LEVY, H. A. & ELLISON, R. D. (1960). *Acta Cryst.* **13**, 270.
LONSDALE, K. (1963). *Acta Cryst.* **16**, A168.
MACINTYRE, W. M. (1963). Private communication.
MACK, M. & SPIELBERG, N. (1958). *Spectrochim. Acta*, **12**, 169.
MATHIESON, A. MCL. (1958). *Acta Cryst.* **11**, 433.
NORTH, A. C. T. (1964). *J. Sci. Instrum.* **41**, 41.
PHILLIPS, D. C. (1964). *J. Sci. Instrum.* **41**, 123.
POTTER, R. (1962). *J. Sci. Instrum.* **37**, 379.
RENNINGER, M. (1937). *Z. Phys.* **106**, 141.
SANTORO, A. & ZOCCHI, M. (1964). *Acta Cryst.* **17**, 597.
WHITTAKER, E. J. W. (1953). *Acta Cryst.* **6**, 222.
WILLIS, B. T. M. (1962*a*). *Pile Neutron Research in Physics. Proc. Int. Atomic Energy Conf., Vienna.*
WILLIS, B. T. M. (1962*b*). *Brit. J. Appl. Phys.* **13**, 548.
WILLIS, B. T. M. (1963). *Proc. Roy. Soc.* A, **274**, 122.
WOOSTER, W. A. & WOOSTER, A. M. (1962). *J. Sci. Instrum.* **39**, 103.
YAKEL, H. L. & FANKUCHEN, I. (1962). *Acta Cryst.* **15**, 1188.
YOUNG, R. A. (1963). *Z. Kristallogr.* **118**, 223.
ZOCCHI, M. & SANTORO, A. (1963). *Acta Cryst.* **16**, A155.

Acta Cryst. (1964). **17**, 1190

Evaluation of Digital Automatic Diffractometer Systems

BY S. C. ABRAHAMS

Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey, U.S.A.

(*Received* 13 *September* 1963)

The ideal automatic diffractometer system is a logical assembly that can measure, *without systematic error* and with little personal intervention, every structure amplitude in the sphere of reflection. Typical sources of error in existing digital systems are discussed and criteria given for their detection. A quantitative measure of departure from the ideal system may be obtained by application of these criteria. Some preliminary results are presented for one system.

Introduction

This paper has three main purposes. The first is to illustrate some of the problems associated with digital automatic diffractometer equipment, the second is to give some criteria for their detection, and the third is to present some typical results for one system. The need for such complex systems should perhaps be briefly justified. Structural crystallographers have long been aware of the difficulties associated with the visual estimation of photographically recorded intensities. There is now a consensus that higher accuracy is required for many physical problems than the photographic method is capable of providing. A parallel difficulty is the large amount of the crystallographer's own time this method consumes.

Attempts at improving accuracy have led to the development of modern counter techniques. While these techniques are inherently more accurate, they can use even more time than the photographic methods they replace. Fortunately, the reason for this disadvantage in manual counter techniques lies in those very repetitive elements which are required for successful automation. Modern automation design has hence been applied to single-crystal diffractometry in an attempt both to improve the accuracy *and* to decrease the time required in making integrated intensity measurements (Abrahams, 1963)*.

Sources of error

This paper has been restricted to the X-ray case, although it is in part also applicable to neutron diffractometry. Limitation of time must necessarily cause some selection among the topics to be considered.

The ideal automatic diffractometer system may be defined as a logical assembly of subsystems that can measure, with the minimum of personal intervention and without systematic error, every structure amplitude in the sphere of reflection. All such systems contain the five logical elements shown in Fig. 1. Manual diffractometers contain all except the automatic control subsystem, so that this discussion also applies to the manual case.

It is apparent that each of these five logical elements has a capacity for introducing error into the total system. A well designed system keeps the sum of all such error below the level required by the final overall accuracy. To control the introduction of error, we may consider each subsystem in Fig. 1 separately.

