ERROR ANALYSIS FOR THE BUERGER PRECESSION CAMERA*

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Abstract

A routine for the reduction of the data from precession x-ray diffraction photographs leads to a direct estimate of the reliability of the cell constants calculated from such measurements. Calibration routines are also discussed.

1. Introduction

The Buerger precession camera (Buerger, 1944) is a very useful instrument for the rapid determination of the cell dimensions and the space group of a single crystal. Although back reflection and other techniques may exceed the precession camera in precision by one or two powers of ten, the latter permits measurements which are quite accurate enough for the cataloging of single crystal cell data (cf. Donnay and Nowacki, 1954) and for the recognition of data previously cataloged. It is also accurate enough to provide cell dimensions which are adequate for the conversion of the results of most modern structure analysis into molecular dimensions.

The accuracy which can be attained by the use of this instrument has been discussed by several authors (Evans *et al.*, 1949; Barnes, 1949; Evans, 1949; Barnes *et al.*, 1951). This paper is written to present a routine for the reduction of the data from precession photographs which indicates the precision attained in the measurement of a given photograph or set of photographs. We find that under ideal conditions, the precision attainable is higher than that suggested by previous writers. Under non-ideal conditions the method of reduction delivers a numerical estimate of the degree of precision which has been achieved. The need for the rediscussion of the accuracy of the camera became apparent in the course of a study of the cell dimensions of a group of alkali citrates (Love and Patterson, 1960).

In a precession photograph taken of a zero layer reciprocal lattice net set accurately parallel to the flat film, the x-ray diffraction spots occur in parallel rows and the net formed by these spots is an image of the reciprocal lattice net in question. The separation X (Fd^* according to Buerger,

1944) of two parallel rows on the film is related to the reciprocal A of the distance between the corresponding rows of the reciprocal lattice by the relation*

$$A = \frac{\lambda F S_m}{XS} \tag{1}$$

in which λ is the wavelength of the radiation, F is the "magnification factor," *i.e.*, the crystal to film distance, X is the measured distance between the rows, S is the distance between the two holes in the cassette which are used to produce fiducial spots on the film. These are found to have a separation S_m when measured at the time the quantity X is determined (see section 3), and permit the correction for shrinkage implied by the ratio S_m/S in (1).

Three of the quantities in (1) *i.e.*, λ, F, S can be eliminated from consideration provided that the camera is calibrated by means of a crystal of known A_0. In this calibration we observe rows of separation X_0 on a film for which the measured distance between the fiducial spots is S_{m0}. In such a case, the quantity A is obtained from

$$A = \frac{X_0}{X} \frac{S_m}{S_{m0}} A_0 \tag{2}$$

provided that the same wavelength is used both for calibration and for the measurement. If two different wavelengths are used, λ_0 and λ respectively, the expression

$$A = \frac{\lambda}{\lambda_0} \frac{X_0}{X} \frac{S_m}{S_{m0}} A_0 \tag{3}$$

must be used.

As is well known from statistical theory, the squared fractional standard deviation in A, i.e., $(\sigma A/A)^2$ as calculated from any of the formulae (1)–(3) is simply the sum of the squared fractional standard deviations of the quantities which enter into the particular formula. An analysis of the expected contribution from each source of error is given in Table 1 and the basis for the estimate of the contribution of each is discussed in the remarks in the table. The only measurements referred to in the table which require further comment are the linear measurements on the film and the way in which they are carried out. These depend on the least count M_0 of the measuring instrument used for this purpose. A discussion of the method we have used for the reduction of our data is given on page 328 and for the measurement of the shrinkage correction on page 329. We comment on the method used for the combination of observations

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* The quantity A is either a translation of the crystal lattice or is simply related to such a translation. See section 6.

TABLE 1. FRACTIONAL STANDARD ERRORS IN THE QUANTITIES APPEARING IN FORMULAE (1)–(3)

For definitions see text.

