(*c*) Characterization of a needle-type texture by parameters. From (1) or from the general results of Roe & Krigbaum one derives easily the following relation between the coefficients A_{2n} and B_{2n} of P_n in a development of $f(\chi)$ and $g(\chi)$ in Legendre functions $P_n(\cos\varphi)$:

$$B_{2n} = P_{2n}(\cos\varphi) \,.\, A_{2n} \,. \tag{2}$$

Hence the coefficients A_{2n} would appear to be the most suitable parameters to characterize the texture. Indeed the results of Fig. 2 and 3 were obtained by a spherical harmonic analysis of the curve of Fig. 2, followed by application of equation (2) and subsequent synthesis.

It is doubtful, however, whether this approach is the most appropriate one if a weak texture has to be eliminated from a number of precision intensity measurements. The distribution of Fig. 2 and 3 is probably typical of the rather broad type of maxima to be expected. The calculation mentioned above has shown that many (here 12) terms are needed to obtain a reasonable degree of accuracy. If the texture itself is only weak, a smaller number may be sufficient, but hardly less than 5 or so. It may be advantageous to sacrifice the simple and linear relationship expressed by equation (2), and to define $f(\beta)$ by some parameters more closely adapted to its expected form. As such, one might think of just two parameters, defining height and width of the maximum, respectively. This leads to much more complicated relations between $f(\chi)$ and $g(\chi)$, which would have to be completely available in order to allow the elimination of such a pair of parameters from a set of measurements.

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DISCUSSION

Weiss: It is true that preferred orientation effects can be disentangled given a thin enough transmission specimen, but I suspect that an accuracy of ~1% is required.

De Wolff: The texture must not be too pronounced; there are techniques for reducing it with transmission specimens.

Weiss: Suppose you use Mo *Kα* on a powder specimen of a transition element, such as iron, it is difficult to make your specimen thin enough, when the 1/*e* thickness is only a few thousandths of an inch.

De Wolff: You should aim at a thickness even less than the 1/*e* value.

Milledge: Those directly concerned with the investigation of orientation use special techniques for their detection. Could these be of assistance?

De Wolff: In principle you are correct, but the materials which are usually studied by powder procedures are generally not of simple symmetry and it is difficult to select reflexions sufficiently strong and sensitive to orientation to be effective.

Alexander: For very thin specimens, the statistical grain size problem is very severe. Appropriate specimen preparation and handling is obviously of importance to smooth out the distribution.

De Wolff: With the appropriate specimen movement, the axis of the distribution can be fixed.

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Conversion of Relative Intensities to an Absolute Scale

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The determination of an absolute scale for X-ray intensities involves the experimental evaluation of a number of constants in the intensity equation whose values are not normally required. The absolute intensities so obtained will not be useful, in the present context, unless the overall accuracy can be maintained at about 1% or better. Some of the difficulties which can occur in making the measurements to the necessary accuracy are discussed.

Introduction

If a Bragg reflection from an ideal powder is measured by scanning a slit through it in the usual way, the integrated intensity, *P*, is related to the structure factor, *F*, by the equation:

$$P = \left(\frac{P_0 N^2 r_0^2 l w \lambda^3}{32\pi R^2 \mu\omega}\right) \left(\frac{j(1+k\cos^2 2\theta)}{\sin^2\theta\cos\theta\,(1+k)}\right) (F^2)\,. \tag{1}$$

P_0 is the total power in the primary beam, N the number of unit cells per unit volume, r_0 the classical electron radius, λ the wavelength, l and w the length and width of the receiving slit, R the radius of the spectrometer, μ the linear absorption coefficient, ω the angular velocity of the receiving slit, j the multiplicity, K the polarization ratio of the monochromator ($K = \cos^2 2\theta$ if the monochromator reflects as an ideal mosaic), and θ the Bragg angle. Since the factors in the first term are all independent of angle, a set of relative intensities can be converted to a set of relative structure factors by consideration only of those factors appearing in the second term. These relative structure factors may then be put on an absolute scale by evaluation of the quantities in the first term, and it is the measurement of these quantities which will be the subject of this paper.