A. X-ray and crystal

Fluctuations, both long- and short-term, in the intensity and spectral distribution of the X-ray supply

---

* An outline of some of the factors which led to automation is contained in a film *Automated X-Ray Diffractometry* which was used to introduce an Informal Discussion on Automatic Single-Crystal Diffractometry at the Sixth International Congress of the I.U.Cr., Rome, September, 1963. Prints of this film (16 mm in colour, with optical sound track) are available on request to the author. — Ed.

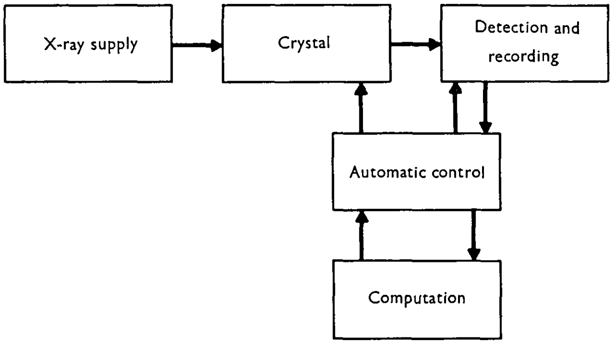

Fig. 1. Assembly of logical elements in an automatic diffractometer system.

are well known, and the literature is well documented on methods of measurement (Parrish, 1962). Variations of several per cent are not uncommon even in 'well stabilized' generators. Failure to measure and control such fluctuation will needlessly complicate the measurement of variation further along the logical path indicated in Fig. 1. In order to discuss those aspects of the system that may be less well known, let us assume the X-ray supply is indeed stable to ±0·5% or better and that the crystal is correctly oriented, of known dimensions, free of anisotropic strain and with accurately determined lattice constants.

B. Detection and recording

We may now consider the detection and recording subsystem in more detail. Fig. 2 indicates the principal components. Of the three most common counter tubes, it is likely that the Geiger tube will not be used in automatic diffractometry, because of its excessive dead time. The greater quantum counting efficiency and longer life of the scintillation crystal and photomultiplier tube make this combination preferable to the proportional counter. A considerable volume of literature has now accumulated on scintillation counters, much of which is not too familiar to X-ray crystallographers. There are several interesting scintillation counter effects which, if not allowed for, may introduce error into the measured intensity.

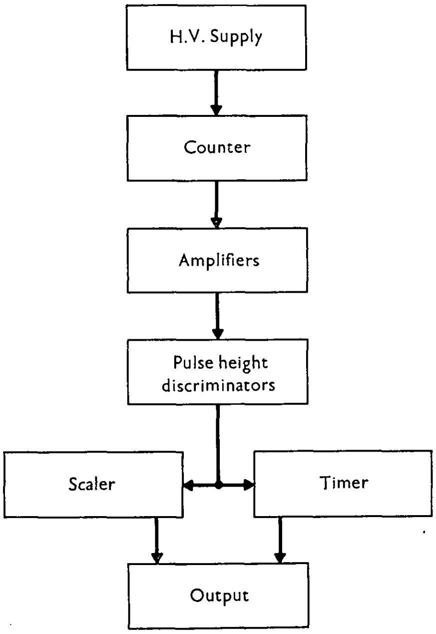

Fig. 2. Principal components in the detection and recording subsystem.

Scintillation crystals such as NaI(Th) have a dead time of about 0·25 μs and with the best available circuitry, the total effective dead time is increased to about 1 μs. The corresponding counting loss (for X-rays produced at constant potential) at a rate of 100,000 per second is then about 10%. Good methods (Short, 1960; Burbank, 1961) now exist for measuring counting losses. At high count rates, an additional effect becomes prominent, as the dynodes in the photomultiplier tube become fatigued. For one system, no evidence of fatigue was present up to apparent (*i.e.* uncorrected for losses) count rates of 100,000 per second. The effect of continuous counting on the apparent count rate above 120,000 per second is shown in Fig. 3. This change of over 35% as a function of time is typical. In any given system, the count rate at which fatigue sets in must be experimentally determined.

