SHORT COMMUNICATIONS

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible.*

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The learnt-profile method in four-circle diffractometry: the variation of reflexion peak width.

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Abstract

The anisotropic functional form previously suggested for the variation of reflexion peak width in reciprocal space does not adequately deal with cases of high anisotropy when measurements are made at different azimuthal angles. A small modification produces considerable improvement.

We have previously reported an application of the learnt-profile method to single-crystal diffraction data collection on a four-circle diffractometer (Clegg, 1981). Essential to the method is the derivation and use of an anisotropic functional form for the width of the α_1 and α_2 components of each reflexion, so that the correct scan parameters can be chosen. We used a seven-parameter function of the form

$$W = \sum \sum a_i a_j A_{ij} + B \tan \theta,$$

where the a_i are the direction cosines of the diffraction vector relative to a crystal-fixed set of Cartesian axes, and A is a symmetric 3 × 3 tensor. The term $B \tan \theta$ allows for wavelength dispersion within α_1 and α_2.

This form has been found to be very satisfactory in most cases, but it assumes that W is independent of the azimuthal angle for which the reflexion is measured. If all reflexions are measured at or close to the bisecting geometry (azimuthal angle = 0), or if the width function is approximately isotropic, this shortcoming is unimportant. If, however, different azimuthal angles are to be used (*e.g.* for application of empirical absorption corrections) and the width function is highly anisotropic, a poor match of expected and measured reflexion width is obtained, and the learnt-profile method breaks down. Such anisotropy of the width function can be caused by non-uniformity of crystal dimensions (*e.g.* for needle and plate crystals), anisotropy of mosaic spread, or both. Thus it is closely related to anisotropy of secondary extinction. Reference to the work of Coppens (1969) and Coppens & Hamilton (1970) suggests that the necessary improvement to the functional form for W is to replace the direction cosines a_i by d_i, the direction cosines of the vector perpendicular to the diffraction plane. Incorporation of this change into the data collection procedure improves the match of expected and measured reflexion widths for measurement in non-bisecting geometries and makes the method applicable for azimuthal scan measurements even in extreme cases of anisotropy.

In such cases, when data are to be collected at different azimuthal angles, it is advantageous to include measurements at a range of azimuthal angles in the preliminary routine which determines the width parameters and an initial normalized reflexion profile, so that these are obtained under conditions as similar as possible to those under which data collection takes place.

References

CLEGG, W. (1981). *Acta Cryst.* A**37**, 22–28.
COPPENS, P. (1969). *Crystallographic Computing*, edited by F. R. AHMED, pp. 255–270. Copenhagen: Munksgaard.
COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A**26**, 71–83.

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Least-squares refinement of unit-cell parameters from precession photographs.

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Abstract

A method is described for the determination of reciprocal-cell parameters by least-squares refinement from (x,y) Cartesian coordinates of reflexions on precession photographs.

An advantage of the precession method of single-crystal X-ray photography over the Weissenberg method is the production of an undistorted record of each reciprocal-lattice level. Reciprocal-unit-cell parameters can easily be obtained by direct measurement of angles and distances on the film. With a suitable single mounting of the crystal, two zero-layer

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photographs can be obtained, giving all three reciprocal-cell lengths and two of the three angles; the third angle is derived from these and from the corresponding direct cell angle, which is the difference in camera dial settings for the two photographs.

We have found it useful to develop a method for deriving precise parameters from precession photographs. This need arose from a set of circumstances including (i) the availability of a precession camera and an accurate device for measurement of (x,y) Cartesian coordinates from films; and (ii) the use of an older type of four-circle diffractometer (Hilger & Watts Y290), for which a previous knowledge of reasonably precise unit-cell dimensions can save considerable time and effort in setting up a crystal for data collection. Devices for accurate measurement of coordinates from films are commercially available from crystallographic suppliers, or a two-direction travelling microscope can be used.