It is possible, of course, to by-pass the evaluation of many of the factors in this first term and still achieve a set of structure factors on an approximately correct absolute scale. This may be done, for example, by comparison with a second substance whose scattering factor is presumed known, and in this case only the absorption coefficients need be measured. Or, one may presume to know something about the scattering factor of the primary substance itself, for example, its value at high sin θ/λ, and effect a standardization without consideration of the first term. However, since these methods do not lead to a completely independent determination of the scattering factor, and since the probable errors are difficult to evaluate, they will not be considered here. Based on the conviction that an absolute accuracy of 1 % in intensity is necessary, the approach taken here will be that each quantity in the first term, with the exception of numerical factors, must be determined experimentally. The measurement of these quantities is, in each case, quite straightforward in principle. Because of the high accuracy required, difficulties arise in many subtle ways, and it is hard for one person to foresee all of the problems with which another may be faced. Therefore, this paper will consist principally of examples taken from the author's own experience, with the hope that these may suggest further improvements in overall accuracy.

Measurement of the primary beam power, P_0

In a typical monochromatic powder diffraction apparatus, the primary beam may contain over 10^8 counts per second. This power is too great to be measured directly with the usual types of X-ray counter; the rate is therefore first reduced by an accurately known factor of about 10^4 to 10^5. A number of methods have been suggested and used to accomplish this reduction. Among these are: the use of absorbers alone, or the use of a perfect single crystal rocked through its reflecting range (Batterman, Chipman & DeMarco, 1961) – the use of a narrow slit scanned through the direct beam plus a lesser number of absorbers (Paakkari & Suortti, 1966, for example) – the use of a type of counter which can count the full primary beam (*cf.* Witte & Wölfel, 1958).

Each of these methods has its own particular difficulties; perhaps a discussion of some of the considerations necessary in carrying out a measurement by the method of absorbers alone will serve as an illustration of the types of difficulties which can be expected in general.

The primary beam coming from the monochromator contains the $K\alpha$ wavelengths plus a small band on either side, and a weak continuum scattered by the monochromator crystal. Further, if the tube is operated at high potential, harmonics of the basic wavelength will be present. Because of their lesser attenuation in the absorbers, the shorter wavelengths may cause appreciable error in the measurement of P_0. Fig. 1 shows pulse height distributions taken with the counter in the primary (Cu $K\alpha$) beam adjusted to have a total (integral) count rate of about 5500 counts per second by operating at: (*a*) 14 kV with Ni absorbers, (*b*) 40 kV with Al absorbers, (*c*) 40 kV with Ni absorbers. At 40 kV, Ni absorbers are clearly better than Al absorbers. But one must still rely on the pulse height analyzer to reject the higher energy counts to the required accuracy, and it is preferable, as we shall see, to set the PHA limits not too close to the peak. Further, these extra counts will affect the dead time correction. However, as shown in Fig. 2, if the tube is operated below the half wavelength voltage [condition (*a*)] the absorption coefficient of Ni is larger for nearly all possible wavelengths than for Cu $K\alpha$. For a small band between Cu $K\alpha$ and the Ni K edge, however, this is not the case and it is possible for significant effects to arise on this account.

In addition, the difference in absorption for the $K\alpha_1$ and $K\alpha_2$ wavelengths must be considered. A straightforward method for measuring the absorption factors of the foils is to use the direct beam with all foils in

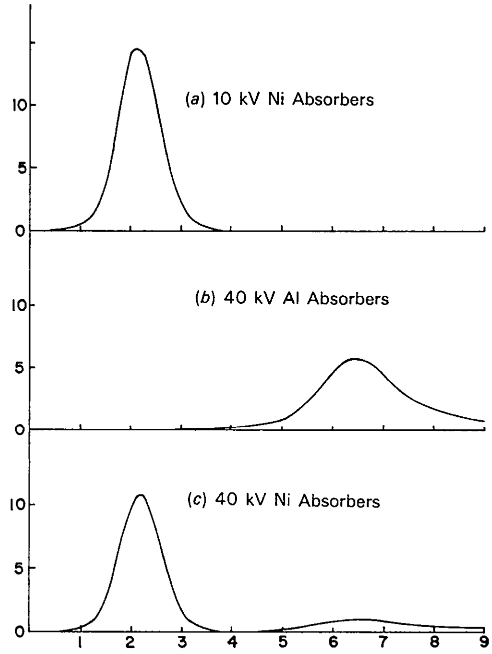

Fig. 1. Pulse height distributions taken with a NaI(Tl) scintillation counter of radiation from a Cu target tube monochromated by a bent LiF crystal. Absorber thickness was adjusted to make the total count rate 5500 cts/sec in each case.

