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Indicators of Accuracy in Structure Factor Measurement

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Objective estimation of the error (σF_{meas}) in each structure factor (F_{meas}), by a procedure such as that outlined in *Acta Cryst.* (1964) **17**, 1327, allows the indicator

$$\mathscr{U}_\alpha = [\Sigma\,(\Delta^2 F_{\text{meas}}/\sigma^2 F_{\text{meas}}) \div \chi^2_{m-n,\alpha}]^{1/2}$$

to be evaluated, where $\Delta F_{\text{meas}} = |F_{\text{meas}}| - |F_{\text{calc}}|$, $\chi^2_{m-n,\alpha}$ is given by the χ^2 distribution at the α-significance level, and the model for which $\Sigma\Delta^2 F_{\text{meas}}$ is minimized contains m independent F_{meas} and n variables. The sensitivity of $\mathscr{U}_\alpha$ to errors in F_{meas} is examined under both real and hypothetical conditions. For the real case, the range in $\mathscr{U}_{0\cdot01}$ for eight recently measured inorganic crystals indicates the average minimum residual error in σF_{meas} to be about 1%, the maximum error to be about 21%. The hypothetical case is considered by propagating several types of error into a set of 772 independent F_{meas} corresponding to a model consisting of 10 independent atoms undergoing isotropic thermal vibration. The indicator $\mathscr{U}_{0\cdot01}$ detects a systematic intensity error at a level in which the maximum intensity error in 97% of the data reaches 5%. Long term drift in the experiment is indicated with considerable sensitivity by $\mathscr{U}_{0\cdot01}$. Systematic error as a function of scattering angle is detectable only if the σF_{meas} contain a component due to the suspected error.

Introduction

Structure factors (F_{meas}) are generally measured, not for the purpose of establishing their intrinsic magnitudes, but in order to derive the values of related physical quantities. Typical of such derived quantities are atomic positions, atomic amplitudes of vibration, atomic scattering factors and electron distributions. The correctness with which these derivations are made depends both upon the *accuracy* of the F_{meas} and also upon the *validity* of the theoretical model. In this paper it is assumed that departures of the model from validity are negligible compared with the errors in the F_{meas}. It is also assumed that the differences between the F_{meas} and the corresponding parameters in the theoretical F_{calc} have been minimized by the method of least squares.

The weakness of the customary R factor as an indicator of fit between F_{meas} and F_{calc} is well known. Errors in F_{meas} that are systematic, with respect to functions that may be varied in the minimizing process, will be improperly absorbed into the derived function. The consequence is not only an R factor that is too small but, more seriously, the possibility of magnitudes for the apparent standard deviations of the derived functions that are also too small (see, *e.g.* Hamilton & Abrahams, 1968).

Based on the assumptions above, which are also implicitly included in the R factor, an alternative indicator of accuracy of the F_{meas} is developed herein, and examples of its use are given. The influence of various kinds of error on this, and on other indicators, is also considered.

Sources of error in F_{meas}

The uncertainties in a derived quantity are correctly calculated only if the uncertainties in the measured set of primary quantities are correctly assigned. Propagation of error theory (see, *e.g.* Birge, 1939) provides the basis for the method of calculation. It is hence necessary to recognize the more important sources of error that remain in the F_{meas} after all corrections have been applied. Other papers at this International Meeting will consider the origin, the possibility of correction, and the magnitudes of many error sources in detail. The principal sources of error in F_{meas} are grouped together, for convenience, in Table 1. A procedure for the evaluation of the errors associated only with the diffractometer itself, neglecting the crystal under study, was given at an Open Session of the Commission on Crystallographic Apparatus held in Rome, 1963 (Abrahams, 1964*a*).

Table 1. *Error sources in* F_{meas}

I. Random
- (*a*) Poisson distribution in the arrival of quanta in the incident X-ray beam.
- (*b*) Short term variations in incident X-ray beam flux.
- (*c*) Short term variations in sensitivity of detection system.

II. Systematic
- (*a*) Differences between measured and actual crystal dimensions.
- (*b*) Incorrect transmission coefficient.
- (*c*) Incorrect extinction correction.
- (*d*) Non-monochromatic incident X-ray beam.
- (*e*) Thermal diffuse scattering.
- (*f*) Multiple scattering.
- (*g*) Inhomogeneous crystal specimen.
- (*h*) Radiation damage.
- (*i*) Mechanical misalignments.
- (*j*) Long term variation in incident beam flux.
- (*k*) Long term variation in sensitivity of detection system.

Estimation of $\sigma F_{\rm meas}$

The variance in $F_{\rm meas}(\sigma^2F_{\rm meas})$ is given, approximately, by equation (1)

$$\sigma^2F_{\rm meas}/F^2_{\rm meas} = \sum_j \sigma^2 f_j(F_{\rm meas})/f_j^2(F_{\rm meas}) \,. \qquad (1)$$

We assume that $\sigma f_j(F_{\rm meas}) \ll f_j(F_{\rm meas})$, where f_j is the jth correction factor for $F_{\rm meas}$. To evaluate equation (1), it is necessary to assign magnitudes to each of the jth variances on the right-hand side of the equation. The variances due to the following random sources of error are readily determined experimentally. The Poisson distribution in the arrival of quanta in the incident beam at the crystal has a variance ($\mathscr{N}$) that is directly related to the number of quanta ($\mathscr{N}$) received by the counter. Numerous examples of the evaluation of this variance based on counting statistics are given in the literature (*e.g.*, Shoemaker, 1968; Cetlin & Abrahams, 1963). The short term variations given in Table 1 under I(*b*) and I(*c*) are related to the diffractometer system stability. These variations may be determined directly (*e.g.* Abrahams, 1964*a*). A stability range of $\pm p$ per cent in I(*b*) and I(*c*) (Table 1) then approximately corresponds to a variance of $4p^2\times10^{-4}F^4_{\rm meas}$.

