

A Geiger-Counter Technique for the Measurement of Integrated Reflexion Intensity

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A Geiger-counter spectrometer for single-crystal measurements is described. Two methods are described by which integrated reflexion intensity may be measured in a short time, despite the non-linear response of the Geiger counter to X-ray intensity. Some advantages and disadvantages of the balanced-filter method of monochromatization are pointed out. The relation between counting rate and X-ray intensity is dealt with from both the theoretical and practical points of view. Results obtained with the counter-spectrometer are compared with those obtained by photographic recording.

1. Introduction

The measurement of the integrated intensity of X-rays reflected from a single crystal is fundamental in X-ray crystallography. At present such measurements are usually made by photographic recording, followed by eye-estimation of intensities. While rapid and convenient in practice, this method is of limited accuracy, and in general does not give the integrated reflexion intensity. A number of integrating photometers are described in the literature, but such instruments are usually slow in operation—an important consideration when a large number of measurements has to be made. Geiger-counter spectrometers for the recording of Debye-Scherrer patterns are now well known, but the suitability of the Geiger counter for single-crystal measurements has only recently been investigated by Lonsdale (1948) and by Wooster, Ramachandran & Lang (1948). These investigators were interested mainly in the measurement of the thermal diffuse scattering of X-rays. The present investigation was undertaken in order to compare the overall accuracy and reproducibility of results obtained with a counter spectrometer with those obtained by photographic methods, and to investigate the possible uses of a counter spectrometer in crystal-structure analyses.

2. Apparatus

A standard 'Unicam' single-crystal goniometer was adapted by attaching a circular scale and arm to carry the counter. This arm can readily be detached and replaced by a microscope, and a cylindrical film holder can be mounted around the axis of rotation of the goniometer arcs, as in the standard instrument. These accessories are used in centring the specimen on the axis of rotation, and in adjusting it so that a crystallographic axis coincides with the axis of rotation. The present apparatus records only zero-layer reflexions, and when used with a horizontally mounted X-ray tube

does not record reflexions at angles greater than 100° . Self-quenching argon-alcohol and krypton-alcohol counters have been used for measurements made with copper and molybdenum characteristic radiations respectively. A typical counter used in this work had the following dimensions:

Cathode: brass cylinder, 1 in. outside diameter, $5\frac{1}{2}$ in. long.

Anode: tungsten wire, 0.004 in. diameter.

Window: aluminium 0.002 in. thick, closing one end of cylinder.

Filling: alcohol pressure, 1 cm.Hg; argon pressure, 20 cm.Hg.

Except for the entrance slits the counter is completely screened and is connected by short lengths of screened cable to a unit supplying a stabilized high voltage and to a counting-rate meter. The latter consists of an amplifier followed by circuits whose action can be briefly described as follows. Amplified pulses from the counter trigger a multivibrator unit to produce pulses of current having a rectangular waveform which is independent, within limits, of the amplitude and duration of the initiating pulse. These pulses are passed to an integrating circuit containing a microammeter, and the circuit is designed so that the deflexion of this meter is directly proportional to the average number of counts recorded per second. The time over which the average is formed can be varied from less than 1 sec. to about 4 min. After each recorded count, the instrument is insensitive to further signals from the counter for a time referred to subsequently as its 'resolving time'. This time is, in fact, equal to the duration of the rectangular pulse produced by the multivibrator and can be measured accurately. The resolving time can be given four different values by the setting of a switch, and, at the same time, the range is varied so that full-scale deflexion of the meter corresponds to either 12.5, 50, 250, or 1000 counts/sec. Over this range the response

is directly proportional to the number of counts recorded per second. The instrument is similar in principle to that described by Schiff & Evans (1936), although different in design.

The counting-rate meter is followed by a standard scaling unit (scale of one hundred electronic recorder plus mechanical recorder) which records the number of counts made in a time selected by the closing of a switch. The resolving time of this instrument is negligible compared with that of the Geiger counter itself. A schematic diagram of the apparatus is shown in Fig. 1.

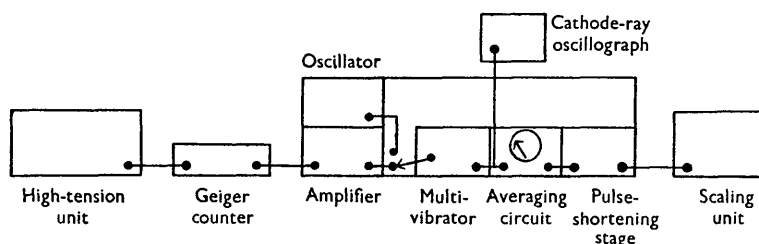


Fig. 1. Schematic diagram of recording apparatus. The oscillator and cathode-ray oscillograph are used only in the initial calibration of the counting-rate meter or in measuring resolving times.

3. Monochromatization of radiation

It is well known that an observation of N counts is subject to a statistical uncertainty \sqrt{N} , so that, for instance, 10,000 counts must be recorded to obtain a standard deviation of 1%. Furthermore, if a source produces N counts in a certain time and these are recorded together with B counts from another (background) source, we can only determine N as $(N+B) - B$. If $N+B$ and B represent two observations made in successive equal time intervals, the standard deviation of N is $\sqrt{(N+2B)}$. If, however, the expected value of B is accurately known as a result of a measurement extending over a long period, the standard deviation of N is $\sqrt{(N+B)}$.

In X-ray work on single crystals, the sources of background are as follows:

- Non-characteristic radiation reflected from another order of the plane being measured.
- Incoherently scattered or fluorescent radiation from the crystal, or radiation scattered from the air near the crystal.
- Cosmic radiation and the natural radioactive contamination of the apparatus.

Thus in order to reduce the standard deviation introduced by background counting, and to enable a sufficient number of counts to be recorded in a reasonable time, it is essential to have as high an X-ray intensity as possible. Experiments with radiation produced by a standard sealed-off X-ray tube and monochromatized by crystal reflexion have shown that in the study of a crystal of an organic compound having dimensions of, say, $0.4 \times 0.2 \times 0.2$ mm. the intensities encountered are such that several minutes would be required to measure even moderately strong reflexions with an accuracy of a few per cent. Filtered radiation gives much higher

intensities, but contains a considerable amount of white radiation which can be detected by the counter. The results shown in Fig. 2 were obtained using copper radiation filtered through nickel foil of thickness sufficient to reduce the $K\alpha$ radiation to one-quarter. The X-ray tube was operated at 40 kV. P. This figure shows the radiation reflected from a crystal of 4-amino,2,6-dichloropyrimidine at angles between those at which the (200) and (400) reflexions occur. In this case, the $\frac{1}{2}\lambda$ radiation reflected from (400) is comparable in intensity with the characteristic radiation reflected from (200).