place. They are then removed and replaced one at a time, and the ratios measured. If the total reduction of the primary beam is taken as the product of the individually measured ratios, one can show that because of the presence of the two wavelengths, the measurement of P_0 will be too small, the factor being:

$$\frac{[x_1+x_2 \exp\{(n-1)(\mu_1-\mu_2)t\}]^n}{[x_1+x_2 \exp\{(n)(\mu_1-\mu_2)t\}]^{n-1}}, \tag{2}$$

where x_1 and x_2 are the relative fractions of $K\alpha_1$ and $K\alpha_2$, in the incident beam, μ_1 and μ_2 are the absorption coefficients of the foils for $K\alpha_1$ and $K\alpha_2$ respectively, t is the thickness of a foil, and n is the total number of foils. For a typical case, $x_1=0{\cdot}67$, $x_2=0{\cdot}33$, $n=5$, $\exp(\mu_1 t)=10{\cdot}0$, $\Delta\mu=3(\Delta\lambda/\lambda).(\mu)=0{\cdot}0181\mu$ for Mo $K\alpha$, and equation (2) yields 0·9964. If a much weaker beam having the same composition as the primary beam were available, the absorption of the foils could be measured one at a time. In this case, the resulting P_0 would be too large by the factor:

$$\frac{[(x_1+x_2 \exp\{n(\mu_1-\mu_2)t\}]}{[x_1+x_2 \exp\{(\mu_1-\mu_2)t\}]^n}. \tag{3}$$

Using the same typical values, this equation yields 1·0039. If the foils were measured in a beam of appreciably different composition, the effects could be larger, but these typical results are, of course, large enough to warrant correction.

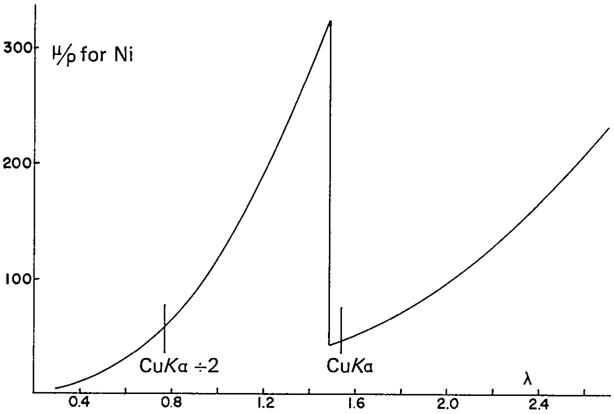

Fig. 2. Mass absorption coefficients of Ni as a function of wavelength.

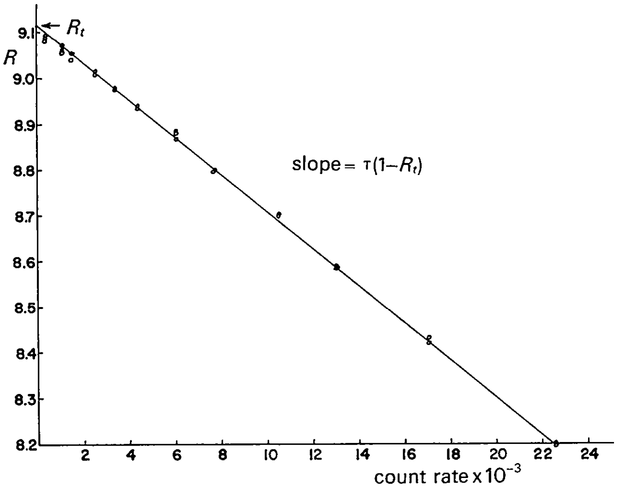

Fig. 3. The absorption factor of a foil *versus* the count rate of the incident X-ray beam. The intercept gives the true absorption factor and the slope is proportional to the dead time, τ.

Measurement of the dead time

It is essential that the dead time of the counting apparatus be measured, and that corrections for dead time effects be made. The simple method outlined below has been in use for some time in our laboratory. We take the relation $N_t=N/(1-N\tau)$ where N_t and N are the true and measured count rates respectively, and τ is the dead time. The absorption factor of a foil is now measured at a number of different incident count rates. This factor is the ratio, R, of the count rate with foil out, N_0, to the rate with foil in, N_i. Using the above relation between N_t and N one can show that:

$$R=R_t-N_0\tau(R_t-1). \tag{4}$$

If each measured R is plotted against its count rate N_0 (foil out), a curve such as is given in Fig. 3 results. The slope of the line gives $\tau(R_t-1)$ and the intercept gives R_t.