Nature of Quantity	Symbol	Remarks	Equation #	Squared Fractional Standard Deviation×10⁸				
				M=0.05 mm.			M=0.025 mm.	
				(1)	(2)	(3)	(4)	(5)
Instrumental Constants	F	Estimated from design $F=60.00\pm0.10$ mm.	$(\sigma F/F)^2$	278				
	S	Direct measurement (Our instrument 122.24 ± 0.03 mm.)	$(\sigma S/S)^2$	6				
Physical Constants from the Literature	λ	It is estimated that the center of mass of a Kα doublet is known to 1/10 of the doublet separation $\sigma\lambda=4\times10^{-4}$ Å	$(\sigma\lambda/\lambda)^2$	7(Cu)		32(Mo)		32(Mo)
	λ_0		$(\sigma\lambda_0/\lambda_0)^2$			7(Cu)		7(Cu)
	A_0	Taken as twice the variation in spacing* of various recorded measurements of samples of natural quartz ($\sigma A_0/A_0=2\times10^{-4}$)	$(\sigma A_0/A_0)^2$		4	4	4	4
Linear Measurements on Films	X	Statistical analysis of measurements on film (section 2)	$(\sigma X/X)^2$	> 35	> 35	> 35	> 9	> 9
	X_0	Calibration repeated until mean error less than least count	$(\sigma X_0/X_0)^2$		35	35	9	9
	S_m S_{m0}	(See section 3)	$(\sigma S_m/S_m)^2$ $(\sigma S_{m0}/S_{m0})^2$	35	35 35	35 35	9 9	9 9
Calculated Spacing	A		$(\sigma A/A)^2\times10^8$ $(\sigma A/A)\times10^4$	>361 > 19	>144 > 12	>183 > 14	>40 > 6.3	>79 > 8.9

* (Keith, 1950).

from several films on pages 330–331. We discuss the accuracy of angular measurements and consider the accuracy of the crystal cell dimensions in terms of the accuracy of the reciprocal net dimensions measured on the precession camera on page 331–332.

2. Reduction of Experimental Data and the Error in X and X_0

In the measuring device* used in the reduction of our data an engraved line on a plastic plate in contact with the film is constrained to move along, and is perpendicular to a scale on which the position of the line can be measured. With the film fixed in the measuring device and illuminated from below, the engraved line is set along each row of spots on the film and the coordinate x_r of each row with respect to the scale is recorded. The rows must, of course, be set accurately parallel to the engraved line before the measurements are made. In the instrument under discussion the vernier first used was calibrated to 0.1 mm. (least count 0.05 mm.) and was read to that accuracy. Columns 1–3 of Table 1 refer to the use of this vernier. In later measurements a vernier calibrated to 0.05 mm. (least count 0.025 mm.) was used. Columns 4 and 5 of Table 1 indicate the increase in accuracy resulting from the use of the more accurate device.

It is assumed that any departure of the set of measured values x_r from a uniform spacing of period X is due to experimental error and a least squares procedure is used to determine the best value of X and of the coordinate ξ of one row to fit the measured sequence of values x_r. If an odd number $(2n+1)$ of rows** is measured as will almost always be the case on a zero layer photograph, it can easily be shown (cf. Whittaker and Robinson, 1924) that the best value of X is given by

$$X = [rx_r]/[r^2] \tag{4}$$

in which the bracket [ ] implies summation over all values of r from $-n$ to n. The corresponding values of the coordinate ξ of the central row is given by the average value.

$$\xi = [x_r]/(2n + 1) \tag{5}$$

The standard deviations in X and ξ are respectively given by

$$(\sigma X)^2 = \Delta_0^2/\{(2n - 1)[r^2]\} \tag{6}$$

and

$$(\sigma \xi)^2 = \Delta_0^2/(4n^2 - 1) \tag{7}$$

* Supplied by Charles E. Supper Co., Newton Centre, Mass.
** We have set up a similar discussion for an even number of rows but we have had no use for it and have not reported it here.

in which the sum of the squares of the residuals is given by

$$\Delta_0{}^2 = [x_r{}^2] - \{[x_r]^2/(2n+1)\} - \{[rx_r]^2/[r^2]\}$$
$$= [x_r{}^2] - \xi[x_r] - X[rx_r] \tag{8}$$

It is useful to remember that

$$[r^2] = (1/3)n(n+1)(2n+1), \tag{9}$$

and it is easy to calculate a table of the values of this quantity to be expected from the crystals under investigation in a given laboratory.