The systematic variances have previously (Abrahams, 1964*b*) been considered by dividing them into anisotropic and isotropic classes. Anisotropic error is detectable by variations among magnitudes of symmetry-related reflections, *i.e.* by pseudo-replication, using equation (2),

$$\sigma^2_{\rm aniso}(F^2_{\rm meas}) = \sum_{j=1}^{P}(F_j^2 - F^2_{\rm meas})^2 \div (P-1)\,, \qquad (2)$$

where $\sigma F_{\rm meas} = \sigma F^2_{\rm meas}/2F_{\rm meas}$, and $F^2_{\rm meas}$ is given by the equation

$$F^2_{\rm meas} = \frac{1}{P}\sum_{j=1}^{P} F_j^2\,, \qquad (3)$$

and P members of a form have been measured. For crystals of low symmetry, or if $P \le 2$ for a given form, equation (2) is not recommended. In such cases, average values for $\sigma^2_{\rm aniso}(F^2_{\rm meas})$ are obtained for each range of $F^2_{\rm meas}$, as described by Abrahams & Reddy (1965). An estimate of anisotropy in the extinction effect, and of the error caused by multiple scattering, may be obtained experimentally by the variation observed in intensity on rotation about the scattering vector.

Direct measurement of the remaining unreplicated error sources is more difficult: instead, if not possible to eliminate experimentally, such as for II(*i*), II(*j*) and II(*k*) in Table 1, a numerical estimate may be made and the corresponding variance derived as in the case of short range stability above. Replacing equation (1) by the equivalent percentage variances, and rearranging, we obtain:

$$\sigma^2F^2_{\rm meas} = \sigma^2(\text{counting statistics}) + \sigma^2_{\rm aniso}(F^2_{\rm meas}) + 4\sum_i k_i^2 \times 10^{-4} F^4_{\rm meas} \qquad (4)$$

where k_i is the estimated percentage error due to sources listed in Table 1 that have not been measured experimentally.

Typical magnitudes for the summation term in equation (4) are given under $4\sum_i k_i^2$ in Table 2.

Accuracy indicators

In addition to the usual R and wR factors obtained on minimization of the difference terms $\Delta F = |F_{\rm meas}| - |F_{\rm calc}|$ by means such as the method of least squares, the S factor is readily calculated by equation (5):

$$S^2 = \sum(\Delta^2F/\sigma^2F_{\rm meas}) \div (m-n) \qquad (5)$$

where there are m observations and n variables used in the minimization process. The expression S^2 is a measure of the goodness-of-fit, and estimates the variance of an observation of unit weight. This quantity, which is routinely calculated by the standard *ORFLS* program of Busing, Martin & Levy (1962), should have a value close to unity if the assignment of $\sigma F_{\rm meas}$ terms is correct, *i.e.* if each observation is correctly weighted, since the weight of $F_{\rm meas} = 1/\sigma^2F_{\rm meas}$.

Table 2. *Experimental indicator values*

Crystal	m	n	$4\sum_i k_i^2$	R	wR	$\mathscr{U}_{0\cdot01}$	$\mathscr{U}_{0\cdot001}$	Reference
$LiNbO_3$	247	8	42	0·0383	0·0501	0·889–1·127	0·863–1·168	Abrahams, Reddy & Bernstein (1966)
$Bi_{12}GeO_{20}$	631	23	98	0·0623	0·0808	0·792–0·919	0·777–0·939	Abrahams, Jamieson & Bernstein (1967)
$GaFeO_3$	772	40	37	0·0465	0·0517	0·918–1·050	0·902–1·071	Abrahams, Reddy & Bernstein (1965)
$DyMn_2O_5$	976	40	61	0·0401	0·0582	1·018–1·147	1·002–1·167	Abrahams & Bernstein (1967)
$Sc_2(WO_4)_3$	1731	78	179	0·0622	0·0895	0·977–1·069	0·965–1·083	Abrahams & Bernstein (1966*b*)
α-$MnMoO_4$	1873	62	70	0·0574	0·0688	1·061–1·156	1·049–1·171	Abrahams & Reddy (1965)
$Fe_3(PO_4)_2.4H_2O$	1919	89	27	0·0336	0·0436	0·890–0·969	0·880–0·981	Abrahams & Bernstein (1966*a*)
α-$ZnMoO_4$	3269	163	91	0·0726	0·0708	0·902–0·962	0·894–0·971	Abrahams (1967)

The deviation of S from unity is a measure of the validity of the weight assignment. This measure is made quantitative if S is compared with the distribution of values expected for experiments with m observations and n variables. Equation (6) gives the value of S that will be exceeded in 100α per cent of replications of such an experiment

$$(S^2)_\alpha=\chi^2_{m-n,\alpha}/m-n\,, \tag{6}$$

where $\chi^2_{m-n,\alpha}$ is the 100α per cent point of the chi-square distribution over $m-n$ degrees of freedom. Tabulated values for this distribution generally do not extend to large values of $m-n$, at the various α-levels of significance. For most crystallographic calculations, the values obtained from equation (7) are amply accurate (Wilson & Hilferty, 1931):

$$\chi^2_{m-n,\alpha}=(m-n)\left[1-\frac{2}{9(m-n)}+u_\alpha\,.\sqrt{\frac{2}{9(m-n)}}\right]^3 \tag{7}$$

where $u_\alpha=2{\cdot}5758$ at the 0·01 level and 3·2905 at the 0·001 level. A simple numerical approximation to the standard deviation in $(S)_\alpha$ is given by $u_\alpha/\sqrt{2(m-n)}$.