Several worthwhile observations relative to the above can be made. First, the measurements lead to a very linear relation between R and N_0 (Fig. 3) showing that a single dead time will handle the correction up to quite high count rates. Statistical errors in the Figure are shown by the size of the circles. Second, if one of the foils to be used in the P_0 measurement has been used to obtain Fig. 3, its absorption factor will be a by-product. Furthermore, the absorption factors of the other P_0 foils can be quickly and accurately measured relative to this foil at high count rates, correcting for the small differences by means of the dead time curve. Third, the often encountered phrase 'linear range for the counter' has no meaning; for a typical five microsecond dead time, a count rate as low as 800 c/s requires a 0·4% correction. This error made for each of five foils would result in an error of 2% in P_0.

Before leaving the subject, perhaps a few remarks on dead time corrections to peak integrals could be included. Here the count rate varies from low to high to low again as the peak is scanned, but if N is taken as the instantaneous count rate, the above relation between N and N_t still holds, and the true peak integral, P_t, is given by $\int N_t dt = \int N/(1-N\tau)dt$. Expanding and replacing N by nh, where h is the count rate at the peak, the integral can be written:

$$P_t = P\left[1 + \tau h \frac{\int n^2 dt}{\int n dt} + \tau^2 h^2 \frac{\int n^3 dt}{\int n dt} + \ldots\right]. \quad (5)$$

The ratios of the integrals in equation (5) can be calculated analytically for some peak shapes. For example, for a Gaussian form, $\int n^x dt / \int n\, dt = 1/\sqrt{x}$. However, these ratios can easily be evaluated numerically for any peak whose shape is known. Hosoya & Yamagishi (1967), using an approximate expression equivalent to the first two terms in equation (5), have calculated the correction for a few special shapes including the Gaussian. For many applications, terms in $\tau^2 h^2$ and higher are indeed negligible. However, for the not too extreme case of $\tau = 5$ microsec and $h = 10^4$ cts/sec, the third term amounts to about 0·15%.

Checks of the counting system

In addition to measurement of the dead time, there are a number of checks which should be made on a counting system before it is used in the accumulation of highly accurate data. Many of these such as periodic checks on background and overall gain stability are well known and will not be discussed. Particularly pertinent to the measurement of absolute intensities, however, is a point which is often overlooked. The direct beam enters the counter in a somewhat different place and with a different distribution than does the diffracted beam (through the receiving slit). The counter must therefore have a uniform sensitivity over at least the entire portion which is used. We have found that (1) scintillation crystals, even when new, may show a change of sensitivity across the face perhaps because of variations in thickness of the beryllium window – (2) scintillation crystals tend to go bad rather quickly presumably because of the intrusion of water through the beryllium (this often occurs within six to twelve months of the time of purchase and lowers the sensitivity drastically in spots) – (3) the gain of the scintillation crystal-photomultiplier combination may depend on position across the face of the counter. Therefore, if the pulse height analyzer is set with upper and lower limits quite close to the pulse distribution for the case of beams hitting near the counter's center, photons hitting away from center may be counted with reduced efficiency.

Other types of X-ray counter may avoid some of the difficulties mentioned above, but will likely have other difficulties of their own. Problems with any type of counter can probably be overcome with care; we favor the scintillation counter because its high efficiency (nearly 100%) ensures that rays entering from different directions will be counted with nearly the same sensitivity.

Measurement of the receiving slit area

Accurate measurement of the receiving slit area presents some challenge, particularly for fairly narrow slits. If the receiving slit itself is scanned through the primary beam in a P_0 measurement, the width is not needed, but care must be taken that the width is constant over the entire length, which must be large enough to include all of the primary intensity. If this method is not used, both width and length must be measured. We have used X-rays in this measurement. If a pinhole is placed in the beam and the slit scanned across the pinhole, a flat topped peak will result. The area of the peak (in counts) divided by the count rate in the flat portion (in counts per second) yields the time-width of the peak in seconds. This times the angular velocity of the slit gives the angular width of the slit in radians, w/R, which is just what is required. The length of the slit, l/R, may be similarly determined if the slit is rotated 90° in its own plane.

