A Type I Intensity Measurement Project

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A representative sample of integrated intensities was measured for each of six different crystals of α-glycine using the same diffractometer. Examination of the results showed that the reproducibility of the diffractometer was of the order of $\frac{1}{2}$% in integrated intensity, and intercomparison of the six sets revealed that the main sources of error were associated with the individual crystals. The errors are principally correlated with increasing intensity and appear to be due to extinction. The analysis indicates that not only the strongest but almost all reflexions were affected, with extinction coefficients which were roughly a linear function with $I^{1/2}$. In addition, there is considerable evidence that the extinction effects are anisotropic.

Introduction

An accurate knowledge of structure factors is of vital importance in gaining a deeper understanding of bonding and vibrational phenomena in the crystalline state. It is difficult to assess accuracy, however, as there is no simple independent technique to compare with the conventional methods of measurement. The work on Pendellösung fringe measurements (*e.g.* Hart, 1969; Kato, 1969) is of great value in special cases, as are intensity measurements from perfect crystals (*e.g.* Jennings, 1969; Renninger, 1969), but because of the stringent experimental requirements the range of results available is rather limited. Intensity-measurement projects, however, are capable of placing a lower limit on experimental error, though by their nature this limit is likely to be optimistic. Mathieson (1969) has classified such projects as shown in Table 1 and described their scope and the kind of information that can be gleaned from each type.

Table 1. *Project classification*

Type I 1 diffractometer is used for measurements from *n* crystals.

Type II *n* diffractometers are used for measurements from 1 crystal.

Type III *n* diffractometers are used for measurements from *n* crystals.

A type II project has been conducted by the American Crystallographic Association using a spherical crystal of CaF_2. The results are analysed by Abrahams, Alexander, Furnas, Hamilton, Ladell, Okaya, Young & Zalkin (1967) and a more detailed account is given by Mackenzie & Maslen (1968). From these papers it appears that, in the main, the instrumental error causes an r.m.s. deviation of about 2–3% in integrated intensity and that some experimental procedures had angle or intensity-dependent sources of error.

The International Union of Crystallography has sponsored a type III project using D-(+)-tartaric acid

as the standard material (Abrahams, Hamilton & Mathieson, 1970). The r.m.s. reproducibility within the intensity measurements from one crystal was approximately 3% which agrees well with the ACA estimate of instrumental error. However, comparison of intensity measurements from different crystals gave a mean discrepancy of about 12%. From this it was concluded that the crystal is a much larger source of error than the apparatus or measuring procedure used. Again both angle and intensity dependent errors were observed and also some techniques were found to yield significantly poorer results than the rest.

To complete the set of project types and if possible to make a more detailed analysis of the nature of the error sources indicated by the I.U.Cr. and A.C.A. work, a type I project has been undertaken, the results of which form the basis of this paper. It is of interest at this point to note the pioneer work of Wheeler-Robinson (1933) who also effectively carried out a type I project almost four decades ago!

Design of the experiments

The initial stage in planning the series of measurements was to list possible sources of error in intensity measurement and the parameters on which they depended. Measurement sequences were then chosen to reveal any dependence of experimental error on these parameters and where possible to indicate the physical phenomena involved. However, as a faulty diffractometer would obscure any differences between crystals, the first measurements took the form of rigorous experimental tests of the diffractometer.

The anticipated sources of error were absorption, extinction, physical or chemical deterioration of the crystal, radiation damage, machine malfunction or instability, variation in air absorption of the X-ray beam and possibly double Bragg scattering. The parameters most likely to be associated with these sources of experimental error were considered to be the size and shape of the crystal, the setting angles and intensity

Table 2. *The hkl, setting angles and intensities for the six α-glycine crystals*

(*N.B.* The *ij*th element of each 10 × 10 array corresponds to the reflexion denoted by the *ij*th set of Miller indices).

MILLER INDICES

X SETTING ANGLES

φ SETTING ANGLES

2θ VALUES

CRYSTAL 1 INTENSITIES

CRYSTAL 2 INTENSITIES

CRYSTAL 3 INTENSITIES

CRYSTAL 4 INTENSITIES

CRYSTAL 5 INTENSITIES

CRYSTAL 6 INTENSITIES

for a given reflexion and the environmental variables: temperature, air pressure and time. Errors arising from incorrect scan procedure or thermal diffuse scattering were considered to be undetectable in these measurements since they are essentially independent of the particular crystal used.

The α form of glycine was chosen as the standard compound for the measurements, as on preliminary test it appeared very stable to X-rays and to the atmosphere, and also as it may be easily crystallized in a wide variety of habits by cooling a warm saturated aqueous solution. Further, these crystals are not prone to twinning, have excellent faces and exhibit very little diffuse scattering at room temperature. The crystal is monoclinic with space group $P2_1/n$ and the structure has been refined by Marsh (1958) on the basis of film data.

The measurement sequence eventually devised, to isolate the error sources mentioned, was as follows. A selection of 100 reflexions were chosen from one quadrant of reciprocal space such that they gave a representative sample of intensity with the diffractometer setting angles χ, φ and 2θ. After these had been measured, the 100 symmetry-related reflexions were to be measured in the same sequence; the ratio of symmetry-related intensities would then reveal any subtle time-dependent errors as well as gross machine errors. Following this a small sample of reflexions were to be measured at $2\pi/11$ intervals about their scattering vectors, to investigate absorption, extinction and, to some extent, double Bragg scattering. The $0k0$ reflexions were selected as all crystals were to be aligned about $+\mathbf{b}$ and hence their scattering vector would coincide with the φ-axis which simplifies matters experimentally. The 004 was nominated as a reference and this was measured at least once every 50 reflexions to monitor crystal deterioration and radiation damage. Atmospheric pressure and ambient temperature were recorded throughout the period of measurement. The indices of the 100 selected reflexions are listed in Table 2.

