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Automatic Absorption Correction using Intensity Measurements from Azimuthal Scans

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A new method of making absorption corrections from azimuthal scans is described. The method is designed to work on an automatic four-circle diffractometer for crystals with high absorption, of arbitrary shape and having at least four general equivalent reflexions. The data are treated by a procedure which expands the transmission factor as a Fourier series in the diffractometer angles. The variation of transmission with 2θ is simulated by tabulated values for a sphere. The method has been tested by correcting for absorption in a crystal of $SmAu_6$ ($\mu R=5{\cdot}9$).

Introduction

Several practical methods of using changes in intensity of X-ray reflexions as a function of rotation about the normals to their reflecting planes are available for calculating absorption corrections (North, Phillips & Scott Mathews, 1968; Kopfmann & Huber, 1968; Katayama, Sakabe & Sakabe, 1972). These methods are intended for use on four-circle or linear diffractometers and have had great success in the treatment of data from protein crystals. Apart from equation (3) of Katayama, Sakabe & Sakabe (1972) they rely on an approximation due to Furnas (1957) which is tantamount to considering the total transmission as the product of the transmission of the primary and reflected beams. This approximation limits the method to crystals with low values of μR.

In the course of a study on rare-earth gold or palladium alloys in our laboratory (Moreau & Parthé, 1972, 1973), the crystal structure of $SmAu_6$ was determined. The absorption is very high ($\mu=1836$ cm^{-1} for Mo $K\alpha$, $R\simeq 0{\cdot}032$ mm, $\mu R=5{\cdot}9$). The crystals do not have well developed faces and tend to be irregular in form. We were thus unable to calculate satisfactorily the transmission factors either by Gaussian integration or by the analytical method of de Meulenaer & Tompa (1965). Hence we have produced a method for absorption correction using intensity measurements from azimuthal scans not needing Furnas's approximation. The present paper describes the theory of this new method and an experimental test on a crystal of $SmAu_6$. The crystal structure analysis results on $SmAu_6$ are described elsewhere (Moreau & Parthé, 1972; Flack, Moreau & Parthé, 1974).

Theory

Let ψ represent the azimuthal angle of rotation about the normal to a reflecting plane. The zero value of ψ is conventionally taken on a four-circle diffractometer as being in the standard position of $\omega=\theta$. The intensity (I) of any reflexion $h'k'l'$ at azimuthal angle ψ' may be written as:

$$I_{h'k'l'\psi'}=A(h',k',l',\psi')I_{hkl}\,, \tag{1}$$

where $A(h',k',l',\psi')$ is a transmission factor to take account of absorption and I_{hkl} is the 'true' intensity of the reflexion in the absence of any absorption. $h'k'l'$ is any reflexion related by symmetry to the reflexion hkl. Since $h'k'l'\psi'$ depend on the diffractometer setting angles $2\theta,\omega,\chi,\varphi$ we may write $A(h',k',l',\psi')$ as $A(2\theta,\omega,\chi,\varphi)$.

Thus (1) becomes

$$I_{h'k'l'\psi'}=A(2\theta,\omega,\chi,\varphi)I_{hkl}\,. \tag{2}$$

Any hkl has a unique angle 2θ due to Bragg's Law and hence (2) may be integrated over ω, χ and φ for a chosen hkl.

Thus writing

$$\langle I_{h'k'l'\psi'}\rangle=\frac{1}{8\pi^3}\int_0^{2\pi}\int_0^{2\pi}\int_0^{2\pi} I_{h'k'l'\psi'}\mathrm{d}\omega\mathrm{d}\chi\mathrm{d}\varphi \tag{3}$$

and

$$\langle A(2\theta,\omega,\chi,\varphi)\rangle_{2\theta} =\frac{1}{8\pi^3}\int_0^{2\pi}\int_0^{2\pi}\int_0^{2\pi} A(2\theta,\omega,\chi,\varphi)\mathrm{d}\omega\mathrm{d}\chi\mathrm{d}\varphi \tag{4}$$

(the subscript is to emphasize that $\langle A\rangle_{2\theta}$ is a function of 2θ only) we obtain

$$\langle I_{h'k'l'\psi'}\rangle=\langle A(2\theta,\omega,\chi,\varphi)\rangle_{2\theta}\,.\,I_{hkl}\,. \tag{5}$$