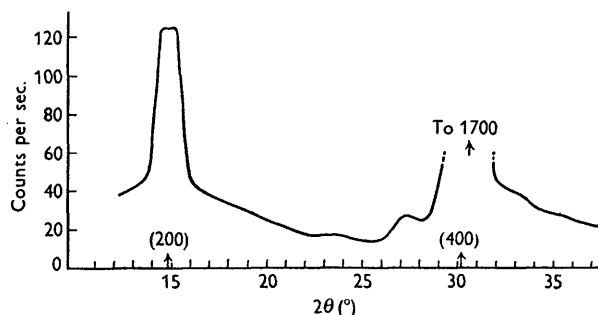


Fig. 2. Illustration of the occurrence of white radiation after filtration of the incident beam through nickel foil. The normal X-ray background has been subtracted but the (200) reflexion appears superimposed on radiation of wave-length about 0.77 Å. reflected from (400). Apparatus set up for stationary crystal method.

(The amount of white radiation present appears somewhat exaggerated by the experimental arrangement, which included a collimator of large aperture and a broad-focus X-ray tube.) This difficulty was overcome by using the balanced-filter method (Ross, 1928). Filters of nickel and iron of approximately the correct thickness were obtained and exact balance for radiation of wave-length 0.77 Å. was found by trial. The balance at other wave-lengths is illustrated in Fig. 3. The method is not entirely satisfactory, because the white radiation within the wave-length limits 1.48–1.77 Å. (the wave-lengths of the Ni_K and Fe_K absorption edges), which is not 'balanced out', is less dispersed at low angles, and so more of it passes through the slits shielding the counter when low-angle reflexions are being recorded than when high-angle reflexions are being recorded. There is no doubt that it would be preferable to use strictly monochromatic radiation when accurate intensity measurements are required,

but this would require the use of larger crystal specimens, or a more powerful source of X-rays, than were available to the writer.

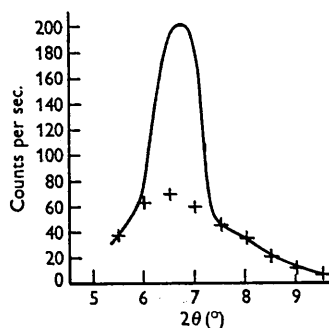


Fig. 3. Illustration of the subtraction of white radiation by balanced filters. The full line connects readings taken with nickel foil in place, the crosses represent readings taken with the iron foil in place. Except in the immediate neighbourhood of a reflexion occurring at $2\theta = 6^\circ 50'$ the two coincide; elsewhere their difference gives the intensity of characteristic radiation. Apparatus set up for oscillating crystal method.

4 (a). Relation between counting rate and X-ray intensity

It has been pointed out by Lonsdale (1948) and by Wooster *et al.* (1948) that beyond about 100 counts/sec. counting rate is not proportional to X-ray intensity. Strictly speaking, recorded counting rate is never proportional to intensity, since any number of counts occurring within the resolving time of the recording apparatus, or of the counter itself if the latter has the longer resolving time, will be recorded as one. The proportion of counts lost in this way is inappreciable at low counting rates. When possible, however, one records at a high counting rate so as to reduce the time required to make the observation to a specified (statistical) accuracy.

When the actuating mechanism causes counts to be made at completely random intervals (e.g. a d.c. excited X-ray tube), an exact correction for lost counts can be calculated. If N_0 is the number of counts recorded in 1 sec., and τ is the relevant resolving time, the corrected counting rate is given by

$$N = N_0 / (1 - N_0\tau) \quad (1)$$

(see, for instance, Lewis, 1948). Correction is more difficult when the intensity of the source varies, as with a self-rectifying X-ray tube. An estimate of the losses to be expected under these conditions has been made by Arndt (1949), and a first-order correction for the general case has been given by Westcott (1948). This

consists in taking

$$N = N_0 + N^2 K \tau, \quad (2)$$

where K is the form-factor of the source, defined by

$$\sqrt{K} = \frac{\text{R.M.S. intensity of source}}{\text{Mean intensity of source}}. \quad (3)$$

A more accurate result may be obtained as follows. Let n be the expected counting rate at any instant t , and n_0 the corresponding rate of recording of counts, so that

$$N = \int_0^1 n dt \quad \text{and} \quad N_0 = \int_0^1 n_0 dt.$$

Since the period of the intensity variation ($\sim 10^{-2}$ sec. for an X-ray tube) is long compared with the resolving times met with in practice ($\sim 10^{-4}$ sec. for a Geiger counter), we have by analogy with (1),

$$n = n_0 + n n_0 \tau. \quad (4)$$

Westcott, in effect, puts $n_0 = n$ in the correcting term $n n_0 \tau$, and this leads directly to (2). Taking $n_0 = n N_0 / N$, which is a better approximation, it may readily be shown that

$$N = N_0 / (1 - N_0 K \tau). \quad (5)$$

An alternative derivation of this equation has recently been published (Alexander, Kummer & Klug, 1949).

This result means that to a good approximation the variation in intensity of the source effectively increases the resolving time of the apparatus by a constant factor K , defined above. An experimental correction based on this result is briefly described below. This method breaks down if 'spurious counts' are being produced by the counter, but in any case such a counter cannot be expected to give reliable and reproducible measurements of X-ray intensity. A characteristic of spurious counts is that they do not occur entirely at random, but follow one another, or a true count, at intervals of time roughly equal to the resolving time of the counter (Putman, 1948). Equation (1) is based on the assumption that counts are distributed randomly in time; any departure from it can therefore be attributed to the occurrence of spurious counts. All counters used were therefore tested as follows. Counts were recorded from a γ -ray source, the resolving times of the counting-rate meter being $\tau_1 = 1760$, $\tau_2 = 440$ and $\tau_3 = 90 \mu\text{sec.}$ for successive readings. We should then have from (1),

$$N = N_1 / (1 - N_1 \tau_1) = N_2 / (1 - N_2 \tau_2) = N_3 / (1 - N_3 \tau_3),$$

or $\tau_1 - \tau_2 = 1/N_1 - 1/N_2$, etc.,

where N_1 is the number of counts recorded in 1 sec. when the resolving time of the apparatus is τ_1 , and N_2 and N_3 are similarly defined. Some numerical results obtained with a particular counter are given in Table 1.