It is convenient to compare S^2 with $(S^2)_\alpha$ directly, by equation (8):

$$\mathscr{U}_\alpha=[S^2/(S^2)_\alpha]^{1/2}\,,\ [S^2/(S^2)_{1-\alpha}]^{1/2}\,. \tag{8}$$

The range of $\mathscr{U}_\alpha$ given by equation (8) corresponds to a confidence interval of $100(1-2\alpha)$ per cent. Hence, $\mathscr{U}_{0\cdot01}$ represents an interval which should not be exceeded in more than one per cent of the replications of the experiment. In case the $\mathscr{U}_\alpha$ range includes unity, the assignment of σF_{meas} may be held valid at the α level. Departure of the $\mathscr{U}_\alpha$ range from unity expresses the error in the mean σF_{meas}.

Experimental test of accuracy indicators

Values of σF_{meas} were assigned to each F_{meas} determined, for a group of eight crystals (Table 2), by the procedure indicated above. The references in Table 2 supply the details of the experiments. These crystals were chosen to give a wide range of m and n. The constant term of equation (4), used to estimate the non-replicated error sources listed in Table 1, is given for each crystal under $4\sum_i k_i^2$. The range in magnitude of this term is also wide, as seen from Table 2. The largest value, for $Sc_2(WO_4)_3$, is due in large part to the 2·2% variation from sphericity of the sample used, together with the magnitude of the linear absorption coefficient $\mu=30{\cdot}96$ mm^{-1}.

Examination of the $\mathscr{U}_\alpha$ ranges in Table 2 shows, at the significance level of 1%, that assignment of σF_{meas} is acceptable for three of the crystals; of the others, the ranges are unacceptably small for three and unacceptably large for the two remaining crystals. The maximum least deviation at this significance level is 8·1% for $Bi_{12}GeO_{20}$: hence, the mean value of σF_{meas} for this crystal is approximately too large by at least 8%. For all eight crystals in Table 2, the average least deviation of the $\mathscr{U}_\alpha$ range from unity, with due regard for sign, is less than 1%.

Propagation of simulated error in F_{meas}

Additional insight into the influence of various kinds of error, both on the accuracy indicators and on some of the derived physical quantities for which the F_{meas} are ultimately used, was sought by propagating such error into a simulated set of $F^{\text{EF}}_{\text{meas}}$. The model necessary for such simulation was chosen to consist of the atomic position coordinates and isotropic temperature factors experimentally determined for $GaFeO_3$ and listed in Table 3 of Abrahams, Reddy & Bernstein (1965). The form factors and dispersion corrections given in that paper were regarded as free from error (EF). The structure factors thereby calculated for the four independent metal and six independent oxygen atoms formed a set of error-free $F^{\text{EF}}_{\text{meas}}$.

The first type of error we consider is random in nature, and the corresponding set of F_{meas} is obtained from equation (9)

$$F_{\text{meas}}=F^{\text{EF}}_{\text{meas}}+N\,.\,\sigma F^{\text{EF}}_{\text{meas}}\,. \tag{9}$$

N, the random normal deviate, is computer generated (Chambers, 1968) and gives a random sequence of deviates normally distributed about zero. The value of $\sigma F^{\text{EF}}_{\text{meas}}$ was chosen according to equation (10), as a reasonable representation of an error distribution:

$$\begin{aligned}\sigma F^{\text{EF}}_{\text{meas}}&=s\,.\,F^{\text{EF}}_{\text{meas}}\ \text{ if }\ F^{\text{EF}}_{\text{meas}}\geq 4F_{\text{min}}\,,\\ \sigma F^{\text{EF}}_{\text{meas}}&=4s\,.\,F_{\text{min}}\ \text{ if }\ 2F_{\text{min}}\leq F^{\text{EF}}_{\text{meas}}<4F_{\text{min}}\,,\\ \sigma F^{\text{EF}}_{\text{meas}}&=s(6F_{\text{min}}-F^{\text{EF}}_{\text{meas}})\ \text{ if }\ F^{\text{EF}}_{\text{meas}}<2F_{\text{min}}\,,\end{aligned} \tag{10}$$

where F_{min} is the smallest value of $F^{\text{EF}}_{\text{meas}}$.

The resulting set of F_{meas} were then used, in a least-squares minimization procedure, to refine the coordinates of an initial model in which each metal atom was randomly displaced by 0·05 Å from the 'correct' position (Table 3 of Abrahams, Reddy & Bernstein, 1965) and each oxygen atom was randomly displaced by 0·10 Å. The metal atom isotropic temperature factors were initially set equal to 0·3 Å^2, the oxygen atom temperature factors to 0·7 Å^2. The effects of three different random sets of error, all with $s=0{\cdot}03$ in equation (10), are contained in Table 3.

It may be noted that the value of R is *smaller* than the 3% error introduced into the F_{meas} on a random basis: the value of wR appears more realistic, *i.e.* over 3%. The $\mathscr{U}_{0\cdot01}$ ranges, for all sets, include unity – which is generally close to the midpoint of the range. This is to be expected, since the values for σF_{meas} in the least-squares refinement are identical with those of equation (9) used to produce the F_{meas} set. Of considerable interest are the quantities $\Delta\xi_{\text{max}}/\sigma\xi$, where ξ is a coordinate. The maximum value for this quantity is 2·9, obtained with the first set of random normal deviates generated.