In practice it is perhaps worthwhile to change the origin of x_r by subtracting the observed value of x_0 from the observed values of x_r thus minimizing the size of all the sums. In the usual zero layer measurements the value of ξ has no direct meaning. It is, however, worthwhile to calculate $\xi + rX$ for all lines. Comparison with the original values for X_r will indicate the presence of a mistake in the calculation or in the original measurements. An exact knowledge of ξ and its accuracy will, of course, be of importance in estimating the shift between the rows in the zero layer and those in a higher layer in monoclinic or triclinic crystals.

If a crystal has been set by standard routines so that only single spots are seen on the measured photographs, we believe that the quantity σX derived from (6) will include in itself all the errors which may arise from missetting, lack of centering, improper film positioning and kindred sources. For this reason we have made no other allowance for these possibilities in the present discussion.

It should be emphasized that the present reduction is not that which will produce the smallest value of σX from a given number of measurements. Repeated measurements of the more widely separated rows would lead to a lower standard deviation than does the present procedure. However, the latter gives a more realistic estimate of the reliability of the measurements made on the photograph.

It is clear that the least squares procedure can lead to ridiculous results, *i.e.*, to values of the standard deviation σX which are below the least count of the instrument. In such cases we have estimated the standard deviation of X by the formula

$$(\sigma X/X)^2 = 2M^2/L^2 \tag{10}$$

where L is the extreme range covered by the film (≈ 120 mm.) and M is the least count of the instrument. When $M = 0.05$ mm., $(\sigma X/X)^2 \approx 35 \times 10^{-8}$ and when $M = 0.025$ mm., $(\sigma X/X)^2 \approx 9 \times 10^{-8}$. These provide reasonable lower limits for the uncertainty in the measurement of X.

3. SHRINKAGE CORRECTIONS

In section 1 we have implied for simplicity that there is a pair of fiducial spots located so that the measurement of their separation S_m can be

made at the angular setting of the measuring device used for the measurement of X. This is only true in the case of an orthogonal net set with one axis along the dial axis. The two fiducial spots along the dial axis will be measured at an angular setting ϕ_0 of the measuring device with the engraved line perpendicular to the line joining the spots. The average of the two measurements at ϕ_0 and $\phi_0 + 180°$ we call S_{mH}. The two fiducial spots perpendicular to the dial axis (Barnes *et al.*, 1951) are then measured at angular settings $\phi_0 \pm 90°$ with an average value which we call S_V. Assuming that the shrinkage is a homogeneous distortion with principal axes perpendicular to the edges of the film, the value of S_m to be used in correcting an X value measured at an angular setting ϕ will then be given by

$$S_m = \sqrt{S_H{}^2 \cos^2(\phi - \phi_0) + S_V{}^2 \sin^2(\phi - \phi_0)} \qquad (11)$$

In Table 1 we have assumed that the average of two measurements for S_H or for S_V will be accurate to the least count of the measuring device *i.e.*, $(\sigma S_m / S_m)^2 = 2M^2/L^2$.

In measuring the angle between two rows on a film, two angles ϕ_1 and ϕ_2 must be measured. Each of these angles is subject to a small correction for shrinkage. The corrected value of ϕ_i is $\phi_i + \Delta$ where

$$\tan \Delta = -(S_H - S_V) \sin 2(\phi_i - \phi_0) / \{(S_H + S_V) + (S_H - S_V) \cos 2(\phi_i - \phi_0)\} \qquad (12)$$

In most cases this correction will be of the same order of magnitude as the uncertainty in the measurement of the angle ϕ (Section 5). In all but the worst cases the approximate formula

$$\Delta = -\{(S_H - S_V)/(S_H + S_V)\} \sin 2(\phi_i - \phi_0) \qquad (12a)$$

is quite accurate enough.

4. Combination of Observations from Two or More Films

If several different observations X_i corresponding to the same A are made on different films or on symmetrically equivalent rows on the same film, the results can be combined as follows. For a given film the ratio X_i / S_{mi} will have a weight w_i given by

$$1/w_i(X_i/S_{mi})^2 = \{(\sigma X_i/X_i)^2 + (\sigma S_{mi}/S_{mi})^2\} = 1/\omega_i \qquad (13)$$

The most probable value of X/S_m will then be

$$X/S_m = \Sigma(w_i x_i/S_{mi})/\Sigma w_i \qquad (14)$$

with a weight $W = \Sigma w_i$, where Σ implies summation over all observations. Thus we have

$$\{\sigma(X/S_m)/(X/S_m)\}^2 = 1/W(X/S_m)^2 = 1/\Omega \qquad (15)$$

The actual calculation is facilitated by recognizing that $(X/S_m) \approx (X_i/S_{mi})$. Then with ω_i and Ω as defined by (13) and (15) respectively.

$$\Omega = \Sigma \omega_i \qquad (16)$$

The lower limit of the relative standard deviation of X has already been given in (10), and in section 3 we have estimated $(\sigma S_m/S_m)^2$ as $2\ (M/L)^2$. Therefore it is clear that a minimum reasonable value for expression (15) is $4\ (M/L)^2$.