Table 1. Analysis of counts recorded from a source of constant intensity

N_1	N_2 (counts/sec.)	N_3	$1/N_1 - 1/N_2$	$1/N_1 - 1/N_3$ ($\mu\text{sec.}$)	$1/N_2 - 1/N_3$
86.4	97.3	100.3	1300	1630	330
171.8	220.4	231.1	1360	1480	120
274.4	426.1	463.7	1290	1480	190
344.1	616.2	713.5	1280	1510	230

Values of $1/N_1 - 1/N_2$ agree with $\tau_1 - \tau_2 = 1320 \mu\text{sec.}$; other results are consistent with $\tau_3 = 250 \pm 40 \mu\text{sec.}$, which must therefore be the resolving time of the counter itself. This figure was roughly checked by oscillographic measurements, using the method of Stever (1942). Counters producing spurious counts were shown up by the fact that τ_3 , calculated in the above way, had a negative value.

The form factor of an X-ray source can be measured by a similar method, the difference being that (1) is now replaced by (5), so that

$$K(\tau_1 - \tau_2) = 1/N_1 - 1/N_2, \text{ etc.}$$

Alternatively, K can be calculated from a knowledge of the waveforms of the voltage applied to, and the current through, the X-ray tube (Arndt, 1949).

An experimental check of (5) was made as follows. Counts were recorded, using X-rays from a tube having a molybdenum anticathode excited by pulsating d.c. of 55 kV.P. Observations were made with different resolving times, and with the monochromatic radiation filtered through different thicknesses of nickel foil. One foil was taken as standard, and the counting rate with m foils interposed was compared with that when m foils plus the standard foil were interposed.

Since the statistical inaccuracy of the results at counting rates less than 50 per sec. is more than 1%, and since the output from the X-ray tube could not be held constant to better than 1%, differences of reciprocals at low counting rates are very inaccurate and have been omitted from Table 2. It will be seen that

values of $1/N_1 - 1/N_2$, etc., are reasonably constant and lead to

$$K = \frac{1/N_1 - 1/N_2}{\tau_1 - \tau_2} = \frac{2540}{1320} = 1.92,$$

$$\text{or } K = \frac{1/N_1 - 1/N_3}{\tau_1 - \tau_3} = \frac{2860}{1510} = 1.90.$$

Values of $1/N_2 - 1/N_3$ are scarcely accurate enough to give a value of K . Taking $K = 1.91$, they lead to $\tau_3 = 220 \mu\text{sec.}$, in good agreement with a previous result. The value of K calculated from current and voltage waveforms was 1.96.

Values of $N = N_i / (1 - N_i K \tau_i)$ for $i = 1, 2$ and 3 are given in Table 3.

Values of N deduced from observations made with the three different resolving times are in good agreement in the region where the correction does not exceed 30%. (These results occur above the dividing lines drawn in Table 3.) After correction, the ratio

$$\frac{\text{Counting rate with } m \text{ foils interposed}}{\text{Counting rate with } m + 1 \text{ foils interposed}}$$

is always within a few per cent of the value 1.93 calculated from the thickness of the standard foil. (The fact that this figure is almost equal to the value of K is, of course, purely coincidental.)

In this case, therefore, recorded counting rate was proportional to X-ray intensity to within 2% up to a counting rate of, at most, 40 per sec., but, after correction, proportionality held up to a counting rate of about 500 per sec. It should perhaps be emphasized that this method involving the use of foils was used only as a check. Normally, the value of K for a particular

Table 2. *Analysis of counts recorded from a source of varying intensity*

No. of foils	N_1	N_2 (counts/sec.)	N_3	$1/N_1 - 1/N_2$	$1/N_1 - 1/N_3$ ($\mu\text{sec.}$)	$1/N_2 - 1/N_3$
6+1	11.3	11.1	11.4	—	—	—
5+1	21.1	21.9	21.5	—	—	—
4+1	38.8	44.1	44.2	—	—	—
3+1	67.7	80.3	83.4	2400	2800	400
2+1	103.5	135.4	146.0	2680	2820	540
1+1	152.0	235.5	258.5	2340	2730	390
1	200.0	380.7	442.7	2410	2740	330
6	20.5	21.3	22.0	—	—	—
5	36.9	39.7	40.5	—	—	—
4	67.2	80.7	84.0	2500	3000	500
3	107.8	145.1	155.2	2390	2830	440
2	151.3	236.7	258.3	2410	2760	350
1	200.0	377.0	440.2	2350	2730	380
0	237.5	543.7	659.2	2370	2690	310

Table 3. *Results corrected for lost counts*

No. of foils $m+1$	Corrected counts/sec.			No. of foils m	Corrected counts/sec.			Intensity ratio
	$i=1$	$i=2$	$i=3$		$i=1$	$i=2$	$i=3$	
6+1	11.7	11.2	11.4	6	22.0	21.7	22.2	1.93
5+1	22.7	22.3	21.7	5	42.2	41.2	41.5	1.87
4+1	44.6	45.7	45.2	4	86.9	86.5	87.1	1.92
3+1	87.2	86.0	86.8	3	168.2	166.6	167.0	1.93
2+1	158	153	157	2	308	296	294	1.90
1+1	309	293	296	1	608	548	552	1.87
1	607	562	560	0	1190	1000	942	—

X-ray tube was determined by making a few observations with different resolving times; equation (5) was then used to calculate corrected counting rates. Measurements with a self-rectifying tube producing copper characteristic radiation, for instance, gave $K=3.4$.

4 (b). Relation between number of counts recorded and integrated intensity

In measuring the integrated reflexion intensity from a crystal plane, the intensity of the source varies if a self-rectifying X-ray tube is used, and as the crystal moves with uniform angular velocity through the Bragg angle, the reflected beam varies in intensity as the reflecting power of the crystal changes. For a given position of the crystal, we have from (5),

$$N = N_0 + NN_0K\tau,$$

provided N is such that not more than 30 % of counts are lost. If the crystal moves uniformly in a time T through the range α over which reflexion takes place, the total number of counts made, which is a measure of the integrated reflexion intensity, is given by

$$M = \int_0^T N dt;$$

the total recorded is

$$M_0 = \int_0^T N_0 dt.$$

We express the fact that the counting rate depends on the crystal setting ϕ by writing $N = N_m F(\phi)$, where N_m is the rate at which counts are made when the crystal is stationary in the position of maximum reflexion. Proceeding as in §4(a), and making similar approximations, we obtain

$$M = M_0 / \left(1 - M_0 K_1 \frac{\tau}{T} \right), \quad (6)$$

$$\text{where } K_1 = K\alpha \int_0^\alpha F^2(\phi) d\phi / \left[\int_0^\alpha F(\phi) d\phi \right]^2. \quad (7)$$

That is

$$\sqrt{K_1} = (\sqrt{K}) \times \frac{\text{R.M.S. reflecting power of crystal over range } \alpha}{\text{Mean reflecting power over this range}}.$$

Equation (6) is very similar to equation (5), and K_1 may be taken as a constant whose value can be directly measured by making observations with different resolving times, as described in §4(a). Experimental verification was obtained by a method similar to that described in §4(a).