There should be no surprise, with random error only present in the F_{meas}, that the best coordinates obtained by least-squares refinement do not coincide with the correct coordinates. The probability that no coordinate belonging to a fitted set of k-coordinates should deviate by $y\sigma$ is given by equation (11).

$$\text{Probability } (|u_i|<y\colon i=1, \dots k) = \left[\frac{1}{\sqrt{2\pi}}\int_{-y}^{y} \exp\,(-\alpha^2/2)d\alpha\right]^k \tag{11}$$

where u_i are unit normal deviates and the expression in square brackets is the normal probability function. For $k=40$, the probability that the maximum deviate is as large as $2{\cdot}9\sigma$ is 13·8%: for $y=2{\cdot}5\sigma$, the probability rises to 39·3%.

These results are completely consistent with the expectation that the measured values of each ξ parameter, if the experiment is repeated many times and if random error only is present, form a normal distribution about the true, but unknown value of ξ, with dispersion $\sigma\xi$.

Four kinds of systematic error were next generated, always in association with random error as given by equations (9) and (10). The term s was kept at 0·03 and the third set of random normal deviates of Table 3 was used throughout.

The first error type of this group was one that varies systematically with intensity, as given by equation (12),

$$I'=I\left(1+A\cdot\frac{I}{I_{\text{max}}}\right), \tag{12}$$

where I is the error-free intensity computed from $F^{\text{EF}}_{\text{meas}}$ and I_{max} is the maximum value of I. The constant A was given values: 0·1, 0·2, 0·4 and ~1·0. It was assumed in the following calculations, in simulation of experiment, that the systematic error of equation (12) was undetected. Hence, the same assignment of σF_{meas} was made as in the case of random error only. The initial coordinates used in the random error case were also used in all the systematic error refinement procedures. A summary of the results thus obtained is given in Table 4 (the entry corresponding to $A=0$ is identical with the third N-set entry of Table 3).

Examination of Table 4 indicates that unexpectedly large values of A are required before any of the accuracy indicators are strongly affected. Thus, it is only for $A=\sim 1{\cdot}0$ that the $\mathscr{U}_{0\cdot01}$ range diverges strongly from unity: even for this A value, the largest displacements of position parameters from the correct value are of relatively low significance, although the temperature factors are very significantly in error.

The large A values required to produce detectable changes in the indicators are understandable in terms of the intensity distribution of F_{meas}, shown in Fig. 1. The value of $I_{\text{max}}\simeq 102{,}000$ on the absolute scale, corresponding to $F(303)$, is far out in the tail of the distribution. Indeed, of the 772 F_{meas}, only 25 have $I>10{,}000$ and only 185 have $I>1{,}000$. Thus, a linearly increasing error in intensity resulting in an error in I_{max} of A per cent will produce an error of less than $A/10$ per cent in the great majority of intensities, that is, approximately an error less than $A/20$ per cent in the remaining 96·8% of the F_{meas}.

A second kind of systematic error is one that linearly increases with scattering angle, as given by equation (13):

$$F_{\text{meas}}=F^{\text{EF}}_{\text{meas}}\left(1+B\cdot\frac{\theta}{\theta_{\text{max}}}\right), \tag{13}$$

where θ is the scattering angle in degrees. The angle $\theta_{\text{max}}=45°$ is the maximum value in the list of $GaFeO_3$ structure factors, using Mo $K\alpha$ radiation (Abrahams, Reddy & Bernstein, 1965). The constant B was given

Table 3. *Effects of random error*

N set	R	wR	$\mathscr{U}_{0\cdot01}$	$\Delta\xi max/\sigma\xi$*	$\Delta B_{\text{max}}/\sigma B$
1	0·0258	0·0331	0·933–1·067	2·9	2·0
2	0·0257	0·0329	0·925–1·058	2·0	1·4
3	0·0249	0·0321	0·903–1·034	2·5	1·4

* ξ represents any position coordinate.

Table 4. *Effects of systematic intensity error*

A in equation (12)	R	wR	$\mathscr{U}_{0\cdot01}$	ΔSF/σSF*	$\Delta\xi_{\text{max}}/\sigma\xi$	$\Delta B_{\text{max}}/\sigma B$
0	0·0249	0·0321	0·903–1·034	1·4	2·5	1·4
0·10	0·0254	0·0323	0·908–1·039	2·8	2·5	1·4
0·20	0·0266	0·0328	0·923–1·056	4·3	2·6	1·7
0·40	0·0294	0·0345	0·975–1·116	6·8	2·4	3·0
~1·0†	0·0375	0·0428	1·217–1·393	11·1	2·0	5·3

* SF is the single scale factor.

† This value of A corresponds to an error of 10% in $I^{\text{EF}}=10000$ (see Fig. 1).

values: 0·1, 0·2 and 0·4. It should be noted that equation (13) introduces the systematic error into the structure factor, and that equation (12) does so into the integrated intensity. As in the case for equation (12), each $F_{\rm meas}$ obtained by equation (13) also included random error (the third N-set of Table 3). The previous initial coordinates were again used in the least-squares refinement.

