensity is 0·25, 0·5 and 1·0 mm respectively in the three calculations. The distribution of true density D_{xy} along a radius is given by the relation $D_x = 2{\cdot}2 \exp(-ax^2)$. At the foot the curve has been made to descend to the base line at a definite point instead of approaching it asymptotically as would an error curve. This makes the numerical and graphical determination of D'_{xy} possible and it in no way affects the value of the comparison with actual photographic spots. If the horizontal and vertical coordinates of the points along the D_{xy} and D'_{xy} curves are denoted x and z respectively, then the volumes under the true and apparent density peaks are given by

$$\int_0^{D_{\max}} \pi x^2 dz \quad \text{and} \quad \int_0^{D'_{\max}} \pi x^2 dz\,.$$

The value of x^2 is plotted against z and the area under the curve is dertermined. If A and A' are these areas the percentage errors listed in Table 5 are given by $100(A-A')/A$.

Table 5. *The percentage error in the measured integrated density for a circular spot having a Gaussian density distribution and a peak density of* 2·0

Diameter of spot at half-density	% Error
0·25 mm	4·4
0·5	1·7
1·0	0·2

In order to ensure that the error is not greater than 1% the diameter at half density must not be less than 0·7 mm. This means that the distance through the centre of the spot from the background on one side to the background on the other side must be at least 2 mm. If the actual spot has sharp edges so that it approximates to the square spot considered above then its size must be still larger.

4. The geometry of scanning

In the previous paragraphs the integrated density has been determined by summation over all points of the spot. In practice such a summation is never carried out. Instead a sampling technique is employed in which the scanning light beam moves relative to the film at a uniform rate along a zigzag path. The same motion is carried out over all spots on a photograph and we are only concerned with the relative values of their integrated densities. In the following analysis we shall suppose the zigzag path to be entirely contained within a square and to consist of lines of equal length, each successive line including with the preceding one an angle of 2φ. The spot will be assumed circular and having the Gaussian distribution of density defined in paragraph 3·2. We assume that the sides of the square are tangential to the spot on the circle of zero density. The integrated density so obtained depends on the precise starting point of the scan and the angle φ. The angle φ must be chosen so that the variation in the integrated density depends on the starting point to less than some chosen figure, say 1%. This angle then determines the relative speeds of movement in the two perpendicular directions. The fast direction of movement (backwards and forwards) will be called Y and the slow movement (always in one direction) will be denoted X. On a projection of the spot, showing contours of equal density with intervals of 0·1 between consecutive contours, lines are drawn corresponding to the zigzag path. The densities along these paths are plotted and the area under each determined. The sum of all such areas gives the integrated density corresponding to what is usually measured. The spot is now moved relative to the zigzag lines and the analysis repeated. In this way the variation of the measured density with the starting point of the scan is determined. At a value of $\varphi = 5°$ the integrated density begins to depend on the starting point of the scan. The difference between the maximum and the minimum integrated density rises uniformly from 5° to 15°, being about 1% at a φ value of 10°. (Wooster & Fasham (1958) found an angle of 5° to be satisfactory in practice.) This implies that the speed of traverse in the Y direction should be at least six times as great as that in the X direction. This result assumes a circular spot and it is necessary to consider how this conclusion is affected by the change in shape and size of spots over a diffraction photograph.

Provided that the area scanned entirely contains the largest spot no error will be caused by a change in size of the spot. This may be seen from the fact that a spot of large size may be regarded as due to the superposition of a number of smaller ones for each of which the above analysis is true.

The profile of the spot becomes important only if the gradient of density becomes greater than a value which is set by the accuracy required. Provided the density at the centre of the spot is not greater than two units above the background and provided that the spot is least 2 mm across and has no sudden variations of density the inaccuracy due to the profile will not exceed 1%.

5. Conclusion

It must be emphasized that all the above considerations apply equally to every form of optical microdensitometer. A variation in resolution can be had by using a fine grain film but only at the expense of longer exposures. A flying spot microdensitometer is subject to the limitations discussed here just as much as an instrument provided with a mechanical scanning device. The most commonly used microdensitometer is the human eye but unfortunately this can be deceived by gradients of density and it is difficult to estimate what accuracy can be obtained by visual comparisons.

A general conclusion arising from this paper is that diffraction spots are usually too small for accurate work. They can be made larger by using an X-ray beam which converges on the crystal. This requires a collimator which permits rays from a larger area of the focal spot to reach the film than is usual, *i.e.* the aperture near the X-ray tube must be large and the aperture near the crystal smaller. This arrangement lessens the exposure time.