5. Measurement of integrated intensity

(a) Stationary-crystal method

If a crystal of width w and mosaic spread δ is held stationary in the reflecting position, the total radiation reflected from the crystal is a measure of the integrated reflexion intensity, provided that X-rays are

produced with uniform intensity over a region of the target of dimensions somewhat greater than $t = W + D\delta$, where D is the distance of the crystal from the X-ray focus. Taking $D=10$ cm., $W=0.1$ mm. and $\delta=30'$ gives $t=1$ mm. Pinhole photographs showed that a Machlett tube was the only one available which might fulfil this condition. When the condition is fulfilled, the intensity of X-rays reflected from the crystal should be independent of the setting of the crystal over a range of a few minutes of arc. This was tested using a crystal of 4-amino,2,6-dichloropyrimidine of dimensions $0.5 \times 0.1 \times 0.1$ mm., the maximum extension being along the c axis, which was set vertical. The result is shown in Fig. 4. Over a range of $15'$ the intensity was constant to within 3 %, over a smaller range it was constant to 1 %. Since for this crystal

$$F^2(hk0) = F^2(\bar{h}k0) = F^2(\bar{h}k0) = F^2(\bar{h}k0),$$

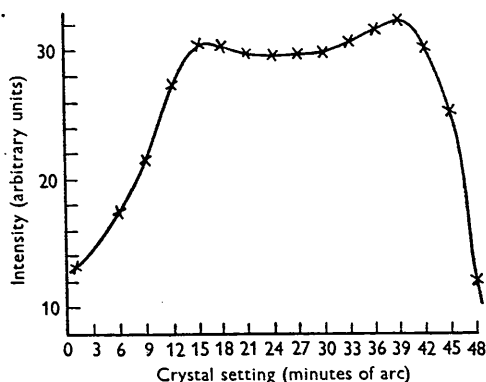


Fig. 4. Reflecting curve for stationary crystal method.

eight independent measurements of the intensity of each $(hk0)$ reflexion could be made. The results for (120) were, for instance, 33.8, 34.3, 35.8, 35.7, 33.6, 34.0, 34.5, 34.2 counts/sec. Readings taken on 10 successive days showed deviations no greater than those expected on statistical grounds. The X-ray tube was not stabilized, but the supply voltage and the current were kept constant by manual adjustment. Results were recorded with the counting-rate meter using an averaging time of either 24 or 120 sec., enough to give a (statistical) accuracy of 1–2 % for the comparatively few reflexions measured by this method. Corrections for background and for lost counts could have been made as described in more detail later, but in practice the method was not used after an initial trial because doubts were felt as to whether the conditions necessary to make a reading a measure of the integrated reflexion intensity were fulfilled by the apparatus available. If such technical difficulties can be overcome, the method is, in principle, as rapid and convenient in operation as any that could be devised for integrated intensity measurements.

(b) Oscillating-crystal method

This is based on the normal method for the measurement of integrated reflexion intensity. By means of a

cam-and-lever system, the crystal was oscillated through a range of 1° or more, one complete oscillation being made in 1 min. The slit shielding the counter was kept sufficiently wide for all characteristic radiation reflected to be recorded. In this case the counting-rate meter was not used to make quantitative measurements, but to amplify and equalize the pulses from the counter and to introduce, when required, an accurately known resolving time. The averaging time of the circuit associated with the microammeter was kept low (about 1 sec.) so that the meter followed the X-ray intensity with very little time lag. It was thus possible to verify, when measuring integrated intensity, that the reading was a maximum at the centre of the range of oscillation of the crystal and fell to background level at either end of the range. The total number of counts occurring in a complete oscillation was recorded by the scaling unit; if necessary the intensity was reduced by inserting nickel foils so that not more than 3000 counts were made in one oscillation of the crystal.

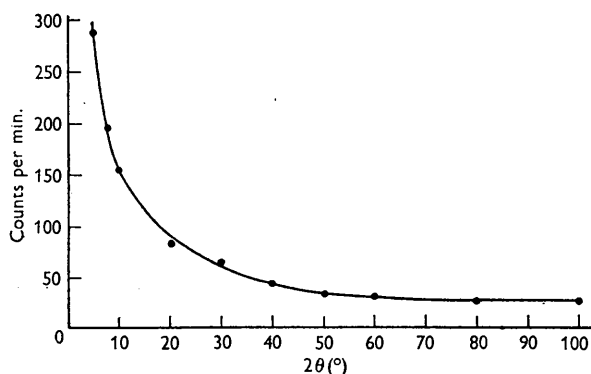


Fig. 5. X-ray background from a small crystal of adenine hydrochloride. Apparatus as shown in Fig. 7.

The following corrections to each reading were necessary:

(i) *Correction for 'natural' and 'X-ray' background.* The natural background counting rate was measured at least twice per day by recording the total number of counts made in a period of 10 min. with the window of the X-ray tube closed. The natural background depends, of course, on the dimensions of the counter, but the figure of 60 counts/min. for the counter whose dimensions are given in § 2 may be taken as typical.

The X-ray background due to radiation scattered from the air near the crystal and (incoherently) from the crystal itself, was measured at a number of angles within the range $5^\circ < 2\theta < 100^\circ$. The crystal and the counter were in each case set so that no reflected radiation could be recorded. Results for a particular case are shown in Fig. 5. The use of these readings to correct a particular observation for background implies that the X-ray background is 'structureless' (that is, the existence of thermal diffuse scattering is ignored), which cannot be exactly correct.

(ii) *Correction for lost counts.* It has already been shown that the corrected number of counts is given approximately by

$$M = M_0 / \left(1 - M_0 K_1 \frac{\tau}{T} \right),$$

where M_0 is the number recorded and K_1 , τ and T are as defined previously. From the definition of K_1 (equation (7)) we see that it depends on the variation with angle of the intensity of reflexion from the crystal and on the form-factor of the X-ray source. As has already been pointed out, we may calculate K_1 from a knowledge of K and the experimentally determined form of $F(\phi)$; alternatively, we can measure K_1 directly by making a number of observations of M_0 with different resolving times, as described in a somewhat different connexion in § 4(a).