Preliminary tests of diffractometer performance

In both the I.U.Cr. and A.C.A. projects, little stress was laid on preliminary testing of the performance of the various functions of the diffractometer. It is, however, possible to test all the theoretical requirements experimentally, and so establish, if not eliminate, the sources of instrumental error. The testing sequence used here revealed several unsuspected error sources all of which may be easily corrected.

The theoretical model, usually used to represent the measurement of a single-crystal integrated intensity, makes the following assumptions about diffractometer performance.*

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* The figures in brackets summarize the estimated standard deviations in integrated intensity found during the course of these tests.

1. The X-ray beam at the crystal is:
   (a) of constant intensity with time ($< 0.07\%$)
   (b) of constant flux across the region occupied by the crystal (0.07%)
   (c) of known degree of polarization ($< 0.25\%$).
2. The crystal is:
   (a) in the homogeneous beam at all times (0.0%)
   (b) is set correctly to the diffracting angle (0.01%)
   (c) is rotated at the same constant angular velocity with respect to the beam for all scans (0.3%).
3. The detector system:
   (a) has constant sensitivity over the whole of the sensitive area (0.4%)
   (b) has constant sensitivity with time ($< 0.07\%$)
   (c) has a linear response within the working range (0.2%)
   (d) either receives or is sensitive only to monochromatic radiation ($< 0.1\%$)
   (e) receives all the diffracted beam (0.0%).

The extent to which each of these conditions was fulfilled was tested in the following way.

First, the mechanical alignment of the machine was examined and the relevant adjustments made. This established that provided the correct setting angles were used, the diffracted beam would always go down the centre of the counter collimator; later the aperture was shown to be more than adequate by slowly closing left/right and top/bottom shutters on an actual reflexion. Thus condition 3(e) was fulfilled. Condition 2(a) was also partially met in that for all possible crystal settings the crystal remained at the same point in space to within ± 0.025 mm, and later it was shown that this point corresponded to the centre of the homogeneous beam.

Next, a lead sheet containing a small pinhole was mounted on a goniometer head in the crystal position and the resulting direct beam was monitored by the stationary detector, which in this case was a NaI(Tl) scintillation counter. Counts of 400 sec were taken at a rate of 10,000 cps over a period of 3 hours and the total variation of the individual counts was $\pm 0.15\%$; the combined e.s.d. for the stability of the X-ray source and the counting chain was found to be less than

Table 3. *Dimensions of crystals (numbered 1–6) used in this Type 1 project*

Lengths quoted are perpendicular distances in microns to the crystal faces from an arbitrary origin within the crystal.

1 Face	d	2 Face	d	3 Face	d	4 Face	d	5 Face	d	6 Face	d
010	57	100	64	010	111	010	49	010	66	010	22·2
0$\bar{1}$0	45	$\bar{1}$00	67	0$\bar{1}$0	141	0$\bar{1}$0	44	0$\bar{1}$0	99	0$\bar{1}$0	26·6
011	104	110	105	601	251	011	68	120	100	011	31·1
01$\bar{1}$	60	$\bar{1}$10	103	$\bar{1}$00	180	01$\bar{1}$	58	$\bar{1}$20	101	01$\bar{1}$	28·9
0$\bar{1}$1	71	0$\bar{1}\bar{1}$	120	011	60	$\bar{1}$10	208	01$\bar{1}$	56	$\bar{1}$10	53·4
0$\bar{2}$1	109	01$\bar{1}$	98	01$\bar{1}$	78	310	192	011	50	110	40·0
$\bar{1}\bar{1}$0	96	011	91	0$\bar{1}\bar{1}$	82						
$\bar{1}$10	82	0$\bar{1}$1	106	0$\bar{1}$1	107						
110	123										

Table 4. *Analysis of reference reflexions*

Count measurements are given in order of time increasing down the column. Crystals numbered as in Table 2.

	1 Peak count	Bg.*	2 Peak count	Bg.	3 Peak count	Bg.	4 Peak count	Bg.	5 Peak count	Bg.	6 Peak count	Bg.
	13237	(275)	20815	(377)	47436	(897)	21443	(409)	19695	(368)	1527	(47)
	13243	(270)	20662	(386)	47457	(863)	20716	(398)	19707	(371)	1501	(46)
	13253	(279)	20793	(381)	47290	(877)	20714	(400)	19523	(358)	1534	(48)
	13289	(275)	20610	(373)	47179	(830)	21415	(−)	19609	(357)	1525	(50)
	13151	(277)	20493	(396)	47224	(851)	21324	(352)	19569	(365)	1535	(49)
	13042	(256)	20551	(378)	47251	(869)	21047	(388)	19604	(355)	1504	(49)
	[12641	(2031)]					21014	(392)				
	[12653	(2132)]					21460	(598)				
							21372	(396)				
							21753	(402)				
Average	13206 ± 83		20654 ± 115		47206 ± 122		21226 ± 322		19618 ± 67		1521 ± 14	
R.m.s. deviation from mean (%)	0·63		0·56		0·26		1·52		0·34		0·92	
% e.s.d. due to counting statistics	0·27		0·22		0·14		0·22		0·22		0·81	
% e.s.d. due to other sources	0·56		0·51		0·23		1·50		0·26		0·44	

*Bg. = background in parentheses.

