Short Communications

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Detector aperture size in the conventional estimation of integrated intensity in the \( \omega/2\theta \) scan mode.

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Abstract

In respect of the traditional wide-aperture procedure for the measurement of integrated intensity, the practice of varying the detector aperture width from reflection to reflection as a function of tan \( \theta \) is shown to be erroneous in relation to the \( \omega/2\theta \) scan mode: in most cases, no adjustment is needed at all.

In perusing publications in recent years reporting structure analyses based on data collected by the conventional wide-aperture procedure (Bragg, 1914) on diffractometers with an aperture control facility, it comes as somewhat of a surprise to read that, using the \( \omega/2\theta \) scan mode, some authors not only adjust their \( \omega \) (crystal) scan range with change of \( \theta \), following a form \( A + B \tan \theta \) to allow for wavelength dispersion, but also adjust the detector aperture using the same functional relationship, but with different numerical constants, e.g. \( C + D \tan \theta \). This means that, taking typical values such as \( C = 2.0 \) and \( D = 0.2 \) to 1.0, the aperture is opened up to a rather considerable extent as one moves from low to high values. However, there seems to be no obvious record in the literature which offers an explanation for this practice.

Using the two-dimensional viewpoint of Mathieson (1982) the situation is illustrated in Fig. 1(i) for a low \( \theta \) reflection and (ii) for a higher \( \theta \) reflection, the three scan modes \( \omega(s = 0) \), \( \omega/\theta(s = 1) \), \( \omega/2\theta(s = 2) \) being represented in Figs. 1(a), (b) and (c) respectively [see Mathieson (1983a) for terminology]. The loci of the fragment/mosaic distribution, \( \mu \), the source distribution, \( \sigma \), and the wavelength distribution, \( \lambda \), are indicated in each case. The outer (thin-line) rectangle represents the \([\Delta\omega, \Delta2\theta]\) area surveyed using the conventional wide-aperture procedure for measurement of integrated intensity. The six-sided (thick-line) figures \( ABCDEFG \) correspond to the designated outer limits of the distributions of \( \mu, \sigma, \lambda \), and represent the areas within which the integration should take place for the measure to be exactly comparable from reflection to reflection. The two dark areas within each six-sided figure represents the \( K_1, K_2 \) components of the peak emission of the source.

It is clear from Figs. 1(a) and (b) that, in the case of the \( \omega \) and \( \omega/\theta \) scan modes, the aperture width, which is given by the horizontal width of the rectangles in Fig 1, must increase as one moves to higher \( \theta \) angles and that the main factor contributing to this increase is the wavelength dispersion, with a possible minor (but not simple \( \theta \)-dependent) contribution from anisotropic mosaic distribution in the case of the \( \omega/\theta \) scan mode. By contrast, in the case of the \( \omega/2\theta \) scan mode, Fig. 1(c), the wavelength dispersion effect, in relation to aperture width, is zero, its full effect being along \( \omega \). In other words, for this particular scan mode, the aperture width remains constant irrespective of \( \theta \) setting. The mosaic distribution, if anisotropic, may require that the aperture width be varied but this will be a minor effect and will be dependent on the location of the Bragg reflection in reciprocal space and not simply on tan \( \theta \).

Diffractometers with an aperture control facility are generally equipped with a perpendicular pre-monochromator. With this configuration, the monochromator dispersion is normal to the specimen crystal dispersion [see Fig. 5 in Mathieson (1968); also Furnas & Beard (1965)] and therefore lies along the vertical dimension of the detector aperture. So it is only the specimen dispersion which influences the (horizontal) aperture size, and hence the treatment of the specimen dispersion in Mathieson (1982) is directly applicable to the discussion of aperture size with a perpendicular monochromator. Where a parallel mono-
chromator is solved, the change of the slope of the distribution in $\Delta \omega, \Delta 2\theta$ space as $\theta$ changes is much more complex than a tan $\theta$ dependence, see Schoenborn (1983).