Values of K_1 derived by the two methods agreed to within 10%. In principle, K_1 is not necessarily the same for all reflexions, since the gradual resolution of the α -doublet and absorption of X-rays in the crystal may change the form of $F(\phi)$ as θ increases; in practice, for a given crystal specimen and X-ray source it was found that K_1 could be taken as constant for all reflexions.

An example will illustrate the order of magnitude of this correction. In a series of measurements on guanine hydrochloride dihydrate, the crystal passed in 1 min. through a range of 1° which included the reflecting position. The value of K_1 found by calculation was 8.5, and by measurement, 8.6 ± 0.8 . In this case the counting-rate meter was operated on a range such that its resolving time of $440 \mu\text{sec.}$ was greater than that of the Geiger counter, $250 \mu\text{sec.}$ Thus with $\tau = 4.4 \times 10^{-4} \text{ sec.}$, $T = 60 \text{ sec.}$ and $M_0 = 2000$ (say), $M = 2280$, from equation (6). We also have from this equation,

$$\frac{\Delta M}{M} = M \frac{\tau}{T} \Delta K_1.$$

Taking $M_0 = 2000$ and $\Delta K_1 = 0.8$ gives $\Delta M/M = 1.3\%$, so that the uncertainty in the value of K_1 was relatively unimportant if not more than 2000–3000 counts were recorded during one oscillation of the crystal.

(iii) *Correction for presence of white radiation.* White radiation of two different wave-length ranges may be distinguished—that which is contained within the wave-length limits 1.48–1.77 Å., and the remainder. Correction for the presence of the latter will be considered first. Weissenberg photographs of the crystal being investigated were very useful in this connexion, as they showed which reflexions were 'overlapped' by non-characteristic radiation from another order of the plane being measured. For such reflexions each reading was duplicated, counts being recorded first with a nickel foil in position and then through a 'balanced' foil of iron. This procedure 'balanced out' radiation reflected from another order of the plane being measured (see Fig. 3).

White radiation within the wave-length limits 1.48–1.77 Å. which is recorded comes only from the plane

whose integrated intensity is being measured, so that at first sight it might appear that no correction is necessary. It has, however, been pointed out that the greater dispersion of this radiation at high angles results in a lesser proportion of it passing through the slits shielding the counter, so that it is advisable to subtract by calculation the effect of this radiation. Unlike the other corrections considered, this is a proportional correction, although the factor of proportionality varies with 2θ . To estimate the magnitude of this correction the following procedure was adopted. The crystal was oscillated through the normal range ($1^\circ 10'$ in these experiments) and the counter was set successively in different 2θ positions to record the radiation arising over a very limited range of 2θ . (The range was limited by reducing the width of a slit in front of the counter to 0.1 mm.) The result for a particular reflexion is shown in Fig. 6. It will be seen that white radiation is recorded over a range on either side of the characteristic radiation, and that the

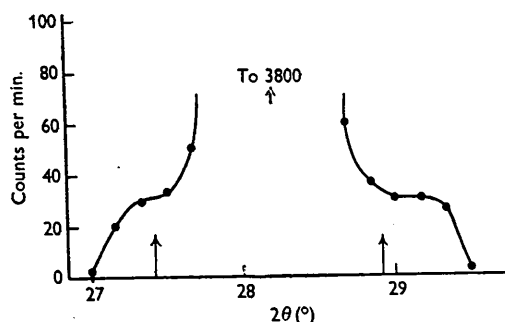


Fig. 6. Illustration of the method of correction for the presence of white radiation for which $1.48 < \lambda < 1.77$ Å. Details are given in the text.

range $2^\circ 20'$ over which this white radiation extends corresponds with the range of oscillation of the crystal, $1^\circ 10'$. Normally, the width of the slit referred to above was such that all radiation between the two arrows of Fig. 6 was recorded by the counter; hence it was calculated that for a reflexion occurring with this value of 2θ , the white radiation was responsible for 2.2% of the intensity normally recorded. The correction for reflexions having other 2θ values was similarly estimated, and varied from 6% at $2\theta = 10^\circ$ to less than 1% at $2\theta = 50^\circ$. When molybdenum radiation was used a corresponding correction was not attempted since readings were confined to the range $40^\circ < 2\theta < 60^\circ$.

(iv) *Correction for 'counter drift'*. In making a series of observations on a particular crystal, one reflexion was taken as standard and was recorded at half-hourly intervals throughout the series. Readings on this particular reflexion sometimes showed a uniform 'drift' throughout the day; the difference between readings taken at the beginning and end of the day depended on the counter used, but was sometimes as much as 5%. The reason for this was not definitely established, but it may have been due to displacement of the counter characteristics by temperature change (Putman, 1948).

It was verified that all counting rates were changed in the same proportion, and since the change was always very gradual a correction could be made by measuring a standard intensity at intervals.

6. Comparison of independent measurements

The accuracy of an observation depends on so many factors—number of counts recorded, relative intensity of background, magnitude of correction for lost counts, etc.—that a detailed analysis of the probable error of a particular measurement would be of little value at this stage. A more convincing demonstration of the accuracy of which the technique is capable was obtained by making two independent sets of readings on the ($h0l$) reflexions from crystals of adenine hydrochloride. The crystal structure of this compound is known (Broomhead, 1948). For the first set of observations a crystal having the dimensions $0.39 \times 0.85 \times 0.10$ mm. in the a , b and c directions respectively was used, and the counter used for intensity measurements had a resolving time of $80 \mu\text{sec}$. The relatively short resolving time is explained

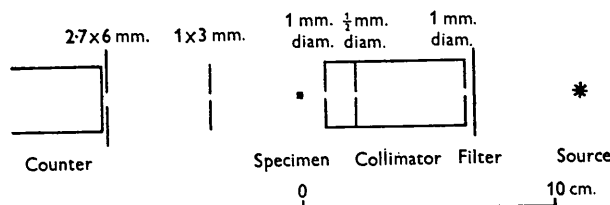


Fig. 7. Dimensions of the apparatus as used in a particular experiment. The vertical scale is exaggerated. The numbers give the dimensions of the apertures.

by the fact that this counter was only $2\frac{1}{2}$ in. long, so that its quantum efficiency for X-rays was also relatively low—about 15%. For the second set of observations a crystal measuring $0.15 \times 0.42 \times 0.13$ mm. in the a , b and c directions was used with a longer counter having a resolving time of $160 \mu\text{sec}$., and an efficiency about twice that of the other. Fig. 7 shows the relevant dimensions of the apparatus as used with the smaller crystal. With the larger crystal four 1 min. observations were made on each reflexion; with the smaller, generally only two were made. In the former case, about 24 hr. in all were required for the measurement of 120 intensities. Readings were corrected for the factors mentioned above, and a correction was made for absorption in the specimens. It should be emphasized that all corrections were independent, since two different specimens and two different Geiger counters were used. A random selection from the results obtained is given in Table 4.