0·07 %. This period includes the maximum fluctuations in supply voltage and ambient temperature which the apparatus was likely to encounter under normal working conditions. Thus the criteria 1(a) and 3(b) are well satisfied.

Using the pinhole as a fine collimator and the X-ray generator as a standard intensity source, a counter step scan was carried out to verify that the active area was of uniform sensitivity. The e.s.d. for a series of 26 constant time counts of about 10^5 at 0·2 mm intervals across the face was 0·45%. This, compared with a counting statistical e.s.d. of 0·27%, means that condition 3(a) is well fulfilled.

As the sheet with the pinhole was mounted on a goniometer head and since the counter response was shown to be uniform over its active area, it was possible to monitor the X-ray flux at the crystal by adjusting the traverse slides and the χ-circle. It was discovered that, at low take-off angles, the beam homo-
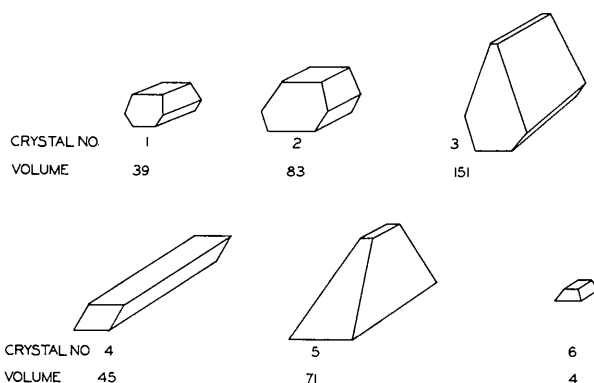
Fig. 1. Sketches of the six crystals used on approximately the same scale. (Volumes are in 10^{-4} mm³).
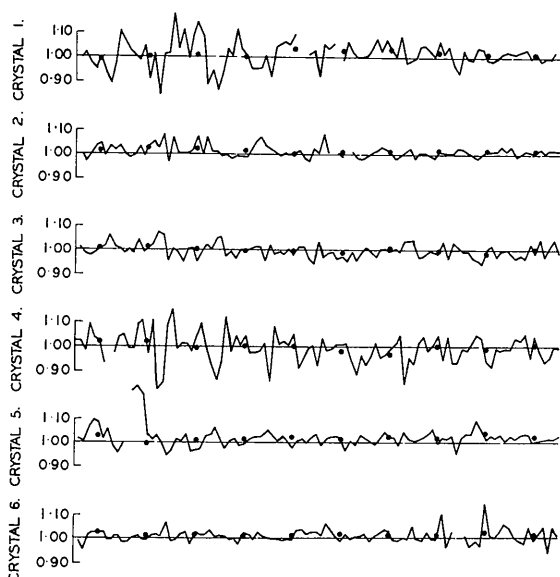
Fig. 2. A plot of integrated intensity divided by the symmetry-related intensity as a function of sequence of measurement.

geneity is substantially affected by absorption of the X-rays in the target (Denne, 1970a) but at 5° the flux over a circle of 1 mm diameter was found to be constant to an e.s.d. of 0·07 % using point counts of about 10^6. Thus condition 1(b) is also adequately satisfied.

By adjusting the pinhole to the centre of the circles and measuring the translation required to reach the edge of the beam in a number of different directions, it was simple to verify that the centre of the circles coincided with the centre of the X-ray beam, as was anticipated from the mechanical alignment procedure.

Crude measurements using a counter and scattering block mounted on the χ-circle have confirmed the findings of Bearden (1928) and Wollan (1928) that characteristic radiation is unpolarized to within 1·0%; further, transmission through typical nickel β-filters does not cause significant polarization in spite of the preferred orientation induced by the rolling of the foils.

The response of the counter was found to be linear to 0·2% up to 12,000 cps by measuring the peak counting rate of a given reflexion against tube current. At 8000 cps, aluminium attenuators are automatically introduced and the reproducibility and calibration of the attenuation factors were also established to better than 0·2%.

The system is made sensitive only to Cu $K\alpha$ radiation by a nickel β-filter and pulse height discrimination. To test the efficiency of this system an NaCl crystal was mounted and the spectrum given by a strong reflexion was recorded from $\lambda = 0·4$ to 3·0 Å. The resulting spectrum showed that at no wavelength was the system's response greater than 1% of that for characteristic radiation and that after background correction, second and third harmonic radiation errors were less than 0·1%.

The constant scan velocity condition, 2(c), was tested using a moiré fringe device and the details of this test are to be published elsewhere (Davies, Denne, Haines, Mackenzie & Mathieson, 1972). The reproducibility was found to be better than 0·3%.

However, repeated measurement of a given reflexion revealed quite appreciable variation, which was traced to play in the goniometer head. This effectively modifies the scanning velocity (Denne, 1970b) so the best conventional head available was used with careful temperature control.*

The remaining stipulation, correct setting to the diffracting condition, is rather difficult to test. Even though in repeated trials the setting mechanism may appear to be working perfectly, faults may be intermittent and/or infrequent. However, the design of the measurement sequence is such that this type of fault should be made evident by the results.

The combined r.m.s. instrumental error was thus found by these measurements to be less than 0·6% in integrated intensity.

* This work was performed before conical goniometer heads were available (Denne, 1971).

Experimental

Crystals of α-glycine were grown by pouring a small quantity of warm saturated aqueous solution onto a large glass slide; crystals up to 0·3 mm across were formed within about 10 minutes and it was hoped that this rapid rate of growth would give rise to a high degree of mosaicity. Six crystals were selected from several different crystallizations; they were chosen to give a wide range of shapes and sizes. Sketches of the crystal habits are shown in Fig. 1 and their dimensions in Table 3.