Generally speaking both for powder film, Weissenberg, and precession photographs the requirements for position measurement and for intensity measurement are opposite. The former requires sharp lines or spots and the latter broad lines or spots.

APPENDIX

Calculation of the error caused by variation of the density over the field of view

In order to simplify the analysis the following assumptions are made. The field of view of the objective lens of the microdensitometer is supposed rectangular having sides a and b respectively. Along any given line parallel to the side b the density is taken to be uniform and along all lines parallel to a the density varies uniformly from D_1 at one end to D_2 at the other. At a distance x from the light end the density is D_x.

The incident light is of intensity I_0 per unit area and the light emerging from a small area at a distance x from the light end has an intensity I_x per unit area. Through an area bounded by a line of length b parallel to one edge of the field of view and another perpendicular line of length dx, there emerges light of intensity dI_x where,

$$dI_x = b\,dx\,I_x\,.$$

The total amount of light transmitted through the whole field of view is thus equal to Iab where

$$Iab = \int_{D_1}^{D_2} dI_x = b\int_{D_1}^{D_2} I_x dx\,.$$

Now, by definition of D_x

$$D_x = \log_{10}(I_0/I_x)$$

or

$$I_x = I_0 10^{-D_x}.$$

Hence,

$$Iab = bI_0\int_{D_1}^{D_2} 10^{-D_x}dx\,.$$

We have assumed that D_x varies uniformly across the area, *i.e.*

$$D_x = D_1 + \frac{(D_2-D_1)x}{a}$$

and

$$dD_x = \frac{(D_2-D_1)\,dx}{a}\,.$$

Hence,

$$\begin{aligned} Iab &= \frac{abI_0}{D_2-D_1}\int_{D_1}^{D_2} 10^{-D_x}dD_x \\ &= \frac{abI_0}{D_2-D_1}\cdot\frac{1}{\log_e 10}[10^{-D_1}-10^{-D_2}] \\ &= \frac{abI_0}{D_2-D_1}\cdot 0{\cdot}4343\,[\text{antilog}\,(-D_1)-\text{antilog}\,(-D_2)]. \end{aligned}$$

The average density measured by the microdensitometer is D' where

$$\begin{aligned} D' &= \log_{10}(I_0/I) \\ &= \log_{10}\left[\frac{D_2-D_1}{0{\cdot}4343\,[\text{antilog}\,(-D_1)-\text{antilog}\,(-D_2)]}\right]. \end{aligned}$$

The true average density is $(D_1+D_2)/2$ and we require the ratio $D'2/(D_1+D_2)$.

We shall put $D_1=0$ when this ratio becomes

$$\frac{2}{D_2}\log_{10}\left[\frac{D_2}{0{\cdot}4343\,[1-\text{antilog}\,(-D_2)]}\right].$$

From this equation the data given in Tables 1 and 2 have been derived.

Reference

Wooster, W. A. & Fasham, J. A. L. (1958). *J. Sci. Instrum.* **35**, 153.

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The Crystal Structures of Low and High Albites at −180 °C

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The structures of low and high albites determined by Ferguson, Traill & Taylor (1958) have been reinvestigated at −180 °C, particular attention being paid to the anisotropic peaks found at the sites of the sodium atoms at room temperature. Refinement of the structures has been conducted by means of (F_o-F_c) projections parallel to the [001] and [100] axes. The peaks found to be anisotropic at room temperature remain anisotropic at the lower temperature, the effect being more pronounced in high albite than in low. No observable change in the ellipticity of the sodium peaks occurs when the temperature is reduced. The structures of the minerals are discussed on the basis of theories of disorder in feldspar structures.

Introduction

The structures of low and high albites determined by Ferguson, Traill & Taylor (1958) showed an unusual feature which has since been the subject of much discussion, namely a marked anisotropy of the electron-density distribution at the site of the sodium atom. The effect was much more conspicuous in high albite than in low. It was to elucidate this feature that the present low-temperature study was undertaken. For practical reasons, it could only be two-dimensional; this, however, allowed convenient comparison with the work of Ferguson, Traill & Taylor.

The difficulty of distinguishing between thermal vibration amplitudes and disorder as a cause of broadening in electron-density peaks has long been recognized. In both cases, the observed distribution represents an average over a large number of unit cells, or subcells, in which the atom occupies a number of different positions. Thermal amplitudes are described by the use of a Gaussian temperature factor; disorder effects, when each atom is more or less

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