Combining (2) and (5) gives

$$\frac{I_{h'k'l'\psi'}}{\langle I_{h'k'l'\psi'}\rangle}=\frac{A(2\theta,\omega,\chi,\varphi)}{\langle A(2\theta,\omega,\chi,\varphi)\rangle_{2\theta}}=A'(2\theta,\omega,\chi,\varphi)\,. \tag{6}$$

Consider the significance of (6) for a spherical crystal of linear absorption coefficient μ and radius R. For all $h'k'l'$ the intensity $I_{h'k'l'\psi'}$ is independent of ψ and thus

$$A'(2\theta,\omega,\chi,\varphi)=1\,, \tag{7}$$

and

$$\langle A(2\theta,\omega,\chi,\varphi)\rangle_{2\theta}=A(2\theta,\omega,\chi,\varphi)=A_s(\mu R,2\theta)\,, \tag{8}$$

where $A_s(\mu R, 2\theta)$ is the transmission factor for a sphere and is readily available in tabulated form (*International Tables for X-ray Crystallography*, 1967*a*). We see that in the case of a sphere the total transmission factor

$$A(2\theta,\omega,\chi,\varphi)=A'(2\theta,\omega,\chi,\varphi)\,.\,\langle A(2\theta,\omega,\chi,\varphi)\rangle_{2\theta} \qquad (9)$$

reduces to

$$A(2\theta,\omega,\chi,\varphi)=(1{\cdot}0)A_s(\mu R,2\theta)\,. \qquad (10)$$

Comparing (9) and (10) it may be seen that the function $A'(2\theta,\omega,\chi,\varphi)$ is related to the shape and orientation of the crystal (spherical: $A'=1$) and $\langle A(2\theta,\omega,\chi,\varphi)\rangle_{2\theta}$ to the volume (or radius). The separation of A into the product of A' and $\langle A\rangle_{2\theta}$ is all the more important since it is possible to estimate A' from intensity measurements and approximate $\langle A\rangle_{2\theta}$ by $A_s(\mu R, 2\theta)$.

Let us consider the experimental determination of A' by use of (6). $I_{h'k'l'\psi'}$ are measurable subject only to instrumental restrictions. $\langle I_{h'k'l'\psi'}\rangle$ may be approximated by the mean value of $I_{h'k'l'\psi'}$ from a series of intensity measurements taken at equal intervals of ψ for *hkl* and each of its symmetry-related reflexions. Clearly it is possible to make measurements of this kind for every reflexion *hkl* in the asymmetric region of reciprocal space. Such a procedure would however be impracticable owing to the very large number of intensity measurements necessary. A more satisfactory approach is to use the experimental measurements of A' from a limited number of reflexions at different values of 2θ. These could be made the basis of an interpolation scheme giving values of A' to be applied to intensities measured during a standard data collection run.

To find a satisfactory interpolation scheme we must examine the properties of A'. A and consequently A' are single-valued and continuous functions which are cyclic in each of $2\theta,\omega,\chi,\varphi$ with periods of 2π. Thus we may write A' as a Fourier series in $2\theta,\omega,\chi,\varphi$. It is convenient to reduce the number of variables in this series. This is possible because on most four-circle diffractometers intensities for a standard data collection are measured in the standard setting with $\omega=\theta$. If we assume this always to be the case it is possible to write A' as:

$$A'(2\theta,\chi,\varphi)\,.$$

The A', a function of three variables $2\theta,\chi,\varphi$, should be taken to imply A', the function of four variables $A'(\omega,2\theta,\chi,\varphi)$, restricted to $\omega=\theta$. It is only the values of A' with $\omega=\theta$ which are necessary for applying an absorption correction for reflexions in the standard position. We write A' as a Fourier series:

$$A'(2\theta,\chi,\varphi)=\sum_{i=-\infty}^{+\infty}\sum_{j=-\infty}^{+\infty}\sum_{m=-\infty}^{+\infty}a'_{ijm}$$
$$\times\cos(i2\theta+j\chi+m\varphi)+b'_{ijm}\sin(i2\theta+j\chi+m\varphi) \qquad (11)$$

where i, j and m are integers.

The geometry of our diffractometer (Philips PW1100) is such that for $\omega=\theta$

$$A(2\theta,\chi,\varphi)=A(-2\theta,\chi+\pi,\varphi)=A(2\theta,-\chi+\pi,\varphi+\pi)$$
$$=A(-2\theta,-\chi,\varphi+\pi) \qquad (12)$$

and the same relation holds for A'. Applying conditions (12) to (11) imposes the following restrictions on the values of a'_{ijm} and b'_{ijm}.