The measurements were taken using Cu $K\alpha$ radiation with a 5° take-off angle, a tube-window to crystal distance of 18 cm, and crystal to detector distance of 24 cm. Integration was by means of an $\omega/2\theta$ scan of 2° in 2θ plus a small θ-dependent increment equal to twice the α_1–α_2 splitting. The scan speed was 0·5°/min in 2θ and point background counts of 40 sec each were taken at both limits of every scan. All crystals were aligned about **b** and had **c*** in the plane of the χ-circle for zero φ.

Apart from runs 1 and 4, the measurements went as planned. Due to computing problems, run 1 was completed in two sections; the first 40 reflexions were followed by the 40 symmetry-related reflexions and the remaining two sets of 60 in the same sequence. After the rotation about φ measurements, a few mispunched instruction cards were run again. During run 4, the output mechanism failed and many cards were punched without recording counts, which entailed re-running a section of the measurements. The crude results are available on request from the author.

Examination of the output revealed that gross machine errors had occurred for 10 reflexions out of the 1500 measured; of these, 6 were not printed out because of card punch failure and the remaining 4 were consecutive measurements in run 5 where the background counts had spuriously high values, possibly on account of mis-setting errors.

The measurements were converted to integrated intensities by subtracting the appropriately scaled background count from the peak count, multiplying by an attenuation factor where necessary and applying an absorption correction by the method of Busing & Levy (1957). Standard deviations were calculated on the basis of counting statistics, due care being taken to use the actual number of photons reaching the detector in

Table 5. *Tests of reproducibility between symmetry-related reflexions*

(*a*) Overall % r.m.s. deviation

Run number	1	2	3	4	5	6
% r.m.s. dev.	5·5	2·7	2·3	6·1	3·1	2·7

(*b*) % r.m.s. deviation as a function of χ

χ range	0–10°	10–20°	20–30°	30–40°	40–50°	50–60°	60–70°	70–80°	80–90°
No. of refs.	15	13	19	15	13	13	7	3	2
Expt. no.									
1	2·8	5·2	7·0	5·0	5·4	7·6	3·7	2·4	1·8
2	3·2	2·2	3·1	1·4	2·3	2·6	1·9	2·9	5·7
3	2·0	1·7	3·1	1·7	1·4	2·1	1·8	4·6	4·5
4	6·1	7·8	5·1	5·8	4·1	7·4	4·3	3·2	11·6
5	5·7	7·9	3·2	3·5	2·7	2·7	3·9	5·7	0·6
6	2·3	2·3	3·6	3·8	2·0	2·2	1·7	1·4	0·2

(*c*) % r.m.s. deviation as a function of φ

φ range	0–20°	20–40°	40–60°	60–80°	80–100°	100–120°	120–140°	140–160°	160–180°
No. of refs.	16	12	6	12	3	5	19	10	17
Expt. no.									
1	7·4	5·5	3·5	3·0	3·5	3·0	4·6	5·8	6·5
2	2·0	3·0	4·3	2·8	0·3	1·5	2·3	2·6	3·0
3	2·3	2·3	1·7	2·1	0·7	2·2	2·7	2·3	2·3
4	10·3	6·3	3·2	3·7	0·7	1·0	2·5	5·2	7·7
5	3·6	2·0	2·0	4·4	2·1	1·9	3·1	6·6	7·4
6	2·4	3·5	5·7	2·7	2·4	1·8	2·2	1·6	2·3

(*d*) % r.m.s. deviation as a function of 2θ

2θ range	0–28°	28–42°	42–57°	57–71°	71–86°	86–100°	100–115°	115–129°
No. of refs.	11	16	13	14	11	14	13	8
Expt. no.								
1	8·8	7·0	6·3	4·8	4·2	3·8	2·8	1·6
2	3·4	3·9	3·0	1·3	3·0	1·5	1·9	1·6
3	2·6	2·7	2·4	2·7	2·1	1·2	2·1	2·3
4	8·3	8·2	5·9	5·5	3·6	6·3	4·4	3·5
5	4·7	9·4	2·7	2·0	2·4	2·4	3·9	1·6
6	2·1	2·0	1·7	1·6	2·6	3·3	4·5	3·1

Table 5 (cont.)

(e) % r.m.s. deviations as a function of intensity

I range	1	2	3	4	5	6	7	8	9	10
Expt. no.				(increasing intensity) →						
1	3·0	2·0	2·6	3·6	4·0	4·5	5·2	7·6	7·0	9·8
2	2·2	1·9	1·4	1·0	1·5	2·4	2·9	3·0	3·0	5·0
3	2·3	1·5	0·8	2·0	1·1	2·5	1·8	2·8	2·6	4·0
4	5·0	3·9	2·8	4·4	4·2	5·0	3·4	10·3	5·1	11·4
5	3·9	1·6	2·6	2·7	6·5	2·4	2·1	3·9	6·6	8·1
6	5·5	4·0	2·4	2·1	2·8	0·8	2·1	1·4	1·3	1·5