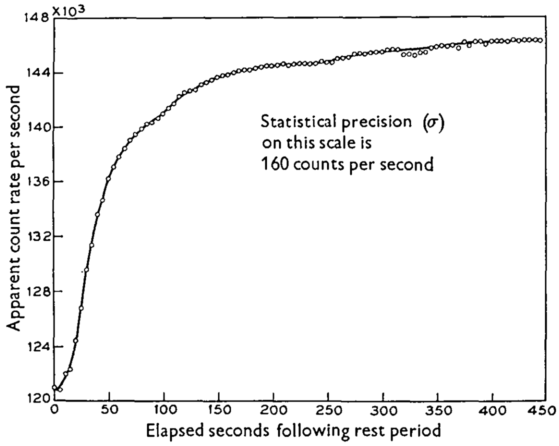

Fig. 3. Variation of apparent count rate as a function of photomultiplier tube fatigue.

Another effect is the temperature dependence of the photomultiplier tube gain. This can conveniently be measured by use of a long-lived radio-isotope. At 10,000 counts per second, obtained from a ^{57}Co (in Fe) source which produces a 7·1 keV Fe X-ray line, a variation of +0·02% per °C was observed in the scintillation crystal and photomultiplier tube assembly of one system. Other photomultiplier tubes have been shown to exhibit larger dependency of either positive or negative sign (Murray & Manning, 1960). Again, this effect must be known in any given system.

The temperature dependence of an entire detection subsystem (Fig. 2) was determined to be $-0{\cdot}04\%$ per °C. Using stabilized X-rays, and measuring the count rate from a peak with no variables except for time and temperature, the temperature dependence was found to be $+0{\cdot}8\%$ per °C.

The stability of the entire detection and recording subsystem, including the voltage levels in the pulse height discriminator, is readily checked by using the radio-isotope. For a typical subsystem, at 10,000 counts per second, the total drift in 24 hours was 0·3%, with the mean deviation in the drift$=(\Sigma|\bar{P}-P_i|)/n.\bar{P}$ ($\bar{P}$ is the average count, P_i is the ith count, n is the number of i-counts) being 0·06%.

C. *Automatic control*

There are two basic areas in which the automatic control subsystem can introduce error, namely

1. Angle location, and
2. Intensity measurement routine.

The angle location logic might typically include readers, memory registers, comparators, encoders and translators. Each of these units contains complex circuitry or mechanisms, and therefore the possibility of error is always present. A few examples of many such types of error that could be given are: excessive tension on the paper tape passing through the reader, causing misalignment of the punched holes with respect to the sensing pins; shorting between the fingers of the rotor in the encoder caused by removal of contacting material; failure in the strobe and store circuitry of optical encoders. Generally, difficulties of this kind are most probable at the information transducers.

To guard against angle location error, we always record the *actual* angle reached, rather than rely upon the instruction being faithfully executed.

In Fig. 4, the effect of error in the counter angle is shown. It should be noted that an error of 1·0° produces no change in the integrated intensity, nor in the position of the maximum, using an ω scan. A 2·0° error, however, gives a catastrophic effect. The change in the 'shoulders' as the angle error increases is significant, and could lead to error in 'background' estimation.

The control routine used to obtain the raw intensity information from which the integrated intensity is later derived is of course one of the most sensitive parts of the system. There is no time in this paper to discuss the various types of routine in any detail. Only two examples of the errors produced by some popular routines can be given. Fig. 5 illustrates a typical intensity profile. Routines that sample the background and peak only at three points to give a measure of the total intensity can clearly be in error for a background point taken at 122° φ in this example. Also, a cumulative sweep from 120° through 130° would similarly be in error.