In Table 4, M_1 and M_2 represent the number of counts made in 1 min. from each of the two specimens. They were obtained by correcting the recorded number of counts for the factors mentioned in §5; the corrected number was then multiplied by a constant which depended on the number of nickel foils in the path of the

Table 4. *Comparison of independent measurements*

(The quantities listed in this table are defined on succeeding pages.)

<i>hkl</i>	M_1	A_1	I_1	M_2	A_2	I_2	I_1/I_2	F_1	F_2	gF_e	F_e
804	1375	0.637	2160	680	0.602	1130	1.91	9.3	9.5	7.7	10.6
704	1320	0.645	2045	640	0.604	1060	1.93	8.7	8.8	8.7	8.8
604	4180	0.654	6390	1915	0.606	3160	2.02	14.0	14.0	13.9	14.0
504	6450	0.648	9955	2845	0.600	4740	2.10	15.8	15.3	15.0	15.0
404	8550	0.636	13440	4020	0.596	6740	2.00	16.4	16.4	16.6	14.0
304	60	0.560	107	25	0.580	43	(2.48)	1.4	1.2	0	1.0
204	20	0.460	44	35	0.580	60	(0.74)	0.8	1.4	0	3.6
104	28500	0.375	76000	21050	0.570	36930	2.06	33.6	33.0	33.7	30.6
004	10100	0.465	21720	6010	0.577	10415	2.08	19.0	18.5	21.6	15.2
104	35000	0.461	75920	22300	0.573	38920	1.95	38.8	39.2	39.6	35.2
204	4110	0.430	9560	2770	0.580	4775	2.00	15.4	15.4	15.8	14.8
304	8350	0.410	20365	5920	0.587	10085	2.01	25.0	24.8	23.3	24.4
404	85	0.430	198	55	0.587	94	(2.11)	2.7	2.6	3.8	1.0
805	245	0.608	405	110	0.602	183	(2.21)	4.0	3.9	3.7	4.0
705	165	0.615	270	80	0.601	133	(2.03)	3.2	3.1	0	0.4
605	575	0.625	920	260	0.601	430	(2.13)	5.5	5.3	6.6	5.8
505	1980	0.617	3210	1000	0.598	1670	1.92	9.4	9.6	9.5	4.8
405	1140	0.592	1925	585	0.594	985	1.96	6.7	6.8	7.7	8.0
305	5800	0.528	10985	3275	0.594	5515	2.00	15.2	15.2	16.0	18.2
205	120	0.425	282	100	0.578	173	(1.63)	2.4	2.6	3.3	0.6
105	80	0.468	171	55	0.580	95	(1.80)	1.9	2.0	3.2	1.6
005	220	0.522	420	90	0.583	155	(2.71)	3.1	2.6	3.4	2.4
105	670	0.528	1270	360	0.585	615	(2.06)	5.8	5.7	6.2	5.6
205	1145	0.520	2200	680	0.590	1150	1.92	8.3	8.5	10.6	5.2
305	8000	0.514	15565	4545	0.590	7705	2.02	23.8	23.6	23.2	22.8
405	1195	0.525	2275	705	0.595	1185	1.92	9.5	9.7	10.2	9.0

reflected beam. A_1 and A_2 are absorption factors, given ideally by

$$A = \int_s e^{-\mu(r+t)} ds,$$

where s is the area of cross-section of the crystal, μ its linear absorption coefficient, and r , t are the lengths of incident and reflected rays inside the crystal. The measured value of μ was 40.2 cm.^{-1} , while the value calculated from the composition of the material was 41.0 cm.^{-1} . The integrals were evaluated numerically for each reflexion by dividing the cross-section of the larger crystal into 64 equal areas and that of the smaller into 16 (Albrecht, 1939).

$I_1 = M_1/A_1$ and $I_2 = M_2/A_2$ are therefore measures of the integrated intensities from the two specimens. The mean value of I_1/I_2 for the 123 reflexions measured was 2.00. If we classify the reflexions somewhat arbitrarily as those which allowed more than 1000 counts to be made in a 1 min. observation on the larger specimen (70% of those measured), and those which had a smaller intensity, we find that for the first class of reflexions the mean deviation between I_1 and $2I_2$ is 3%, and for the second class 10%. (For the latter class, the ratio I_1/I_2 is given in brackets in Table 4.)

F_1 and F_2 are given by

$$F_1 = \frac{1}{2}(pLI_1)^{\frac{1}{2}} \quad \text{and} \quad F_2 = \frac{1}{2}(pLI_2)^{\frac{1}{2}}.$$

The quantity pL denotes the Lorentz-polarization factor, and the factor $\frac{1}{2}$ was introduced since comparison with calculated values showed that it would put the observed structure factors approximately on an absolute scale for which $F(000) = 186$.

Values of F_e given in Table 4 were obtained by calculation from the co-ordinates given by Broomhead (1948), so that they are independent of the experimental

measurements, except in so far as the latter were used to estimate the constant B in the equation

$$f = f_0 \exp[-B \sin^2 \theta / \lambda^2].$$

Taking $F_0 = \frac{1}{2}(F_1 + F_2)$, we find, for those $F(h0l)$'s for which $2\theta < 100^\circ$,

$$R_0 = \Sigma |F_1 - F_2| / \Sigma |F_1| = 2.6 \%,$$

and

$$R_e = \Sigma |F_0 - F_e| / \Sigma |F_0| = 17 \%.$$

It is anticipated that further refinement of atomic parameters will reduce R_e to a value more nearly equal to R_0 . Corresponding coefficients measured photographically are listed under gF_e . They will be discussed in a later section.

The integrated intensities of a further 135 ($h0l$) reflexions were measured using molybdenum radiation. A few comparatively strong reflexions were measured using both Mo and Cu radiations so that all could be placed on the same scale (Table 5).

Table 5. *Comparison of measurements made with Cu and with Mo radiations*

<i>hkl</i>	$F(\text{Cu})$	$F(\text{Mo})$
307	10.0	9.4
406	8.6	7.8
505	17.0	17.2
603	21.2	21.8
701	15.2	16.0
801	5.0	5.0
806	10.4	10.6
807	9.8	9.6

7. Direct comparison with photographic measurements

Measurements were made on the ($\bar{1}06$) reflexion from the crystal measuring $0.15 \times 0.42 \times 0.13 \text{ mm}$. For this reflexion $\sin \theta / \lambda = 0.318$, $F_e = 32.6$ and $A = 0.584$ (copper

radiation). The dimensions of the apparatus were as shown in Fig. 7, and photographs were taken by placing the film immediately in front of the counter window. From the data published by Friedman (1945), the quantum efficiency of the argon-filled counter was estimated as 30 %, while that of the krypton-filled counter used for measurements with molybdenum radiation was estimated as 40 %.