(f) Variation of r.m.s. Δ with σ based on counting statistics

Crystal no.	1	2	3	4	5	6
r.m.s. Δ	9·8	4·6	3·6	9·2	4·1	1·7
Counting statistical σ	(0·10)	(0·13)	(0·13)	(0·13)	(0·13)	(0·20)
r.m.s. Δ	9·3	3·7	2·4	6·2	4·0	1·1
Counting statistical σ	(0·15)	(0·15)	(0·14)	(0·15)	(0·15)	(0·40)
r.m.s. Δ	6·4	3·2	3·0	9·7	3·4	2·1
Counting statistical σ	(0·17)	(0·17)	(0·15)	(0·17)	(0·17)	(0·52)
r.m.s. Δ	5·3	1·2	3·1	11·0	1·8	1·6
Counting statistical σ	(0·22)	(0·19)	(0·16)	(0·19)	(0·20)	(0·70)
r.m.s. Δ	5·2	2·1	3·0	6·0	2·7	0·7
Counting statistical σ	(0·25)	(0·21)	(0·16)	(0·20)	(0·22)	(0·86)
r.m.s. Δ	3·7	1·5	2·2	3·9	2·4	3·1
Counting statistical σ	(0·32)	(0·26)	(0·18)	(0·25)	(0·27)	(1·1)
r.m.s. Δ	4·0	0·8	2·1	4·6	2·6	2·3
Counting statistical σ	(0·37)	(0·30)	(0·21)	(0·29)	(0·31)	(1·3)
r.m.s. Δ	2·4	1·3	2·5	3·2	2·7	2·3
Counting statistical σ	(0·44)	(0·35)	(0·23)	(0·33)	(0·37)	(1·6)
r.m.s. Δ	1·8	1·7	3·1	3·8	1·6	3·6
Counting statistical σ	(0·63)	(0·49)	(0·32)	(0·46)	(0·51)	(2·4)
r.m.s. Δ	3·3	2·1	2·7	5·2	3·8	5·5
Counting statistical σ	(1·1)	(0·81)	(0·52)	(0·76)	(0·86)	(5·0)

All quantities expressed as percent.

$$\Delta = 100\ (I_t - I_i')/(0{\cdot}5 \times (I_t + I_i')).$$

Analysis of the results

(a) Standard reflexions

The standard reflexions for each of the six crystals are listed in Table 4 with the relevant statistics. No deterioration is detectable for any of the crystals and there are no significant machine drifts. The last two standards for crystal 1 are badly out compared with the rest, but examination of the background counts shows that this is due to a misorientation error. The reference reflexion had a scan range of 0·6° less than the corresponding general reflexions to make it more sensitive to mis-setting. Careful examination of the background counts for the intervening reflexions revealed that none appear to have been affected by this error.

The r.m.s. percentage deviation from the mean is much greater for run 4 than anticipated. The most likely source of this error seems to be the goniometer head which for this particular setting must be presumed to have been less stable than usual.

Since the only errors affecting reproducibility of the reference reflexions (apart from deterioration and drift) are counting statistics and machine error, the observed variance less that due to counting statistics yields an e.s.d. for machine errors. This is given in Table 4 and evidently varies from run to run but in the main is about 0·5%, which is consistent with the value predicted from tests of the individual diffractometer functions.

(b) Consistency between symmetry-related measurements

As mentioned earlier, the symmetry-related set of intensities was measured in the same sequence as the original set, so the time-dependent errors should also be sequence-dependent. In Fig. 2 the ratio of each intensity to its symmetry related value is plotted against sequence. The counting statistics are better than 1% for almost all points but the last 20 in run 6. It is evident that systematic trends with time are a very minor source of error; this is confirmed by plotting the mean of each 10 successive points, none of which turn out to be significantly different from unity. The maximum corrections for variation in air absorption due to atmospheric pressure fluctuations are of the order of 1% and are thus quite insignificant in these plots. However, the sequence test shows quite well the decrease in statistical accuracy towards the end of run 6, the four

consecutive machine faults in run 5 and the very significant difference in reproducibility for runs 1 and 4 compared to the remainder.

The results of the analysis of the r.m.s. percentage deviation between symmetry-related measurements as a function of run number, χ, φ, 2θ, intensity and counting statistical σ are given in Table 5. It is very evident from 5(a) that the reproducibility in runs 1 and 4 is not in the same class as in runs 2, 3, 5 and 6, and that the agreement between symmetry-related measurements is between 4 and 10 times worse than that between reference reflexions. It therefore appears that instrumental error (and the goniometer head) makes a very minor contribution to the differences between symmetry-related measurements. Table 5(b) shows that