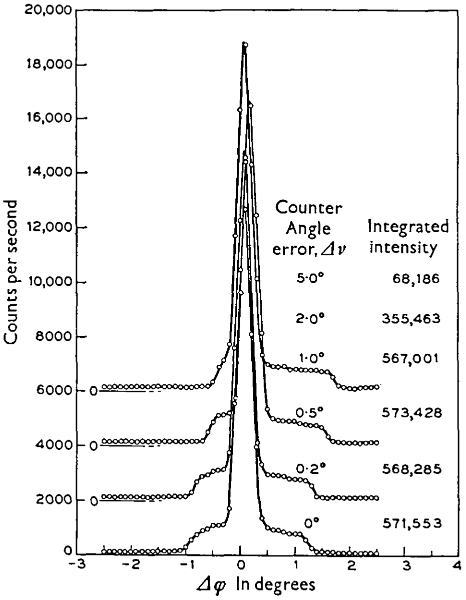

Fig. 4. Variation of intensity profile as a function of error in the counter angle.

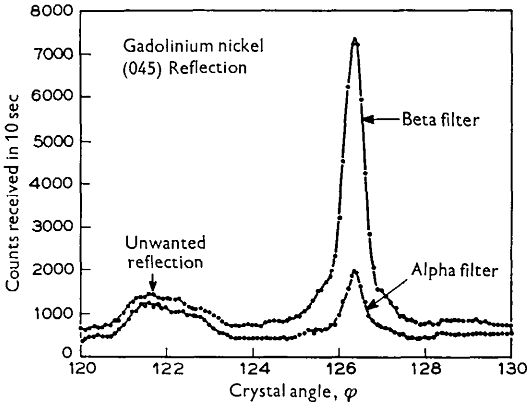

Fig. 5. Example of systematic variation in the 'background' of a typical reflection.

The advantages of moving crystal–stationary counter (ω) *versus* moving crystal–moving counter ($\theta{:}2\theta$) scans and of crystal monochromatized *versus* balanced filter methods are highly important topics which have recently been discussed by Burbank (1964) and by Ladell & Spielberg (1964).

D. *Computation*

This area of the total system is probably familiar to most crystallographers. A critical part of the computational scheme is the detection and elimination of error in the information received. Two common examples of error are (1) in the scaler output, caused by

Table 1. *Reproducibility of structure factors*

hkl	Number of measurements	$\bar{F}$	$\sigma\bar{F}$	Prec. $\bar{F}$	Max. spread in F	Total elapsed time (hr)
200	41	4448·3	12·3	0·024	33·1	24
040	160	481·5	1·4	0·003	4·6	40

GdNi crystal, $a=3{\cdot}772$, $b=10{\cdot}307$, $c=4{\cdot}251$ Å.

component failure or by statistical aberrations of low probability, and (2) in angle location. More subtle errors are caused by real variation in the background. A series of tests for many types of error, together with programs for computing structure factors, standard deviations and other functions from the raw intensity and angle information, has been given by Cetlin & Abrahams (1963).

System evaluation criteria

Let us assume all the components in the automatic diffractometer system have been thoroughly checked and are now assembled. How do we detect complete-system errors? This may be done by using the complete system to measure a quantity that is already well known, as a function of all the variables in the system.

A set of criteria has been proposed (Abrahams, 1962*a*) for this purpose. These criteria include

1. Selection of small spheres of sodium chloride as a standard. Sodium chloride was chosen since it has no position parameters, B(Na) and B(Cl) are fairly well known (*International Tables for X-Ray Crystallography* (1962) gives the experimental ranges 1·25–1·82 for B(Na) and 1·00–1·60 Å^2 for B(Cl)), very pure material is readily available and it is close to ideally imperfect. The difficulty of grinding perfect small spheres is a disadvantage, but small rectangular prisms are equally good if absorption and extinction are properly handled.
2. Measurement of all the equivalent reflections accessible to the diffractometer. The great redundancy in $Fm3m$ allows the use of valid statistical methods in estimating the standard deviation in the mean value of the structure amplitudes.
3. Measurement of the Poisson statistical precision of each integrated intensity, and comparison with that obtained in (2) above.
4. Use of a statistically significant number of different crystals of sodium chloride followed by internal comparisons of the structure amplitudes, preferably using an experimentally determined absolute scale.