For $j=2n$, $m=2n$:

$$a'_{i,j,m}=a'_{-i,j,m}=a'_{i,-j,m}=a'_{-i,-j,m}; \qquad (13a)$$

for $j=2n+1$, $m=2n+1$:

$$a'_{i,j,m}=-a'_{-i,j,m}=a'_{i,-j,m}=-a'_{-i,-j,m}; \qquad (13b)$$

for $j=2n$, $m=2n+1$:

$$a'_{i,j,m}=a'_{-i,j,m}=-a'_{i,-j,m}=-a'_{-i,-j,m}; \qquad (13c)$$

for $j=2n+1$, $m=2n$:

$$a'_{i,j,m}=-a'_{-i,j,m}=-a'_{i,-j,m}=a'_{-i,-j,m}\,. \qquad (13d)$$

The same restrictions hold for b_{ijm}. Rearranging (11) with (13) we obtain:

$$A'(2\theta,\chi,\varphi)$$
$$=\sum_{i=0}^{n_1}\sum_{j=0}^{2n_2}\sum_{m=0}^{2n_3}\cos(i2\theta)\cos(j\chi)$$
$$\times\{a_{ijm}\cos(m\varphi)+b_{ijm}\sin(m\varphi)\}$$
$$+\sum_{i=0}^{n_1}\sum_{j=1}^{2n_2+1}\sum_{m=0}^{2n_3}\sin(i2\theta)\sin(j\chi)$$
$$\times\{a_{ijm}\cos(m\varphi)+b_{ijm}\sin(m\varphi)\}$$
$$+\sum_{i=0}^{n_1}\sum_{j=0}^{2n_2}\sum_{m=1}^{2n_3+1}\cos(i2\theta)\sin(j\chi)$$
$$\times\{a_{ijm}\cos(m\varphi)+b_{ijm}\sin(m\varphi)\}$$
$$+\sum_{i=0}^{n_1}\sum_{j=1}^{2n_2+1}\sum_{m=1}^{2n_3+1}\sin(i2\theta)\cos(j\chi)$$
$$\times\{a_{ijm}\cos(m\varphi)+b_{ijm}\sin(m\varphi)\}\,. \qquad (14)$$

Although in principle the limits n_1, n_2 and n_3 of this summation are all $+\infty$, in practice it is necessary to restrict them to finite values. The utility of (14) is clear. The A' may be measured from a series of reflexions as described above. The values of the a_{ijm} and b_{ijm} may thus be determined by inversion of (14) and these used to give A' at other arbitrary values of $2\theta,\chi,\varphi$. It is not possible to use standard inversion formulae (*cf. International Tables for X-ray Crystallography*, 1967*b*) for the Fourier series (14) since the measurements of A' will not span the whole of $2\theta,\chi,\varphi$ space in equal intervals. Hence we have used a least-squares method (see, for example, Hamilton, 1964). It should be noted that the a_{ijm}'s and b_{ijm}'s are linearly dependent on the A'.

Experimental

A crystal of $SmAu_6$ of approximate dimensions $100\times 50\times 50$ μm was used. Intensities were collected on an automatic four-circle diffractometer (Philips PW1100) with Mo $K\alpha$ radiation ($\lambda_{K\alpha}=0{\cdot}71069$ Å) reflected from a graphite monochromator. The $\omega/2\theta$ scan mode was used. 948 independent reflexions were measured for the standard data collection out to a limit of 0·7 Å^{-1} in $\sin\theta/\lambda$ ($\theta=30°$).

For the absorption correction the reflexions indicated in Table 1 were used. The intensities of these reflexions (Laue symmetry $4/mmm$) were measured at intervals of 10° in ψ for the range 0 to 170° (1440 measurements). An $\omega/2\theta$ scan was used. Measurements were also performed on the following reflexions: 110, $2\theta=5{\cdot}5°$; 12,11,3, $2\theta=69{\cdot}0°$; 16,11,2, $2\theta=83{\cdot}8°$. These results were however not used in the calculation of the absorption correction. 110 was chosen because it was a reflexion with a small value of 2θ, but of the four equivalent reflexions only two could be measured with the crystal oriented as it was. The value of $\langle I\rangle_{2\theta}$ would thus be very uncertain. The other two reflexions 12,11,3 and 16,11,2 were rejected, as giving too many 'weak' measures of intensity although these reflexions were the strongest in the neighbourhood of their particular 2θ values.