there is no significant χ-dependence of this lack of agreement except possibly that run 1 shows poorer results at $\chi=45°$ than 0° or 90°; Table 5(c), however, shows that there is a definite φ-dependence for runs 1 and 4, the disagreement being at its worst when c^* is in the plane of the χ-circle. Table 5(d) shows that errors are greatest at low θ values for runs 1, 2, 4 and 5 and as might be expected because of the high correlation of intensity with angle, Table 5(e) indicates that errors increase with intensity for these same runs. Run 6 however, shows the reverse trend in both cases, but Table 5(f), which compares the r.m.s. observed discrepancies as a function of counting statistical accuracy, shows that this is due entirely to low counts at high angles and low intensities. It is of interest from the point of
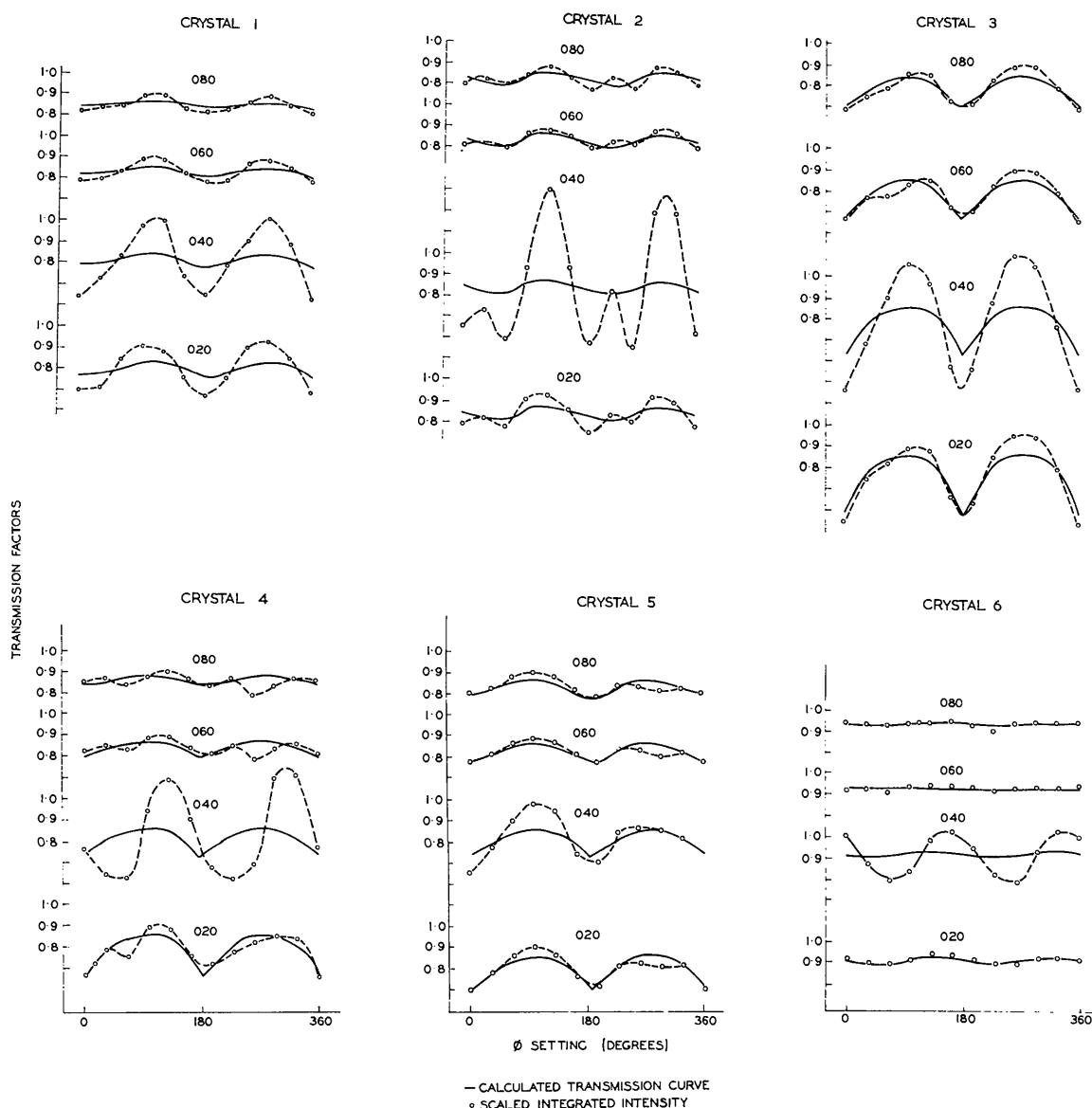
Fig. 3. A plot of the integrated intensity of 020, 040, 060 and 080 measured at $2\pi/11$ intervals about b^*. The continuous curves are absorption corrections on approximately the same scale.
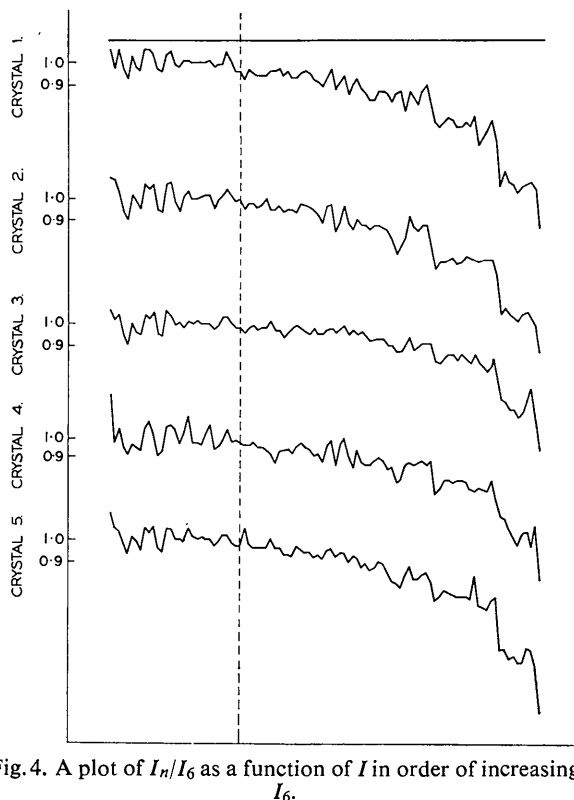
Fig. 4. A plot of I_n/I_6 as a function of I in order of increasing I_6.

view of assessing weights for structure factor least-squares that in these measurements reproducibility bears no relation to counting statistics for a statistical precision of better than about 2%. It is also worthy of note that the largest crystal, number 3, shows the best agreement between the symmetry-related reflexions and the errors seem to be substantially independent of all the parameters tested in Table 5.