Reproducibility of measurement

A simple test of the reproducibility of the *entire system*, and one that is essentially independent of the analyzing crystal itself, assuming the crystal is stable to X-irradiation, is to measure the structure amplitude of the same reflection repeatedly, as a function of time. Table 1 illustrates such measurements for F(200) and F(040) of GdNi. Each of the 41 F(200) and 160 F(040) individual measurements (Table 1) includes every step normally taken by the complete system in measuring structure factors. Each intensity point

Table 2. *Sodium chloride* (*Crystal No.* 1) *structure factors at* 294·7 °K*

hkl	F_{meas}	F_c	Difference	σ	Precision	σ/prec.	Diff./σ
111	19·84	19·79	+0·04	0·18	0·06	3·0	+0·2
200	79·34	83·43	−4·09	0·55	0·05	11·0	−7·4
220	66·96	67·03	−0·07	0·40	0·06	6·7	−0·2
311	10·90	10·08	+0·81	0·44	0·13	3·4	+1·8
222	57·39	56·73	+0·66	0·31	0·05	6·2	+2·1
400	50·17	49·55	+0·62	0·25	0·04	6·3	+2·4
331	9·86	9·56	+0·30	0·36	0·13	2·8	+0·8
420	44·97	44·16	+0·81	0·27	0·08	3·4	+3·0
422	39·99	40·03	−0·04	0·34	0·08	4·3	−0·1
333	10·00	9·99	+0·01	0·38	0·13	2·9	+0·1
511	10·11	9·99	+0·12	0·35	0·11	3·2	+3·4
440	32·78	33·23	−0·45	0·17	0·08	2·1	−2·6
531	9·76	10·10	−0·34	0·53	0·12	4·4	−0·6
442	30·47	30·62	−0·15	1·61	0·08	20·1	−0·1
600	30·42	30·62	−0·20	1·22	0·05	24·4	−0·2
620	28·76	28·24	+0·52	0·63	0·07	9·0	+0·8
533	9·15	9·87	−0·72	0·67	0·09	7·4	−1·1
622	24·18	26·07	−1·89	0·35	0·05	7·0	−5·4

* F_{meas} is the average of all the independent members of each form actually measured. F_c is based upon form factors for Na$^+$ and Cl$^-$ in *International Tables for X-ray Crystallography* (1962), with B_{Na^+} and B_{Cl^-} given in Table 3.

along each $I(200)$ profile was measured for 20-sec count periods, along each $I(040)$ profile for 10-sec periods. The Zr member only of a pair of balanced filters was used. Table 1 not only shows reproducibility in the one per cent class, but also illustrates the value of standard deviations based on population statistics.

Use of suggested criteria

The criteria suggested earlier have now been applied under various experimental conditions. The extended results will be given (Abrahams & Bernstein, 1964) in a paper specifically evaluating PEXRAD* (Abrahams, 1962*b*). Some typical results will be presented here, based on two sodium chloride crystals, both spheres, of radius 0·125 mm for sphere No. 1 and 0·143 mm for No 2. Cu $K\alpha$ radiation was used with nickel filters, with a fixed aperture of 3° and pulse height discrimination.

Table 2 presents the first 18 reflections, to $\Sigma h^2=44$. With Mo $K\alpha$ our results extend to $\Sigma h^2=200$, but there is insufficient time to discuss these in this paper. The principal feature of interest in Table 2 is the difference between σ (based on population statistics) and precision (based on Poisson intensity statistics). The *ratio* of these measures ranges from 2·1 to 24·4. Based on σ, several F_{meas} are significantly different from F_c, despite $R=0{\cdot}021$. The scale factors B(Na) and B(Cl), obtained by least-squares refinement, are given in Table 3. The values of F_{meas} in Table 2 and 4 have been corrected for anomalous dispersion (Patterson, 1962). Without correction $R=0{\cdot}032$.