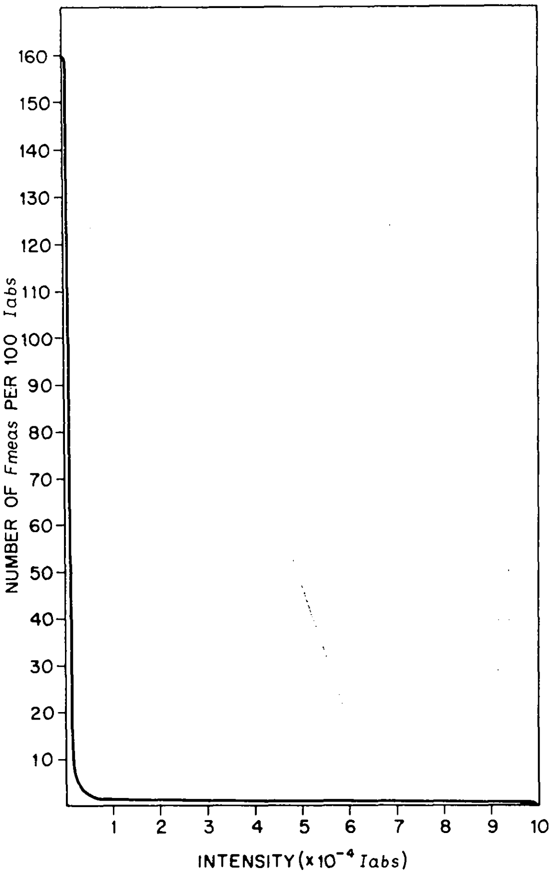

Fig. 1. Distribution of the number of $F_{\rm meas}$, by intensity.

Table 5 shows that none of the accuracy indicators are sensitive to errors systematic in scattering angle; indeed, R and wR become slightly *smaller* as the error increases. This systematic error is absorbed entirely into the scale factor and the temperature factors. The distribution of $F_{\rm meas}$ by angle is presented in Fig. 2, and is close to normal considering the upper angular limit of 45° θ.

A third kind of systematic error is designed to simulate a long term drift in the experiment. The structure factors were regarded as being measured in the sequence given in Table 1 of Abrahams, Reddy & Bernstein (1965) in which the Miller index h varies most rapidly and the index l least rapidly. This sequence is approximately analogous to one that might have been followed with an equi-inclination type diffractometer. An essentially linearly increasing error with time was used, as indicated by equation (14):

$$F_{\rm meas}=F^{\rm EF}_{\rm meas}\left(1+C\cdot\frac{P}{772}\right) \tag{14}$$

where P is the position of the $F_{\rm meas}$ term in the above sequence. The constant C was assigned the values: 0, 0·1, 0·2 and 0·4. The previously defined errors, weights and initial coordinates were again used.

The results of this third kind of error are presented in Table 6. It is apparent that this error is detected with considerable sensitivity by $\mathscr{U}_{0\cdot01}$, and to a lesser extent by the usual R and wR factors. Thus, at $C=0\cdot05$, $R\simeq0\cdot029$ and $wR\simeq0\cdot033$, only slightly larger than the values for $C=0$ (Table 6). However, for $C=0\cdot05$, $\mathscr{U}_{0\cdot01}\simeq1\cdot05\text{–}1\cdot18$ indicating a minimum error in the assignment of $\sigma F_{\rm meas}$ of 5%.

A fourth kind of systematic error is in the absorption coefficient for a spherical crystal of radius R. The 'correct' value of $\mu R=0\cdot9037$ (Abrahams, Reddy & Bernstein, 1965) was replaced by the $\mu R'$ given in equation (15):

$$\mu R'=\mu R(1+D)\,, \tag{15}$$

where D was assigned the values 0, 0·1, 0·2 and 0·4. These absorption corrections were applied to the *inten-*

Table 5. *Effects of systematic error in angle*

B in equation (13)	R	wR	$\mathscr{U}_{0\cdot01}$	ΔSF/σSF	$\Delta\xi_{\rm max}/\sigma\xi$	$\Delta B_{\rm max}/\sigma B$
0	0·0249	0·0321	0·903–1·034	1·4	2·5	1·4
0·1	0·0237	0·0303	0·905–1·036	11·1	2·5	10·8
0·2	0·0227	0·0288	0·918–1·051	21·5	2·4	21·4
0·4	0·0222	0·0271	0·937–1·125	42·2	2·4	41·5

Table 6. *Effects of systematic error in time*

C in equation (14)	R	wR	$\mathscr{U}_{0\cdot01}$	ΔSF/σSF	$\Delta\xi_{\rm max}/\sigma\xi$	$\Delta B_{\rm max}/\sigma B$
0	0·0249	0·0321	0·903–1·034	1·4	2·5	1·4
0·1	0·0319	0·0408	1·207–1·381	10·2	2·5	4·1
0·2	0·0473	0·0589	1·832–2·097	13·2	2·2	5·6
0·4	0·0792	0·0948	3·272–3·744	15·2	2·0	6·2

sities corresponding to the $F^{\text{EF}}_{\text{meas}}$, and then reconverted to F_{meas} which were used in least-squares refinement procedures similar to those carried out with the previous systematic errors.

The results of error in μR are given in Table 7, and are seen to be comparable to those in Table 5: the indicators R and wR decrease slightly as the error increases, and $\mathscr{U}_{0\cdot01}$ remains within an acceptable range. By far the greatest error is found in the scale factor, and to a lesser extent, in the temperature factors.

Discussion

The results obtained experimentally with the accuracy indicators, and the effects produced both on the indicators and on the model parameters by the deliberate introduction of several kinds of error into the F_{meas}, are considered in this section. A brief discussion on the selection of weights in least-squares refinement is also presented.