From these tests it appears that the worst disagreements, which occur in runs 1 and 4, are a function of increasing intensity and decreasing θ as well as the crystal direction in which the scattering vectors occur. This is very unlikely to be an instrumental error in view of the exhaustive preliminary tests, the excellent agreement of the reference reflexions and the considerably better agreement for runs 2, 3, 5 and 6. It is also unlikely to be an effect associated with crystal habit such as absorption, in view of the similarity of results for crystals of such widely different shapes. The intensity dependence suggests extinction and the fact that differences occur between symmetry-related reflexions indicates that the extinction must be anisotropic.

(c) The effect of rotation about a scattering vector

Fig. 3 shows a plot of integrated intensity against the orientation of the crystal about the scattering vector for the 020, 040, 060 and 080 reflexions; the relative intensities are roughly 10:160:3:5 respectively. The absorption correction using the Busing & Levy (1957) procedure is given on a similar scale for comparison.

It is evident that even though the experimental points approximately follow the absorption curves, the fluctuations are considerably greater in all cases. In addition it appears that the deviations are greater the larger the intensity. Abnormally high absorption which increases with increasing intensity is the hallmark of extinction; it seems reasonably convincing, therefore, that extinction should be the source of the discrepancies shown in Fig. 3. In which case, the displacement of the minima compared with the 040 absorption curve for crystal 4 and the multiple troughs in the curves for the crystals 2 and 4 are very compelling evidence for the anisotropy of the extinction effects.

Only for the smallest crystal, number 6, do the absorption curves give some measure of fit and even there the 040 reflexion shows considerable anomaly. The lack of twofold symmetry about the scattering vector in runs 3 and 5 is interesting. In view of the careful alignment work and the regularity of the 040 plot in run 3, it is unlikely that the crystal is straying into the non-homogeneous periphery of the beam. It seems that further investigation of these observations could prove useful.

A technique, similar to that of Willis (1961) was applied to the data for the different $0k0$ orders of crystal 1 and 'g' parameter values of $1{\cdot}7 \times 10^{-4}$, $3{\cdot}5 \times 10^{-4}$, $2{\cdot}0 \times 10^{-4}$ and $1{\cdot}3 \times 10^{-4}$ respectively were obtained to describe the mosaicity. Though there is some consistency for the 3 weaker reflexions it is evident that this method is not adequate for the 040 and comparison with the 040/080 ratio for crystal 6 indicates correction based on even the $3{\cdot}5 \times 10^{-4}$ value for 'g' is 40% too low.

(d) Intercomparison of the six sets of data

In view of the strong indications of extinction, the first comparison test was to determine the intensity dependence of the interset discrepancies, and this was done in the following way. The run 6 data were arranged in sequence of increasing intensity and the other five sets were placed in the same order; for convenience of interpretation the six sets were scaled on the basis of the 30 weakest reflexions. The ratio of I_n/I_6 was then plotted for the first 5 sets of data against the sequence number resulting from ordering the set 6 data, and the result is shown in Fig. 4; the mean of every 20 successive points on Fig. 4 are replotted in Fig. 5 to minimize the effects of other random errors.

Crystal 6 was chosen as the standard as the results of the previous section showed it to exhibit the least extinction; however, the curves in Figs. 4 and 5 show such an overwhelming fall-off with intensity that it was suspected that run 6 might be subject to some unsuspected error systematic with intensity in the opposite sense to extinction effects. To provide a check, therefore, measurements were taken from a crystal (7) which was only 40% of the size of crystal 6. The results in Figs. 4 and 5 indicate good agreement with run 6 over most of the range but at the highest intensities

the run 7 data seem also to be slightly extinguished. It appears therefore that the fall-off of intensity is a real effect.

The extinction errors themselves are very large; even on the optimistic assumption that run 6 represents an unextinguished set of data, the largest intensities in runs 1 to 5 require an increase of approximately 400% to be comparable with run 6; over 42% of the intensities of these 5 sets suffer 10% or greater reduction in intensity and 25% have greater than 20% extinction errors. It is noteworthy that it is not just the few intense reflexions which are affected but almost the whole range of intensities investigated; in fact Fig. 6 shows that the error is roughly linear with $I^{-1/2}$.

In the limited number of crystals studied there appears to be very little relation between extinction characteristics and size and shape. Fig. 4 shows that the performance of the minute crystal 7 was slightly worse than crystal 6 and yet Fig. 5 shows that the largest crystal 3, gave slightly better results than nos. 1 and 4, both of which were considerably smaller.

In view of such large discrepancies between the various sets of data and the excellent way in which they tie in with the extinction effects suggested in the earlier part of the analysis, it seemed fruitless to pursue the interset comparison further in the hope of detecting the remaining smaller error sources. However, the r.m.s. percentage deviation in intensity matrix was calculated and the values are shown in Table 6. Though the numbers seem quite large in comparison with the ωR and R indices obtained in Table 5 of the I.U.Cr. Report (Abrahams, Hamilton & Mathieson, 1970), they are, in fact, comparable. The present work makes reference to intensities rather than structure factors, which will double the percentage differences, and

in addition, a uniform sample of intensity against θ has been collected which emphasizes the contribution of the larger reflexions compared with the complete sphere of data as collected in the I.U.Cr. case, which contains many more small intensities.

Table 6. *The r.m.s. % agreement between intensities measured for the six different crystals used*

Crystal No.	1	4	3	2	5	6	V
1	—	7	6	23	30	78	39
4	7	—	8	20	27	76	45
3	6	8	—	28	31	77	151
2	23	20	28	—	9	61	83
5	30	27	31	9	—	54	71
6	78	76	77	61	54		4

It is of interest that run 6, which appears to be the least extinguished and hence the best set of data, is an outlier. This bears out the comments of Mathieson (1969) that the mean value of a set of project data is not necessarily the true set, and also that the outlier, while it may be better or worse than the average, is in general a diagnostic of a systematic trend.