Table 3. *Least-squares refinement of sodium chloride* (*No.* 1)

B(Na)	B(Cl)	R
1·60 ± 0·12 Å^2	1·17 ± 0·09 Å^2	0·021

Another criterion involves the measurement of a significant number of different specimens of sodium chloride. We have done this for several crystals under a variety of conditions. For this paper, only the results from a second crystal will be given. This crystal was measured in two separate series of experiments. Between series, the crystal and goniometer head were physically removed from the diffractometer. No other changes were made in the measurement conditions. Table 4 presents the two sets of structure factors, each on least-squares-derived 'absolute' scales. The scale factors relating this 'absolute' scale to the original measured scale, together with the corresponding temperature factors from the least-squares calculation, are given in Table 5. The two sets of measurements are not on significantly different scales, indicating good reproducibility in the conditions of measurement. It should be noted that the F_{meas} in Table 4 are on different scales from those in Table 2. If the F_{meas} in Table 4 are arbitrarily placed on the Table 2 scale, the resulting least-squares values for B(Na) and

Table 4. *Comparison of two independent sets of measurements on one sodium chloride crystal* (*No.* 2)

hkl	$F_{\text{meas(1)}}$	$\sigma(1)$	$F_{\text{meas(2)}}$	$\sigma(2)$	Diff.$_{\text{(meas)}}$	Diff./$\bar{\sigma}$*
111	19·10	0·13	19·42	0·39	−0·32	1·6
200	74·48	4·62	69·24	9·12	+5·24	1·0
220	62·52	0·47	61·99	1·28	+0·53	0·8
311	10·56	0·29	10·20	0·28	+0·36	1·8
222	51·75	0·27	53·29	1·42	−1·54	2·1
400	47·36	0·27	48·11	0·37	−0·75	3·3
331	8·70	0·68	8·99	0·34	−0·29	0·8
420	40·26	0·89	39·83	0·25	+0·43	0·9
422	34·83	0·57	35·80	1·09	−0·97	1·6
333	8·08	0·65	8·64	0·15	−0·56	1·7
511	8·45	0·30	8·99	0·27	−0·54	2·7
440	26·49	0·91	29·15	0·93	−2·66	4·1
531	8·02	0·24	8·36	0·19	−0·34	2·1
442	25·47	0·86	25·84	0·38	−0·37	0·8
600	25·66	0·71	26·51	0·70	+0·15	0·3
620	23·48	0·54	23·99	0·88	−0·51	1·0
533	7·49	0·40	7·56	0·10	−0·07	0·3
622	20·94	0·62	21·33	0·51	−0·39	1·0

* $\bar{\sigma}=\frac{1}{2}\sqrt{(\sigma(1)^2+\sigma(2)^2)}$.

Table 5. *Least-squares refinement of sodium chloride* (*No.* 2)
(*Two independent series of intensity measurements*)

Meas. No.	Scalo factor	B(Na)	B(Cl)	R_{init}	R_{final}
1	0·912 ± 0·025	2·25 ± 0·12 Å^2	1·84 ± 0·10 Å^2	0·064	0·038
2	0·959 ± 0·018	2·14 ± 0·09	1·75 ± 0·07	0·095	0·044

---

* Programmed Electronic X-Ray Automatic Diffractometer.

B(Cl) respectively become $1{\cdot}85 \pm 0{\cdot}14$ and $1{\cdot}40 \pm 0{\cdot}08$ Å^2 for measurement No. 1 and $1{\cdot}75 \pm 0{\cdot}11$ and $1{\cdot}33 \pm 0{\cdot}06$ Å^2 for measurement No. 2. The corresponding values of R become 0·043 for measurement No. 1 and 0·049 for measurement No. 2. It is considered that use of β-filters only, together with fixed counter apertures, results in systematic deviations in the intensity measurements. The F_{meas} in Tables 2 and 4 should hence be regarded as illustrative of the evaluation method, and not as error-free data.