(a) Copper radiation

Radiation from a sealed-off Victor tube operated at 30 kV.P., 15 mA., was filtered through nickel foil of thickness sufficient to reduce the $K\alpha$ radiation to one-quarter. When additional thicknesses of nickel foil having a total reduction factor of 4.00 were inserted in the path of the reflected beam, 2420 counts were recorded in a 1 min. observation during which the crystal was oscillated through a range of $1^\circ 10'$ which included the (106) reflexion. Subtracting the natural and X-ray backgrounds, making a small correction for lost counts, and multiplying by 4.00 gives the number of counts made under 'standard' conditions as 9760 per min. Under the same standard conditions this reflexion was just visible on a double-coated Ilfex film after an exposure time of about 30 sec., while after an exposure time of 5 min. the spot had a density which, as experience of this method has shown, could have been measured by eye comparison with a scale with an accuracy of 5–10 %. Thus a reflexion of intensity corresponding to about 3000 counts/min., which when all sources of error are taken into consideration could certainly have been measured on the counter-spectrometer in 1 min. with a standard deviation of 5 % (cf. § 6) would have required an exposure time of 15–20 min. before it could have been measured by eye estimation with comparable accuracy. Wooster *et al.* (1948) found that 5000 counts from a small crystal corresponded to a just-detectable density on a photograph. The exact agreement with the figures given above is largely fortuitous since conditions were different in the two experiments.

Experiments were made to determine the proportion of the radiation absorbed in the film. It was found that 22 % of the radiation was absorbed in the emulsion and 38 % in the film-base, while 40 % was transmitted.

(b) Molybdenum radiation

The source of X-rays was a Machlett tube operated at 55 kV.P., 15 mA., and the radiation was filtered through a zirconium foil of thickness sufficient to reduce the $K\alpha$ radiation to one-third. With nickel foil of reduction factor 7.5 inserted in the path of the reflected beam, 2595 counts were recorded in a 1 min. observation on the (106) reflexion. This corresponded to 20,400 counts under standard conditions. Under these conditions this reflexion was just detectable by photography in 1 min., and could have been measured by eye

estimation with an accuracy of 5–10 % from a photograph of exposure time 10 min. In this case, therefore, a reflexion sufficiently intense to enable 3000 counts to be recorded in 1 min. would have required an exposure time of about 1 hr. before it could have been measured with comparable accuracy by photography. In this case it was found that 5 % of the radiation was absorbed in the emulsion and 15 % in the base, while 80 % was transmitted.

8. Indirect comparison with photographic measurements

Any comparison of the relative efficiencies of the photographic and Geiger-counter methods of intensity measurement must be somewhat arbitrary since the latter measures integrated intensity while the former, as generally used, does not. For instance, if the film had been placed nearer the specimen in the experiments described above, the reflexion would have been detected after a shorter exposure time, but the intensity as measured by a Geiger counter in this position would have been unchanged. Again, the use of a specimen having twice the vertical extension would have doubled the integrated intensity, but would have had only a small effect on the intensity as measured by eye estimation. The photographic measurements on adenine hydrochloride hemihydrate, of which a selection is given in Table 4, were made by J. M. Broomhead using a specimen of dimensions almost identical with those of the larger specimen used in this work. The Weissenberg camera used had a radius of 2 cm., and the maximum exposure time with the crystal oscillating through a range of 190° was 25 hr. The range covered was $0 < \sin \theta / \lambda < 0.64$. Details of the method of correction for absorption are given in the original paper (Broomhead, 1948). If we denote a photographically measured coefficient by F_e , it is found that the ratio $g = \bar{F}_0 / \bar{F}_e$, where the averages are taken over a number of reflexions having approximately the same value of 2θ , is not constant but decreases uniformly by about 43 % between $2\theta = 10^\circ$ and $2\theta = 100^\circ$. It follows that in this case the eye-estimation method measured a quantity proportional to the integrated intensity, but the 'constant of proportionality' varied with 2θ . There is reason to believe that this will generally be the case when eye-estimation methods have been used, but this does not necessarily mean that the use of F_e 's as coefficients in a Fourier series will give atomic co-ordinates which are seriously in error (Clews & Cochran, 1949).

The time required to measure the intensities of 260 reflexions using the counter spectrometer was about 40 hr. (This does not include the time spent in repeating the measurements with another specimen.) Approximately half the measurements were made using copper radiation, the remainder using molybdenum radiation. The range covered was $0 < \sin \theta / \lambda < 0.72$. Comparison of

the measurements, of which a selection is given in Table 4, gave

$$\Sigma |F_1 - F_2| / \Sigma |F_1| = 2.6\%,$$

and

$$\Sigma |F_0 - gF_e| / \Sigma |F_0| = 9\%.$$

No reflexion having $F < 1$ was detected using the counter spectrometer; the corresponding limit of photographic measurement occurred at about $F = 3$.

Comparative measurements have also been made on crystals of guanine hydrochloride dihydrate. The counter-spectrometer measurements were made using a specimen of dimensions $0.4 \times 0.4 \times 1.5$ mm., the direction of maximum extension corresponding to the c axis, which was set vertical. Four 1 min. observations were made on each reflexion. Weissenberg photographs of maximum exposure 25 hr. were taken using a specimen of dimensions $0.2 \times 0.2 \times 1.0$ mm., other conditions being as described above. No corrections for absorption were made in this case as rough calculations using Albrecht's method (Albrecht, 1939) showed that the variation of A from one reflexion to another would not exceed 5% and would generally be considerably less than this. A selection of the results obtained is given in Table 6.

Counter-measured intensities are given as one-sixtieth of the total number of counts made in 1 min.— $M/60$ in the previous notation. Calling the photographically measured intensity I (unity corresponds to a reflexion which could just be detected on the film of longest exposure time) it is found that $M/(60I)$ shows no systematic variation with 2θ and has a mean value

of 15.3. It follows that in this case the eye-estimation method measured integrated intensity, at least over the range $10^\circ < 2\theta < 100^\circ$. The quantity $M/(60 \times 15.3)$ is given in Table 6 and may be compared with I . Of the 154 reflexions examined, 52 were not detected by photography and 7 were not detected using the counter spectrometer. Any reflexion which was detected photographically could be measured by the counter spectrometer in 4 min. with a statistical uncertainty of at most 2%, and about 60% of the total could be measured in this time to within 1%. By comparison of I and $M/60$ the standard deviation of a photographically measured intensity has been estimated as 12% for $I > 5$ and 18% for $I < 5$. The point of division is, of course, somewhat arbitrary.