Structure factors, in common with other quantities, cannot be measured accurately if the experiment contains unknown systematic error. If such error is known, it can either be eliminated experimentally or compensated for theoretically. In the typical diffractometer experiment, many of the sources of error listed in Table 1 can be completely eliminated neither experimentally nor theoretically. It is hence necessary to *estimate* the error in each F_{meas}, in the knowledge that each σF_{meas} also contains residual error. Alternatively, numerous independent sets of F_{meas} for a given material can be determined under various experimental conditions. If there is a normal distribution of each systematic error over these experiments, the true value of each F_{meas} may be obtained together with a detailed knowledge of the errors associated with each experiment. The American Crystallographic Association Single-Crystal Intensity Project (Abrahams, Alexander, Furnas, Hamilton, Ladell, Okaya, Young & Zalkin, 1967) and the International Union of Crystallography Single-Crystal Intensity Project (Abrahams, Hamilton & Mathieson, 1968) are the first large scale attempts at this alternate approach. It may be noted here that the interexperimental agreement obtained therein necessarily indicates an accuracy level that is too high, unless the above distribution of error has been complied with.

It is clearly desirable to develop indicators internal to a given experiment, by means of which the accuracy may be determined. Such indicators should ideally depend only on the experiment. The customary crystallographic R factor is based entirely on the theoretical model. The wR factor may be calculated with or without reference to the experiment: the matter of correct weights is taken up again later in the discussion. The indicator $\mathscr{U}_\alpha$ [equation (8)] can only be properly evaluated by reference to the experiment, as well as to the model, since it depends on the use of objective σF_{meas} determined *before* any refinement is undertaken.

Table 2 contains the values of R, wR and $\mathscr{U}_\alpha$ for the eight crystals used in the experimental test. With but one exception, R is calculated smaller than $wR = [\Sigma w\Delta^2 F_{\text{meas}} / \Sigma wF^2_{\text{meas}}]^{1/2}$, for which w was taken as $(\sigma^2 F_{\text{meas}})^{-1}$. The range of R and wR in Table 2, from 0·034 to 0·089, is close to the contemporaneously

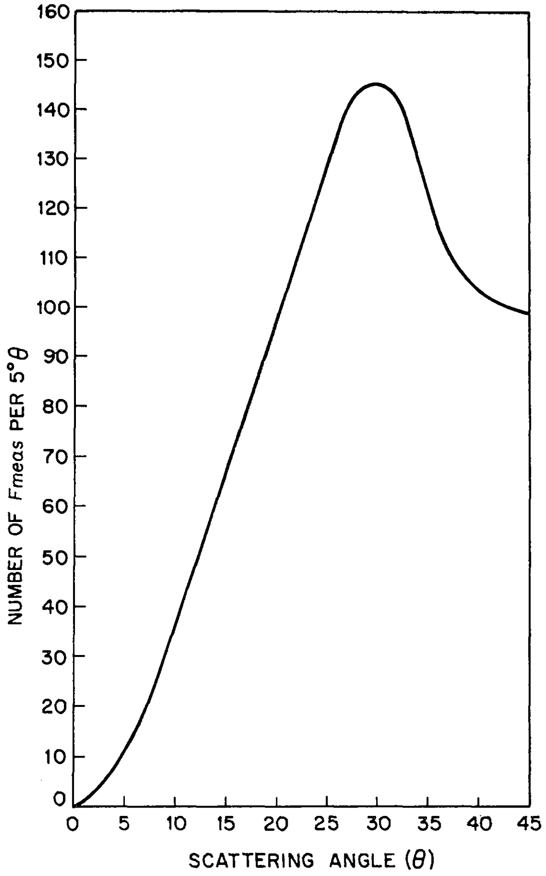

Fig. 2. Distribution of the number of F_{meas}, by scattering angle.

Table 7. *Effects of error in μR**

D in equation (15)	R	wR	$\mathscr{U}_{0\cdot01}$	$\Delta\text{SF}/\sigma\text{SF}$	$\Delta\xi_{\text{max}}/\sigma\xi$	$\Delta B_{\text{æax}}/\sigma B$
0	0·0249	0·0321	0·903–1·034	1·4	2·5	1·4
0·1	0·0236	0·0304	0·903–1·034	25·3	2·6	2·0
0·2	0·0224	0·0288	0·905–1·036	49·6	2·5	4·0
0·4	0·0203	0·0261	0·916–1·048	101·8	2·0	9·5

* μR is product of absorption coefficient and radius of sphere.

'acceptable' limits for these values. However, these magnitudes provide only a measure of agreement with the model. The $\mathscr{U}_\alpha$ intervals not only give an indication of the state of the refinement, but on completion of the refinement, the residual error in the average σF_{meas} is also indicated. From Table 2 it can be seen that the average minimum residual error in σF_{meas} at a 1% significance level, for all eight compounds, is about 1%. The maximum residual error in σF_{meas} is about 21%.

The effect of known error on the indicators and model parameters is now considered. Table 3 shows, for a random error of about 3% in F_{meas}, that R tends to calculate about 17% too low, whereas wR calculates about 10% too high. With a probability of 13·8% that one of the 40 parameters in the model might differ from the correct value by as much as $2{\cdot}9\sigma$ [see equation (11)], the maximum deviation in a model parameter in Table 2 appears entirely acceptable.

Table 4 shows that a systematic error in intensity is likely to remain undetected by the indicators at moderate error levels. However, at such levels, the resulting errors in the model parameters are no greater than in the absence of systematic error. The lower limit of the $\mathscr{U}_{0\cdot01}$ interval does not exceed unity until $A \simeq 0{\cdot}48$. At this error level, the maximum error in intensity for 96·8% of all reflections (see Fig. 1) is only 4·8%.