In summary, it is suggested that the criteria developed in this paper be applied to each diffractometer system built. Analysis of the results thus obtained should enable us to evaluate each system, not only in comparison with other systems, but also on an absolute basis.

It is a pleasure to thank J. L. Bernstein for his careful operation of PEXRAD and for the many computations performed on the IBM 7090.

References

ABRAHAMS, S. C. (1963). *Chem. Engng News*, **41**, 108.
ABRAHAMS, S. C. (1962*a*). ACA Meeting, Paper I–3, Villanova, Pa.
ABRAHAMS, S. C. (1962*b*). *Rev. Sci. Instrum.* **33**, 973.
ABRAHAMS, S. C. & BERNSTEIN, J. L. (1964). To be published.
BURBANK, R. D. (1961). *Rev. Sci. Instrum.* **32**, 368.
BURBANK, R. D. (1964). *Acta Cryst.* **17**, 434.
CETLIN, B. B. & ABRAHAMS, S. C. (1963). *Acta Cryst.* **16**, 943.
International Tables for X-ray Crystallography (1962). Vol. III, 202, 240. Birmingham: Kynoch Press.
LADELL, J. & SPIELBERG, N. (1964). To be published.
MURRAY, R. B. & MANNING, J. J. (1960). *IRE Trans. Nucl. Sc.* NS **7**: 2–3, 80.
PARRISH, W. (1962). *Advances in X-ray Diffractometry and X-ray Spectorgraphy*. Eindhoven: Centrex.
PATTERSON, A. L. (1962). Private communication.
SHORT, M. A. (1960). *Rev. Sci. Instrum.* **31**, 618.

Acta Cryst. (1964). **17**, 1195

Single-Crystal Diffractometry: The Improvement of Accuracy in Intensity Measurements

BY LEROY E. ALEXANDER AND GORDON S. SMITH
Mellon Institute, Pittsburgh 13, *Pennsylvania, U.S.A.*

(*Received* 13 *September* 1963)

Some important experimental factors are considered which must be chosen so as to satisfy a valid concept of integrated reflection intensity when using an incident X-ray beam taken directly off the target of the X-ray tube. The general superiority of the 2θ scan over the ω scan is demonstrated by an analysis of pertinent factors. A basic reason is that spectral dispersion can be readily allowed for in the 2θ scan by proper choice of the scan range, whereas in the ω scan it must be accomplished by regulation of the receiving aperture. Thus the ω-scan technique demands excessively wide apertures at large θ's when β-filtered radiation is employed and over very large ranges of θ when balanced filters are used. Very feeble reflections can often be measured more accurately by taking peak (I_p) rather than integrated (I_i) intensities, but such I_p data must be transformed into the equivalent I_i's by means of empirical correction curves for the crystal concerned. Other practical recommendations are made, and the results of five structure refinements are presented to illustrate the efficacy of the 2θ-scan technique.

1. Introduction

The success of diffractometric intensity measurements depends upon adherence to a valid working concept of integrated reflection intensity, $I_i(hkl)$. When the incident beam is taken directly off the target of the X-ray tube, a satisfactory concept can be based upon the experimental requirement that every point on the crystal be enabled to 'view' every point on the focal spot. It follows that when a crystal of negligible absorption is turned through the angular reflecting range of a set of planes (hkl) corresponding to a characteristic wavelength λ_0, every volume element contributes with equal weight to the overall (integrated) reflection intensity.

The present paper is devoted to a consideration of the important experimental factors which make it possible to conform in actual practice to the above definition of I_i. A working concept based on crystal-monochromatized radiation is more difficult to define and is not proposed. We devote our attention to three- or four-circle diffractometers of the normal-beam