Conclusions

From these measurements it appears that the diffractometer, if rigorously tested, is capable of functioning as required by theory to better than 0·6% in integrated intensity, and that the major source of error in intensity measurement is the crystal itself. The most obvious explanation of the observed discrepancies in the present case is anisotropic extinction, which appears to explain the four- to tenfold worse agreement between symmetry-related measurements compared with the repeated measurement of reference reflexions and the dependence of this disagreement on intensity. It also explains the large, complicated and intensity dependent variations of integrated intensity with respect to crystal orientation about the scattering vector. In addition, extinction would account for the overwhelming downward trend with increasing intensity of the measurements of the first 5 runs compared with those of run 6, which seems from Figs. 2 and 3(a) to be the most extinction-free.

No evidence was found of the inadequacy of absorption corrections, or of effects dependent on time, temperature or pressure. The only effect of crystal size was that the very smallest exhibited least extinction (runs 6 and 7). On the other hand the five larger crystals showed no smooth trend between extinction and size.

The discrepancies in the I.U.Cr. project data can also be shown to be essentially intensity dependent in a similar manner (Mackenzie, 1972) while the predominance of extinction errors in hydroxy apatite was also the principal finding of Sudarsanan & Young (1969). It therefore appears that α-glycine is by no means an atypical compound.
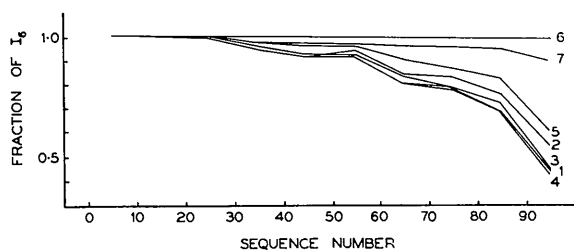

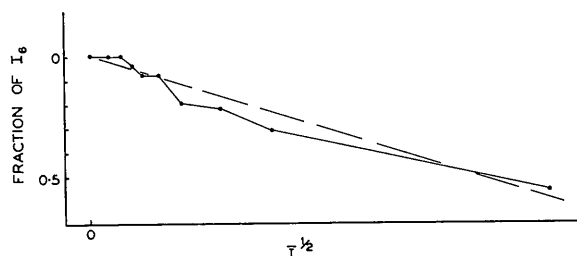Fig. 5. A plot of the mean of each successive ten points in Fig. 4.

Fig. 6. The trace for crystal 1 in Fig. 5 plotted against $I^{-1/2}$ instead of sequence number.

From these measurements it seems that a dramatic improvement in accuracy of structure factor determination may well result from the effective correction or experimental removal of extinction errors. It is also evident that a successful theoretical correction must take account of quite complicated anisotropic extinction in view of Fig. 3.

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Anomalous Scattering by Oxygen: Measurements on (+)-Tartaric Acid

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The structure of (+)-tartaric acid has been used as a test case to study the feasibility of absolute configuration determinations of compounds in which oxygen is the heaviest atom. Based on about 1100 Ni-filtered Cu $K\alpha$ reflections ($-7 \leq k \leq 7$) measured on a Picker automatic diffractometer the $(2R,3R)$ and $(2S,3S)$ configurations could be refined to $R=0.0228$ and $R=0.0231$ respectively. 94 selected enantiomer sensitive reflections gave $R(2R,3R)=0.0336$ and $R(2S,3S)=0.0374$ ($\Delta f''_O=0.032$). Among the 38 most sensitive Bijvoet differences only one had the incorrect sign. A value of 0.041 (4) for $\Delta f''_O$ (Cu $K\alpha$) was derived from 36 observed Bijvoet differences. Similar measurements with Cr $K\alpha$ radiation also permitted the unequivocal assignment of the correct absolute configuration; however, Cr $K\alpha$ radiation was not found to offer any overall advantage over Cu $K\alpha$ radiation. The cell dimensions used in this study are $a=7.7291$ (5), $b=6.0069$ (2), $c=6.2118$ (3) Å, $\beta=100.147$ (2)° (space group $P2_1$; $Z=2$).

Introduction

In a recent study of (+)-methyl-p-tolyl sulfoxide (De la Camp & Hope, 1970) the two enantiomeric structures were refined to $R=0.034$ and $R=0.044$ for the correct and the incorrect enantiomer respectively. This large difference in R indices caused by the anomalous scattering of Cu $K\alpha$ radiation by sulfur ($\Delta f''_S \simeq 0.6$) suggested to us that oxygen in a carbon–hydrogen environment might give rise to measurable anomalous scattering effects, assuming the value of $\Delta f''_O$ to lie in the range 0.03 (Zachariasen, 1965) to 0.10 (*International Tables for X-ray Crystallography*, 1962).

Based on available literature data (+)-tartaric acid seemed a reasonable choice for a test case. The molecule is relatively small, the structure was well deter-

mined (Okaya, Stemple & Kay, 1966), there was no doubt about the absolute configuration (Bijvoet, Peerdeman & van Bommel, 1951) and good crystals could be easily obtained. As it turned out the crystals were not as stable under X-ray irradiation as expected, thereby giving rise to some undesirable effects which, however, were not serious enough to thwart a successful outcome.

Preliminary accounts of this work have been given earlier (Hope & de la Camp, 1969; Hope, de la Camp & Thiessen, 1969).

Experimental

From the outset we planned both to investigate the feasibility of absolute configuration determinations