The treatment of the data was carried out with a program (*CAMEL JOCKEY*) written in FORTRAN for a CDC 3800. The measured intensities were corrected for background. The $\langle I_{h'k'l'\psi'}\rangle$ were then calculated, no adjustment being made for ψ values which it had not been possible to measure because of restrictions in the diffractometer geometry. Hence the A' were derived for those measurements made in the standard setting. The a_{ijm} and b_{ijm} were determined from these A' values by full-matrix least-squares, minimizing $\sum w(A'_{\text{obs}}-A'_{\text{calc}})^2$ where w is an experimental weight, $w=1/\sigma^2$ for each A'_{obs}. The standard deviations σ of A' were estimated from counting statistics. The value of a_{000} was fixed to be unity. The maximum values of i, j and m were chosen to be 1, 3 and 3 respectively with $i^2+j^2+m^2\le 13$. Such a choice gave 19 parameters for 76 observations in the least-squares analysis. The maximum value of i was made smaller than those of j and m to reflect the limited range of observations in θ. The in-

Table 1. *Reflexions and their intensities used to estimate the A' transmission factor*

The two sets of columns give the intensities before and after correction for absorption. Reflexions of negative or zero measured intensity have been omitted.

h	k	l	$2\theta°$	I_{obs}	$\sigma_{I\text{obs}}$	I_{corr}	$\sigma_{I\text{corr}}$
2	1	1	9·7	5·0	4·3	789	689
−2	1	1		9·3	3·3	1656	607
2	−1	1		6·2	4·0	841	545
−2	−1	1		5·2	2·7	1865	1017
2	1	−1		3·6	5·7	991	1549
−2	1	−1		5·0	5·2	787	814
2	−1	−1		7·3	4·6	1057	669
−2	−1	−1		3·1	3·7	1128	1327
1	2	1		3·8	4·7	1015	1270
−1	2	1		8·3	3·5	1113	479
1	−2	1		3·6	4·3	551	662
1	2	−1		2·5	5·2	901	1835
−1	2	−1		5·5	4·0	1125	827
1	−2	−1		12·7	2·7	1609	363
−1	−2	−1		2·8	3·4	768	947
4	1	2	18·3	93·7	2·4	8916	676
−4	1	2		44·0	1·6	8707	877
4	−1	2		106·5	3·2	10561	803
−4	−1	2		27·3	1·8	8909	1412
4	1	−2		59·2	1·8	9686	897
−4	1	−2		69·9	2·0	9118	745
4	−1	−2		66·2	3·7	7821	692
−4	−1	−2		44·2	2·0	8066	949
1	4	2		54·7	3·1	8548	1022
−1	4	2		75·1	14·5	8114	1707
1	−4	2		61·2	2·0	7205	542
−1	−4	2		46·3	2·2	6752	615
−1	−4	−2		56·6	2·0	8031	796
1	4	−2		21·0	1·4	7537	1235
−1	4	−2		24·9	1·9	6035	801
1	−4	−2		106·0	6·5	10947	1058
7	2	1	29·1	28·7	1·2	2314	223
−7	2	1		15·1	1·7	2635	520
7	−2	1		35·2	3·8	2527	347
−7	−2	1		7·5	0·9	3006	982
7	2	−1		29·1	1·2	2766	291
−7	2	−1		17·2	1·2	2390	352
7	−2	−1		36·8	2·7	2696	307
−7	−2	−1	29·1	6·5	0·9	2320	739
2	7	1		11·3	1·3	2470	567
−2	7	1		25·4	2·1	3376	555
2	−7	1		38·8	2·1	2662	251
−2	−7	1		40·1	1·3	3480	331
2	7	−1		9·4	0·9	3036	827
−2	7	−1		16·2	1·0	3041	554
2	−7	−1		41·8	1·4	2887	255
−2	−7	−1		27·2	1·2	2520	277
8	2	6	41·9	8·2	0·6	312	34
−8	2	6		1·5	0·5	205	96
8	−2	6		6·6	0·6	322	50
−8	−2	6		1·6	0·5	449	248
8	2	−6		5·7	0·6	461	83
−8	2	−6		4·9	0·6	399	87
8	−2	−6		3·4	0·6	206	44
−8	−2	−6		2·7	0·6	320	98
2	8	6		4·4	0·6	250	47
−2	8	6		6·3	0·6	283	44
2	−8	6		5·6	0·6	316	50
−2	−8	6		7·6	0·6	512	75
−2	8	−6		0·3	0·5	154	256
2	−8	−6		4·8	0·6	309	64
−2	−8	−6		3·4	0·6	269	66
11	1	7	54·3	4·0	0·5	112	18
−11	1	7		0·5	0·5	113	114
11	−1	7		3·8	0·5	119	21
−11	−1	7		0·1	0·5	40	166
11	1	−7		1·8	0·5	83	26
−11	1	−7		2·8	0·5	190	50
11	−1	−7		3·5	0·5	140	26
−11	−1	−7		1·0	0·5	86	24
1	11	7		3·1	0·5	123	30
−1	11	7		3·2	0·5	116	27
1	−11	7		5·6	0·7	201	30
−1	−11	7		4·6	0·5	176	27
1	−11	−7		2·3	0·5	108	30
−1	−11	−7		1·8	0·5	90	31