Perhaps the most important consideration is the shape of the receiving slit. Fig. 4 shows cross sections through three different shapes. For shape (*a*), the width of the slit depends strongly on the direction of the incoming ray. If w is 0·25 mm and t is 1·5 mm, rays traveling in a direction only 1° away from the central ray will find that the slit appears to be about 10% narrower. Shapes (*b*) and (*c*) are both good; however, for (*c*), care must be taken to make the slit edge not too sharp because of X-ray penetration effects. Shape (*a*) is often the one supplied by manufacturers of X-ray equipment.

One further technique which reduces the difficulties mentioned above is the use of a wide receiving slit, that is one which is as wide as the range over which the narrow slit would be scanned. Here the slit is used in a fixed position, and only the length, which is easier to measure accurately, is required. Count rates will be

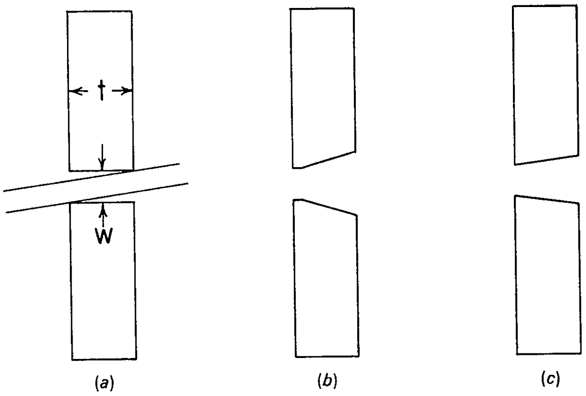

Fig. 4. Three possible receiving slit profiles.

much higher and therefore high statistical accuracy much easier to obtain. In the measurement of the background one may make use of an additional narrow slit, but since this correction is small, the width of the slit need not be known as accurately.

Measurement of the absorption coefficient

The most pertinent thing to be said about absorption coefficients is that in general the tabulated values are not accurate enough for the present purpose. Measurement of the absorption, for ordinary wavelengths and materials from which uniform foils can be obtained, is very easy in principle. In practice the difficulties are, uniformity of the foil, measurement of the thickness, and control of the X-ray wavelength distribution. Table 1 shows some recent measurement of the absorption coefficient of Ni for Cu $K\alpha$ radiation, and the spread in values for this fairly easy case gives some idea of the care required for a useful measurement. Also shown are the values from the International Tables (1935) and (1962). The smoothing done in the preparation of these tables does not always result in the best individual values.

Table 1. *Values of the mass absorption coefficients of* Ni *for* Cu$K\alpha$ *radiation, from various sources*

48	Allen (1926)
48·12	Deslattes (1958)
49·45	Ehrenfried & Dodds (1960)
49·6	Bucklow & Woodhouse (1964)
48·96	Cooper (1965)
48·3	Hosoya (1968)
49·2	International Tables (1935)
45·7	International Tables (1962)

Further effects of the wavelength distribution

We have already discussed some of the problems which result from the real wavelength distribution. The purpose of this section is to point out that there are other factors in equation (1) which depend on wavelength. Consider only the effects arising from the presence of $K\alpha_1$ and $K\alpha_2$. Each will have its own wavelength (appearing as λ^3), absorption coefficient, Bragg angle and hence Lorentz and polarization factors, and dispersion correction. These effects can be quite large, but can easily be calculated for each case. For example, for the 331 reflection of Ni with Cu radiation, the integrated intensity differs by 4·7% for the two wavelengths. Therefore, if the assumed average wavelength differs from the actual average wavelength by one tenth of the α_1–α_2 difference, the correction would amount to about 0·5%.

Summary and conclusions

The determination of accurate absolute structure factors depends, of course, on the accuracy of the relative intensities themselves, and it is most important that the sample and the apparatus conform closely to the conditions for which the intensity formula was derived. We refer to considerations such as extinction, preferred orientation, purity, surface roughness and porosity in the sample, and alignment of the apparatus which are beyond the scope of this paper. Having assured ourselves regarding these considerations, there remain many corrections such as those for background and thermal diffuse scattering above background, for polarization, for atomic vibration (Debye–Waller factor), for dispersion, *etc.*, which again are not covered here. Throughout all of these operations we must keep in mind that if absolute scattering factors cannot be experimentally determined with accuracy higher than that given by theory, they are of little use. There are enough factors to be determined that to hold a useful overall accuracy of 1%, we must try to maintain about 0·1% on each individual measurement.