The discussion of sections 2–4 applies equally well to the measurement of X_0 and S_{m0} corresponding to the calibration spacing A_0. The number of films measured for calibration purposes should be sufficient to reduce the value of the expression (15) below the limit $4\ (M/L)^2$, and this has been assumed in Table 1, but it is not profitable to go beyond this number of measurements.

5. Error in the Measurement of Angle

Two types of angular measurements can be made with the Buerger precession camera: (i) angles between nets, and (ii) angles between rows in a net.

Measurements of type (i) are made on the dial axis of the precession camera (calibrated to 5′) and depend for their accuracy on the precision with which a given net can be set parallel to the film. Experience shows that under the best conditions a missetting of the order of 0.2 mm. on the film can be detected, corresponding to about 3′ in angle. Thus allowing for a least count of 2.5′ the best accuracy to be achieved for a single angular setting will be about 4′. The measurement of angle will then be accurate to about 5′ or 6′. In any given experiment the investigator must estimate for himself the accuracy which he has been able to achieve in setting the two nets whose angular separation is to be measured. We have been unable to devise a reasonable method for the statistical analysis of this error.

Measurements of type (ii) are made on the film using the measuring device described above. This is provided with a circle calibrated to 5′. Independent measurements of the direction of a given family of rows may be made on the individual rows and also on these rows with the film holder rotated through 180°. The accuracy with which the device may be set parallel to a given set of rows depends very critically on the size of the crystal and the spots which it produces and also on the accuracy of the setting of the net. We have found standard deviations for a single setting as high as 17′ in the worst case we have met, but in the best cases measurements can be repeated to the least count. It is recommended that sufficient number of settings be made to establish a statistical estimate for the standard deviation of a single setting.

6. Error in Reduction of Data from a Single Net to Cell Dimensions

It must be noted that quantity A of Eqs (1)–(3) is a lattice translation a only if the two reciprocal nets which produce the rows in the pre-

cession photograph are perpendicular to the plane of the photograph. If they make an angle χ with this plane then

$$a = \frac{A}{\sin \chi} \tag{17}$$

and we must calculate the error in a from

$$(\sigma a/a)^2 = (\sigma A/A)^2 + (\sigma \chi)^2/\tan^2 \chi \tag{18}$$

in which the last term is negligible for angles near 90°. It may be too that the angle χ is not directly measured and that $\sin \chi$ must be calculated from other angles. In such cases the error analysis for the formula used must be carried out. Even though it may be necessary to use the exact formula for the calculation, the error analysis in terms of the exact formula may be cumbersome. In such cases the approximations for triclinic formulae discussed elsewhere prove useful (Patterson, 1952).

7. Discussion

Examination of the column of Table 1 corresponding to equation (1) indicates that provided the manufacturing accuracy and adjustment is maintained a fractional accuracy of 20×10^{-4} can be expected in the measurement of a high quality film without calibration. This is to be compared with the figure of 20–30×10^{-4} given by Evans (1949) and by Barnes and his coworkers (1951). When a careful calibration has been carried out and equation (2) or (3) can be used, errors respectively equal to 12 or 14×10^{-4} can be expected with the 0.10 mm. vernier and 6.3–8.9×10^{-4} with the 0.05 mm. vernier. The contribution of the wave length error is much more important with the more accurate venier.

If all lattice translations are measured with approximately the same fractional accuracy, the contribution to the fractional error in a bond length by the errors in the lattice parameters will be approximately equal to the error in the lattice parameters. Thus a fractional error of 12×10^{-4} in these parameters would correspond to an error in a carbon single bond of about 0.002 Å so that cell parameters determined on the precession camera will in general be adequate for all but the most precise structure analyses.

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