verse least-squares matrix was used to give the correlation and variance–covariance matrices. The latter provides estimated standard deviations on the a's, b's and A''s calculated from the a's and b's.

$\langle A\rangle_{2\theta}$ was approximated by $As(\mu R,2\theta)$. The value of R was taken as the semi-dimension of a cube of volume equal to that of the crystal.

Results

Table 1 shows the values of the intensities and standard deviations of five reflexions and those related by symmetry to these five. One set of intensities (I_{obs}) is 'as measured' and the second set has been corrected for absorption. All these measurements were made in the standard setting ($\omega=\theta$). Those intensities which were measured as negative or zero have been omitted from this Table. The improvement in the intensities of equivalent reflexions after correction may be seen more readily in Table 2. Here a residual R, $R=\sum|I-\langle I\rangle|/\sum I$, where $\langle I\rangle$ is the mean intensity, is given for each group of reflexions before and after correction for absorption. In Table 3 the values of a_{ijm} and b_{ijm} with standard deviations are presented and in Table 4 the elements of the correlation matrix which are greater than 0·7.

Table 2. *Values of R, an intensity residual, for the five groups of reflexions in Table* 1

h	k	l	R_{obs}%	R_{corr}%
2	1	1	37·4	24·9
4	1	2	33·3	11·7
7	2	1	44·4	10·4
8	2	6	43·7	23·3
11	1	7	50·8	26·1

Table 3. *Values of a_{ijm} and b_{ijm} with their e.s.d.'s*

Apart from a_{000}, other values not appearing in the Table are undefined.

i	j	m	a_{ijm}	b_{ijm}
1	1	0	1·08 (77)	–
0	2	0	−0·039 (39)	–
1	3	0	−0·36 (20)	–
1	1	1	−0·72 (21)	0·67 (51)
0	2	1	0·084 (91)	−0·14 (12)
1	3	1	−0·29 (23)	−0·07 (53)
0	0	2	0·453 (86)	−0·278 (85)
1	1	2	0·34 (52)	0·69 (49)
0	2	2	−0·160 (91)	−0·010 (93)
1	1	3	0·08 (16)	−0·31 (13)
0	2	3	0·06 (13)	0·102 (72)

The intensities from the standard data collection were used to refine the positional and isotropic temperature factors of $SmAu_6$. One refinement was carried out with the intensities corrected for absorption assuming a spherical crystal. This gave a residual R ($R=\sum|\Delta F|/\sum|F|$) of 20·2%. A second refinement with the absorption method described in this paper reduced this R to 12·8%. There was no significant shift in the positional parameters of the atoms.