A zero-layer of the reciprocal lattice is described by three parameters, which we can take to be a^*, b^* and γ^* without loss of generality. The photograph is laid on the measuring device with its centre in an arbitrary position (with coordinates X, Y), such that the $+a^*$ axis is rotated anticlockwise from the instrument x axis by an arbitrary angle φ and the $+b^*$ axis by the angle $\gamma^* + \varphi$. Pairs of (x,y) coordinates are measured for a number of reflexions (typically 10–20), preferably well distributed over the film. These are used for a non-linear least-squares refinement of the six parameters a^*, b^*, γ^*, X, Y and φ, in which the quantity $\sum[(x_0 - x_c)^2 + (y_o - y_c)^2]$ is minimized. The basic equations are

$$x = X + S\lambda[ha^* \cos \varphi + kb^* \cos (\varphi + \gamma^*)]$$

$$y = Y + S\lambda[ha^* \sin \varphi + kb^* \sin (\varphi + \gamma^*)],$$

where S is the crystal-to-film distance, λ is the X-ray wavelength in Å, and a^* and b^* have the units of Å^{-1}. Derivatives are obtained analytically and for photographs displaying crystallographic symmetry any of the constraints $a^* = b^*$, $\gamma^* = 60°$ or $\gamma^* = 90°$ can easily be applied. Approximate starting parameters are required, and convergence is reached in a few cycles.

Table 1. *Comparison of reciprocal-cell parameters calculated from precession photographs and diffractometer measurements*

	*hk*0	*h*0*l*	Diffractometer
a^* (Å^{-1})	0·1272 (1)	0·1273 (1)	0·12715 (3)
b^*	0·0810 (1)		0·08082 (2)
c^*		0·0542 (1)	0·05424 (1)
γ^* (°)		77·91 (6)	77·98 (2)
Number of reflexions	12	10	
R.m.s. deviation (mm)	0·018	0·036	

We have found that the results obtained are usually not significantly different from the final values obtained by refinement from diffractometric measurements. A precision of *ca* 0·1% in a^* and b^*, and 0·05° in γ^* is easily attainable. As in all precession measurement methods, the value of S must be accurately known (Buerger, 1964).

A computer listing in Basic for the Hewlett–Packard 2000 series of computers is available from the author on request. Translation into other dialects of Basic or into Fortran would not be difficult.

Example

*hk*0 and *h*0*l* photographs were measured for the monoclinic substance $Mo_2(O_2CCH_3)_2(CH_3COCHCOCH_3)_2$ (Garner, Parkes, Walton & Clegg, 1978). 12 and 10 reflexions respectively were measured, and the results are summarized in Table 1, and compared with the reciprocal-cell parameters derived from diffractometer measurements.

This work was carried out in the University of Newcastle upon Tyne, England. I thank the Crystallography Laboratory and the Computing Laboratory for the use of their equipment.

Reference

Buerger, M. J. (1964). *The Precession Method in X-ray Crystallography*. New York: Wiley.

Garner, C. D., Parkes, S., Walton, I. B. & Clegg, W. (1978). *Inorg. Chim. Acta*, **31**, L451–L452.

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Corrections to equations in § 3 of *International Tables for X-ray Crystallography*, Vol. IV.

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Abstract

Two misprinted equations in *International Tables for X-ray Crystallography*, Vol. IV [(1974). Birmingham: Kynoch Press], should be corrected.

Misprints have been found in § 3 (*Angle Settings for Four-Circle Diffractometers*) of *International Tables for X-ray Crystallography*, Vol. IV (1974).

1. P. 277, paragraph 3.2.2.4., equation (2): Replace $a^*c^* \cos \alpha^*$ by $b^*c^* \cos \alpha^*$.
2. P. 280, paragraph 3.4.3., equation (3): Replace $(a^*c^* \cos \beta^* - t_{12}t_{32})\,t_{11}$ by $(a^*c^* \cos \beta^* - t_{12}t_{32})/t_{11}$.

Reference

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

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