It is convenient to consider next long term drift, *i.e.* systematic error as a function of time. Table 6 reveals that errors of this nature are very readily detected by the $\mathscr{U}_\alpha$ indicator. In fact, the error indicated by the lower limit of the $\mathscr{U}_{0\cdot01}$ interval is very close to the absolute error introduced into the F_{meas}, for the 'theoretical' crystal under study.

The effects of errors in F_{meas} that vary systematically with scattering angle are demonstrated in Tables 5 and 7. It has already been noted that both R and wR appear to improve as the error is increased. The failure of $\mathscr{U}_{0\cdot01}$ to detect this kind of error is due to the compensating failure to assign correct values for σF_{meas}. The σF_{meas} used for both Tables 5 and 7 are based on equation (10) and correspond to a situation in which the experimenter is completely unaware of this systematic error in his measurement. To determine the effect on $\mathscr{U}_{0\cdot01}$ of an assignment of σF_{meas} that correctly estimates the systematic error in F_{meas}, the appropriate value of $4k^2$ [equation (4)] for each D value in Table 7 was included in a new set of $\sigma' F_{\text{meas}}$. Table 8 contains both the $4k^2$ terms and the indicator and parameter displacement values corresponding to those in Table 7 but obtained with use of 'correct' $\sigma' F_{\text{meas}}$.

With correct weights, although R and wR again fail to detect the presence of large systematic error in the F_{meas}, the $\mathscr{U}_{0\cdot01}$ range is depressed far from unity, strongly indicating error. It is to be expected that $\mathscr{U}_{0\cdot01}$ would similarly indicate error of the type given by equation (13) if σF_{meas} in that case were correctly assigned.

Finally, some comments are made on the use of weights in crystallographic least-squares refinement. The majority of current reports based on this technique make use of some kind of 'weighting' scheme: a minority merely assume (incorrectly) that all their observations are equally good and hence apply the same weight to all F_{meas}. Of the various weighting schemes, few are directly related to the experiment itself. A critical analysis of four common schemes, as they applied to one crystal, was given by Abrahams & Reddy (1965). It was shown that, for this case, the Hughes (1941) scheme was superior to Cruickshank's (1961), and also to those based purely on population statistics (Shoemaker, Donohue, Schomaker & Corey, 1950) or on counting statistics.

Central to the correct use of the Method of Least Squares is the solution of a set of normal equations derived from conditional equations of equal weight, *i.e.* an observation F_{meas} of weight W enters the conditional equation as if there were W separate equations each of unit weight (*cf.* Whittaker & Robinson, 1944). Hence, in addition to the possibility of calculating $\mathscr{U}_\alpha$ as an indicator of accuracy, the σF_{meas} derived experimentally by equation (4) also allow the weights $(\sigma^2 F_{\text{meas}})^{-1}$ to be correctly applied in the least-squares refinement of structural parameters.

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Table 8. *Effects of error in μR, with compensating weights*

D in equation (15)	$4k^2$	R	wR	$\mathscr{U}_{0\cdot01}$	ΔSF/σSF	$\Delta\xi_{\max}/\sigma\xi$	$\Delta B_{\max}/\sigma B$
0	0	0·0249	0·0321	0·903 – 1·034	1·4	2·5	1·4
0·1	57	0·0236	0·0315	0·596 – 0·682	23·9	2·7	1·9
0·2	218	0·0225	0·0306	0·363 – 0·416	45·6	2·9	4·2
0·4	857	0·0205	0·0281	0·181 – 0·207	90·3	3·0	9·5

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DISCUSSION

HAMILTON: One should look at this indicator, not only as a single quantity but as a function of various variables. Thus, (at Brookhaven) after refining with the best weights we have been able to devise, we look at this indicator as a function of at least $\sin\theta/\lambda$ and the intensity. Then we adjust the final weighting scheme to make the curves flat. In our view, this is quite a legitimate procedure since it is an empirical measure of σ which is just as valid as some others used.

ABRAHAMS: Having done this, isn't it proper to decide what is the experimental reason for the trends observed in the curves? Having detected the operative reasons, the experiment should be modified; the new curves should then have no indication of trend.

SHOEMAKER: Are the r.m.s. changes in parameters produced by introducing these artificial errors similar to the maximum errors that you have considered on your slide (Table 3)?

ABRAHAMS: The distribution is more or less normal. My interpretation is that many of the errors make little difference to the derived atomic position coordinates – a view we have all tended to take from our own experience.

JEFFERY: One problem in attaining high accuracy in low-symmetry crystals is that of producing a well-ground sphere of uniform radius. We must measure the deviations from sphericity. We have often found the relationship between the observed deviations in a particular direction and the observed intensities in that direction to be linear: we can then arrive at a measure of the error on a single reflexion comparable with that which we could have achieved if there had been a full set of symmetry related reflexions. The trouble is that errors in the sphericity may be partly random and partly systematic and they are difficult to separate. It is probably only the random errors that have a linear relationship with the errors in intensity.

ABRAHAMS: We probably know neither the radius nor the absorption coefficient exactly. An error in μ of 10% would have serious effects.

DR. G.I. SMOLIN (Institute of Silicate Chemistry, Academy of Sciences of the USSR, Leningrad) submitted a written communication on 'Errors in Absorption Corrections for Spherically or Cylindrically Ground Crystals'. As this communication has been published in the normal literature (Smolin, 1968) only the main points are quoted here, which are very relevant to the discussion.