Table 4. *Elements of correlation matrix greater than* 0·7

ijm		
a 110–	*a* 130	−0·79
–	*a* 111	0·79
–	*b* 111	0·93
–	*a* 131	−0·71
–	*b* 131	−0·94
–	*a* 112	−0·90
–	*b* 112	0·90
a 130–	*b* 112	−0·73
a 111–	*b* 111	0·79
–	*a* 131	−0·74
–	*b* 131	−0·80
–	*b* 112	0·79
b 111–	*a* 131	−0·72
–	*b* 131	−0·96
–	*a* 112	−0·89
–	*b* 112	0·81
b 021–	*a* 023	−0·70
a 131–	*b* 112	−0·78
b 131–	*a* 112	0·89
–	*b* 112	−0·79
a 002–	*a* 022	−0·71
b 002–	*b* 022	−0·72
a 112–	*b* 112	−0·74

Discussion

For some measurements of reflexions 12,11,3 and 16,11,2 (measured in the same way as those reflexions in Table 2), the intensity was either zero or negative. Most of the other measurements of these reflexions were weak (*i.e.* $I\le 3\sigma_I$). This produced values of $\langle I\rangle$ and consequently A' with large errors. When the measured intensity at $\psi=0$ was zero or negative, the problem was even more serious. These led to interpolated values of A' which were negative or very small and absorption corrections which were negative or very large. Thus, we judged it safer to omit these observations in the determination of the a_{ijm} and b_{ijm}. It is nevertheless clear that the absorption correction has permitted a considerable improvement in the structure refinement of $SmAu_6$. The R value of 12·8% corresponds approximately to the worst corrected intensity R value presented in Table 2. For certain ranges of θ it seems likely that a further reduction in R might be possible. Table 2 also shows that reflexions where the absorption correction has the most beneficial effect lie in that range of 2θ ($15°<2\theta<35°$) where the ψ scan intensity measurements were of the highest accuracy. Presumably the system of weights used in the determination of the a_{ijm}'s and b_{ijm}'s favoured these measurements and forced the a's and b's in the main to be conditioned by them.

It should be made clear that $\langle A\rangle_{2\theta}$ has been chosen to be $A_s(\mu R,2\theta)$ by analogy and that no attempt at a rigorous derivation of this proposition has been made. Indeed it is only necessary that $\langle A\rangle_{2\theta}$ and $A_s(\mu R,2\theta)$ be equal to the same order of accuracy as the intensity measurements themselves. We trust that this is the case.

A point of more practical consideration is how to choose the value of R to use in $A\ (\mu R, 2\theta)$. We suggest three simple prescriptions:

(*a*) $R=(3V/4\pi)^{1/3}$ where V is the volume of the crystal. This gives the radius of a sphere of volume equal to the crystal.
(*b*) $R=\frac{1}{2}(V)^{1/3}$ which gives the semidimension of a cube of volume equal to the crystal.
(*c*) $R=\frac{1}{2}\bar{x}$ where $\bar{x}$ is the mean linear dimension of the crystal.

For our $SmAu_6$ crystal (*a*), (*b*) and (*c*) give $R=39$, 31 and 33 μm respectively each with an error of 10%. As (*b*) (our first attempt) produced temperature factors in the least-squares refinement (mean value 1·6 Å^2) which are larger than one normally expects for an alloy like $SmAu_6$, it seemed fruitless to try (*a*) or (*c*). The choice of (*a*), (*b*) or (*c*) for other crystals must depend on their shape. For approximately spherical crystals (*a*) is likely to be the best choice whilst for non-spherical crystals (*b*) or (*c*) should be used.

In a previous section we have described how the limits on the values of i, j and m were fixed. Statistical tests (*cf.* Hamilton, 1964) are available which allow the significance of changing the number of parameters in a least-squares procedure to be assessed. In our present computer program statistical tests of this kind have not been included and it is necessary to select the maximum values of i,j,m and $i^2+j^2+m^2$ at the outset.

The present method of absorption correction has been designed for crystals with high absorption and of arbitrary shape. Clearly it is also applicable to crystals contained within an enclosure of arbitrary shape (*e.g.* glass capillary). Since many reflexions at non-zero values of ψ have to be measured, the method is best suited to automatic operation on a four-circle diffractometer. To have confidence in the values of $\langle I_{h'k'l'\psi'}\rangle$, we require a crystal where the number of general equivalent reflexions should be at least four or perhaps even eight. We would not expect the method to work with triclinic crystals and are doubtful for monoclinic crystals. In comparison to our method those of North, Phillips & Scott Mathews (1968) and Kopfmann & Huber (1968) offer the advantage of a smaller number of experimental measurements and are unimpeded by symmetry considerations. However the approximation on which they are based breaks down as the absorption is increased.

Experimental or 'semi-empirical' methods of absorption correction are of limited accuracy. They cannot compete with the Gaussian integration or analytical methods (de Meulenaer & Tompa, 1965) from the point of view of accuracy but can nertheless be exceedingly useful for routine structure determinations.

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