Even with 'correct' adjustment of the detector aperture width, the traditional procedure involves integration over an area (thin-line rectangles in Fig. 1) in excess of that defined by the appropriate ranges of $\mu, \sigma, \lambda$ (thick-line six-sided figures ABCDEF in Fig. 1), and this excess constitutes an inbuilt systematic error in the classical prescription for the measurement of integrated intensity, see Mathieson (1982). A more sophisticated dynamic use of aperture control to eliminate this error source has been described recently (Mathieson, 1983b).

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References


Error in $2\theta$ from single-crystal diffractometers due to sample absorption in a divergent primary beam.

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Abstract

The primary-beam divergence of an X-ray four-circle diffractometer is the source of an error in the measured scattering angles from absorbing single crystals. A correction for this error is included in a least-squares program for lattice-constant determination. It is shown with $\alpha$-LiIO$_3$ as an example that both accuracy and precision are enhanced. The $2\theta$ corrections are typically as large as 0.03° for a spherical crystal with $\mu R = 1.5$ and $R = 0.15$ mm. The results indicate an obtainable accuracy of about 0.02% in lattice constants even if $\mu R \geq 1$.

In the course of a study of the thermal expansivity of hexagonal $\alpha$-LiIO$_3$ (Abrahams, Liminga, Marsh, Schrey, Albertsson, Svensson & Kvick, 1983) lattice constants determined as a function of temperature by X-ray and neutron single-crystal four-circle diffractometers were compounded with lattice constants from a Bond diffractometer (Bond, 1960; Barns, 1967) and with thermal expansion data by dilatometry. It was then evident that the X-ray lattice constants were systematically underestimated. Although the linear absorption coefficient of $\alpha$-LiIO$_3$ is moderate, $\mu \approx 115 \text{ cm}^{-1}$, the error was recognized as due to sample absorption in a divergent primary X-ray beam.

X-ray single-crystal four-circle diffractometers are not designed for accurate lattice-constant determination. Nevertheless, they are often used for such purposes with quite high precision. For example, the software of the Enraf–Nonius CAD4 diffractometer includes routines for calculation of the center of gravity of the reflexion profile and for calculation of the scattering angle $2\theta$, by what is called a modified Bond method, from measurements at two different crystal settings. A precision of $\sigma(\alpha)/\alpha \approx 10^{-4}$ is obtained without special arrangements through examination of a large number of high-angle reflexions followed by least-squares analysis. However, the first requirement of the Bond (1960) method, a well collimated primary beam, is not met by commercial four-circle diffractometers. With a divergent primary beam one must expect errors in measured Bragg angles because of both crystal eccentricity and absorption.

This paper gives an approximate correction to the error caused by primary-beam divergence and absorption; the crystal is assumed to be adjusted with its center of mass at the instrument center. The derivation is based on an equatorial-geometry diffractometer with angle optimization such that the intensity-weighted center of gravity of the crystal, as seen from the detector, is set at the Bragg angle, and with $2\theta$ determined from two crystal settings. Similar corrections have been used before for cylindrical crystals (see Buerger, 1942) and recently for the analysis of line profiles from absorbing samples in the Debye-Scherrer method (Tempest, 1976, 1977).

The calculation of the intensity-weighted center of gravity, at radius vector $r$, (cf. Fig. 1), is simplified by assuming an impinging parallel beam. The error thus introduced is

\[
\frac{r_1}{r} = \frac{x_1}{x} + \frac{y_1}{y} + \frac{z_1}{z}\]

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Fig. 1. Projection of a spherical crystal on the equatorial plane of the diffractometer and the coordinate system used for calculation of the intensity-weighted center of gravity, C, of the crystal. Radius vector $r$, has fractional coordinates $(x, y, z)$. 

$\Delta \omega, \Delta 2\theta$ space as $\theta$ changes is much more complex than a tan $\theta$ dependence, see Schoenborn (1983).