9. Discussion

As a means of measuring intensity a properly designed Geiger counter must always be more sensitive and more accurate than a photographic film, since the quantum efficiency of the former for X-rays may be made to approach 100%. Furthermore, the counter measures intensity directly by detecting individual quanta, and in principle no more precise method of intensity measurement is possible. Intensity measurement from a photograph is essentially indirect and is subject to a number of random experimental errors. Results given in other sections show that under practical conditions greater accuracy and sensitivity can be obtained for roughly the same time of measurement when the

Table 6

h	k	$M/60$	I	$\frac{M}{60 \times 15.3}$	h	k	$M/60$	I	$\frac{M}{60 \times 15.3}$	h	k	$M/60$	I	$\frac{M}{60 \times 15.3}$
0	2	683	38	44.7	2	13	28	2	1.8	5	6	378	20	24.7
0	4	2300	140	144	3	1	51	3	3.3	5	7	6	0	0.4
0	6	310	18	20.3	3	2	1620	108	106	5	8	8	0	0.5
0	8	24	1	1.6	3	3	2884	207	189	5	9	29	2	1.9
0	10	681	40	44.5	3	4	260	16	17.0	5	10	192	10	12.6
0	12	7	0	0.5	3	5	108	8	7.1	5	11	0	0	0
1	1	1940	140	127	3	6	5	0	0.3	5	12	1	0	0.7
1	2	274	16	17.9	3	7	683	41	44.7	6	0	2885	194	188
1	3	2290	142	150	3	8	5	0	0.3	6	1	201	12	13.1
1	4	185	10	12.1	3	9	4	0	0.3	6	2	995	60	65.0
1	5	3	0	0.2	3	10	33	2	2.2	6	3	117	9	7.7
1	6	12	0	0.8	3	11	4	0	0.3	6	4	13	0	0.9
1	7	48	4	3.1	3	12	1	0	0.1	6	5	278	18	18.2
1	8	629	37	41	3	13	2	0	0.1	6	6	49	3	3.2
1	9	7	0	0.5	4	0	11	0	0.7	6	7	44	4	2.9
1	10	36	2	2.3	4	1	1520	92	99.2	6	8	118	8	7.7
1	11	9	0	0.6	4	2	2210	152	145	6	9	2	0	0.1
1	12	9	0	0.6	4	3	539	36	35.2	6	10	198	11	12.9
1	13	0	0	0	4	4	2120	140	138	6	11	39	3	2.6
2	0	4445	360	291	4	5	108	8	7.1	6	12	8	0	0.5
2	1	1065	60	69.5	4	6	183	12	12.0	7	1	27	2	1.8
2	2	1350	88	88.2	4	7	86	5	5.6	7	2	15	1	1.0
2	3	3150	217	206	4	8	130	9	8.5	7	3	89	6	5.8
2	4	310	18	20.3	4	9	27	2	1.8	7	4	720	38	47
2	5	55	4	3.6	4	10	7	0	0.5	7	5	247	16	16.2
2	6	1430	88	93.5	4	11	145	9	9.5	7	6	4	0	0.3
2	7	22	2	1.4	4	12	0	0	0	7	7	27	2	1.8
2	8	52	4	3.4	5	1	1230	72	80.5	7	8	149	9	9.8
2	9	9	0	0.6	5	2	1230	86	80.5	7	9	4	0	0.3
2	10	29	2	1.9	5	3	1430	100	93.5	7	10	10	1	0.7
2	11	16	1	1.0	5	4	274	18	17.9	7	11	28	2	1.8
2	12	3	0	0.2	5	5	91	7	6.0					

counter-spectrometer rather than a Weissenberg camera is used in the investigation of small single crystals.

It has been suggested (Lonsdale, 1948) that intensity measurements should preferably be made by measuring the time for a given number of counts rather than the number of counts recorded in a fixed interval of time. The latter procedure can, in this case, be justified as follows: In the ideal case where the standard deviation of an observation depends only on the number M of counts recorded, we have

$$\text{Standard deviation of } M = \sigma(M) = \sqrt{M},$$

and

$$\sigma(F)/F = \frac{1}{2}\sqrt{M},$$

since $M \propto F^2$. That is, $\sigma(F)$ is the same for all values of F .

In practice, we must take into consideration the standard deviation introduced by the subtraction of background readings (see §3), and the proportional errors caused by possibly inadequate correction for counter 'drift' or for lost counts. Results discussed in §6 show that, with proper precautions, the proportional standard deviation, as distinct from the purely statistical standard deviation, will not exceed 3%. It may then be shown that $\sigma(M) \doteq (M + B + 0.001 M^2)^{\frac{1}{2}}$.

With the apparatus described above the relation $M \doteq 10F^2$ held for the specimen of adenine hydrochloride of volume $8 \times 10^{-3} \text{ mm.}^3$ when copper radiation was used.

Taking the X-ray background as 40 counts/min. (see Fig. 5), and the natural background as 60 counts/min., leads to

$$\sigma(F) \doteq \frac{1}{2} \left(\frac{1}{10} + \frac{1}{F^2} + 0.001 F^2 \right)^{\frac{1}{2}}.$$

A few numerical values are given below:

F	1	2	5	10	15
$\sigma(F)$	0.5	0.3	0.3	0.2	0.3

Even in this case, therefore, the standard deviation of a measured structure amplitude was nearly independent of its magnitude when the time spent in measuring the intensity of each reflexion was the same.

Against the advantages of the counter spectrometer

we can set the fact that it is not self-recording. In using a counter spectrometer to make single-crystal measurements there are so many points at which the judgement of the observer is required that it is difficult to see how such an instrument could ever be made fully automatic. Neither does the counter show spatial relationships in the direct way that they can be shown on a photograph.

The real value of the counter spectrometer in crystal-structure investigation is as a means of measuring integrated intensity with great accuracy. As such it will generally only be used when a preliminary study of the crystal has been made by photographic methods. A comparison of electron densities and bond lengths in adenine hydrochloride obtained by photographic and by counter-spectrometer methods will be made in a later paper.

I should like to thank Prof. Sir Lawrence Bragg and Dr W. H. Taylor for their continued support, and the other members of the laboratory who have given advice or practical assistance in the course of this work. The original suggestion of the 'stationary crystal method' came from Mr K. B. Hirsch.

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