I would like to thank L. D. Jennings who has been a co-worker for many years. A number of the ideas presented here are due to him.

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DISCUSSION

POST: (1) Have you used cylindrical slits?

(2) What stability do you find in respect of scintillation crystals?

CHIPMAN: (1) No.

(2) Extremely variable. We get a rare one which remains reliable but most are poor or become poor within a year. We insist that the design be such that we can remove the crystal from the photomultiplier so that they can be inspected visually. This simple procedure provides a ready method of detecting deterioration. Part of the problem arises from the porosity of the beryllium.

YOUNG: Many people have avoided step-scans in the past because of the large amount of numerical output. However, a step-scan with an individual dead-time correction on each step gives us the only accurate way of making counting-loss corrections.

LADELL: There are electronic circuits which are capable of making counting corrections automatically up to 10^6 c.p.s. I do not know if these are commercially available.

HOSOYA: They are from JOEL.

WEISS: All these devices introduce an error of perhaps 10% in the correction. So you must make sure that the correction itself is small.

ROGERS: Dr Hughes at Cardiff found that when the peak counting rates with an unattenuated beam were such as to lead to 25–30% counting losses, he could avoid these losses by suitable attenuation at a cost of only an extra 10% in the total time taken for his experiment.

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Assessment of Accuracy in Powder Intensity Measurement

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The assessment of the overall accuracy in powder intensity measurement involves the estimation of the error of virtually every term in the intensity equation. Problems related to the accuracy of those quantities which are needed for the determination of relative structure factors are discussed. An example of the consideration of errors in an absolute measurement is given.

Introduction

The attainment of experimental structure factors F of high precision and the assessment of their absolute accuracy are current problems of considerable consequence to crystallography and its applications. Many possible sources of error exist in the individual techniques used in X-ray intensity measurements and in the transformation of the measurements to F values. Investigation of these factors is therefore of prime importance in defining the accuracy to be associated with different levels of experimental sophistication. The purpose of this paper is to discuss the assessment of accuracy in powder intensity measurement. Consideration will be limited to measurements made using the symmetrical Bragg method, counter technique and monochromatized radiation, on centrosymmetric crystals of known structure.

The square of the absolute F value of a Bragg reflexion from a powder specimen can be expressed as (James, 1962)

$$F^2 = \left[\frac{16\pi\omega\mu R^2 V^2}{r_0^2 \lambda^3 A P_0}\right] \left[\frac{\sin\theta\sin 2\theta}{p(\theta,\theta_M)}\,\frac{E}{j}\right], \qquad (1)$$

where ω is the angular velocity of the detector, μ the linear absorption coefficient, R the distance from the specimen to the receiving slit, V the volume of the unit cell, $r_0 = e^2/mc^2$ the classical electron radius, λ the X-ray wavelength, A the area of the receiving slit, P_0 the total power in the primary beam, θ the Bragg angle, θ_M that of the monochromator crystal, $p(\theta, \theta_M)$ the polarization factor, j the multiplicity, and E the total diffracted energy for a reflexion.

The mosaic crystal formula (1), which assumes symmetrical geometry, proper focusing and correct diffractometer alignment, is valid for a specimen free of preferred orientation, extinction, surface roughness and porosity. It is essential that the effects of deviations from these conditions be considered in accurate measurements. In addition, virtually every term in equation (1) requires careful consideration. We shall discuss mainly the problems related to the accuracy of the quantities in the second term of equation (1); the measurement of the quantities in the first term – the scale factor – has been the subject of the contribution by Chipman (1969).

Measuring geometry and diffractometer alignment

The effects of deviations from idealized diffraction conditions are important for low-angle reflexions, particularly if the receiving slit is very narrow, as is necessary when a diffracted-beam monochromator is used. Horizontal divergence and an asymmetrical intensity distribution in the primary beam cause systematic effects on E values, which added up can be of the order of 1% at $\theta \simeq 10°$ (Suortti & Paakkari, 1966). However, the most serious errors are caused by maladjustment of the specimen. For instance, an inaccuracy of 0·2° (in 2θ) in the zero alignment of the X-ray focus, the centre of the goniometer, the specimen surface and the receiving slit may result in an error of $\simeq 5\%$ in E at $\theta = 10°$, if the receiving slit is very narrow. To attain

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* Read by K. Kurki-Suonio.