Dr Smolin points out that the surface layer of a spherical or cylindrical crystal produced by abrasive treatment has a density, and, therefore, a linear absorption coefficient, which may be quite different from that of the bulk material. The depth of the seriously affected layer is about one-fifth of the particle size of the abrasive powder. He calculates the effect on the absorption correction for cylindrical crystals and shows that the use of the standard tables can produce gross errors, especially for heavily absorbing materials at low Bragg angles. He concludes that these tables can be used only for crystals which have been polished or ground with a very fine abrasive. He goes on to describe an improved sphere grinder of the type in which the crystal is tumbled inside an abrasive cavity. A particular feature of the device is that interchangeable components allow a selection of the optimum cavity size and abrasive. The method has been used both for hard silicates and for soft organic crystals.

DIAMOND: (*a*) If there are systematic errors present, the separate observations may be correlated: that is, the errors will not be independent. This complicates the issue further (but should be partly resolvable by reference to the inverse covariance matrix).

(*b*) Is the structure centric or acentric? The atomic positions are more critically dependent on the phase angle than on F and this fact may account for the small change in atomic parameters if the structure is centric.

ABRAHAMS: The structure is polar.

HAHN: Apparently the only quantities which were invariant were the chemically important bond lengths and angles.

ABRAHAMS: Yes. However, you must be very careful if you wish to measure physically significant quantities such as the absolute intensity, the Debye temperature *etc.*

MEGAW: I would like to make two points. The intensity distribution cannot be expected to be normal unless atomic position coordinates are roughly random. This is a generalization which may not be true for $GaFeO_3$, but does apply to a good many oxides. If the positions *approximate* to special positions (even if the actual symmetry is low) this is not true; errors due to incomplete refinement will not be Gaussian, and the trial value of the parameters will influence the path of refinement. Secondly, the weighting scheme appropriate to the final stages is *not* always correct for the earlier stages, especially when the position parameters are non-random (without being special); without separate consideration of different classes of intensities, misleading trial models may be found.

ABRAHAMS: This particular structure (based on space group *Pba*2) does not closely approximate a higher symmetry space group.

ALEXANDER: (*a*) We have noted the tendency to apply factors of the order of 1·5 to 2·0 to conventional *R* values to soak up the inaccuracies that we realize to be present, but still the figures do not put us on a correct statistical basis.

(*b*) The χ^2 distribution method for the detection of systematic error may have a parallel with the work of the late Mr K. Beu on the determination of precise lattice parameters.

LADELL: Would you consider chemical structural results as allowable as an internal check, *e.g.* the coplanarity of five particular atoms in a structure?

ABRAHAMS: I suppose it is permissible to refer to internal consistency in respect of chemical features, provided this is specifically stated; *e.g.* if there are two molecules in the asymmetric unit, conclusions may be derived on the assumption that these are in fact identical. However, the experimental accuracy of the measured *F* cannot easily be assessed quantitatively in this way.

RIVA DI SANSEVERINO: Concerning your criticism of the use of unit weights, when do you consider that a statistically acceptable weighting scheme should be used?

ABRAHAMS: I would consider it correct to use the estimated weights, as outlined above, at all stages.

HAMILTON: In the early stages of analysis while one is still trying to solve the structure, or before one has reached the linear range of least squares, perhaps one may choose to use artificial weighting schemes to reject or down-weight weak or strong terms or modify terms in a selected angular range.

RIVA DI SANSEVERINO: In your alteration of the weighting scheme, you may be adjusting the situation to what you expect or desire.

SANDOR: The study of the effect of simulated systematic errors on a hypothetical structure shows hardly any correlation between the errors in the positional and thermal parameters of the atoms. I wonder how far this apparent lack of correlation applies to real cases where various types of systematic and random errors occur simultaneously.

Would it not be worth extending the present study by mixing various types of errors and study their combined effect on the errors of the positional and thermal parameters of a hypothetical structure?

ABRAHAMS: We plan to do this.

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Real Crystals as a Source of Error

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Specimen-dependent properties of real crystals which influence the accuracy of intensity measurement are size, shape, homogeneity, stability and environment. Variations of any of these will affect the corrections necessary to allow for absorption and extinction in a given experimental measurement; these in turn will affect the evaluation of the absolute intensity, and the two principal tests for internal and external consistency, namely variation within any form $\{hkl\}$, and variation of mean values $I\{hkl\}$ between different specimens. They may also affect the relative values of $I\{hkl\}$ within one data set, leading for example to spurious anharmonicity in the temperature factors derived for an ellipsoidal crystal. Examples of practical solutions of actual problems involve waxes instead of glues for crystal mounting, miniature films or intensifying screens for use in unstable situations or with very small crystals, integrated oscillation photographs for intensity measurements from poor specimens, rotation photographs for high symmetry crystals, the use of Laue photographs for the detection of order-disorder phenomena, and the incorporation of an iron-55 source in an automated diffractometer to provide an internal standard for intensity measurements.

Introduction

The influence of specimen-dependent properties of real crystals on the accuracy with which the intensities can be measured may be summarized in the diagram in Fig. 1. The existence of these effects has been known for many years, and the purpose of this paper is to focus attention on the fact that because many of these problems often confront the average experimenter simultaneously, the precision attainable in individual counter measurements (better than 1 %) can seldom be utilized to achieve structure amplitudes of comparable accuracy. Even the precision of individual photographic intensity measurements, at best about 2 %, cannot generally be transferred to the final list of $F(hkl)$.

The fundamental problem, therefore, consists firstly in recognizing what type of errors introduced by the nature of the specimen will seriously affect the type of