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Electronic and Mechanical Sources of Error in Diffractometry

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The possible sources of error which arise from mechanical and electronic design features are discussed. The need for a self-checking procedure for off-line operation and the advisability of an automatic restart procedure after fortuitous stoppage is stressed. Various features of mechanical design are dealt with in relation to physical stability. In particular, the need for careful expert alignment procedures is pointed out. It is suggested that this aspect rightly belongs in the hands of the manufacturer rather than of the user. Comments on the essential features in the design of goniometer heads are given and the design for a special 'orientation inverter' head particularly suitable for quarter-circle Eulerian cradle diffractometers is described.

Introduction

There is no question but that automatic single-crystal diffractometers can deliver very accurate data even if used in an entirely conventional way. It is possible, for example, to determine and to refine the hydrogen atoms in quite complicated organic structures. To demonstrate the possibilities of the method, Fig. 1 shows a difference Fourier synthesis of an organic structure with 20 C atoms, 8 O atoms, 20 H atoms in the asymmetric unit, which was measured in our laboratory without any special precautions. However the high accuracy potential of the counter principle can of course only be realized if all necessary corrections are made and if the electronic and mechanical errors are kept as low as possible. It is the latter aspects which will be dealt with in this paper. The philosophy underlying such an approach may be somewhat different in different laboratories. My report will certainly concentrate on solutions which we have found useful. On the other hand there are general principles underlying the various specific precautions and I shall try to highlight these.

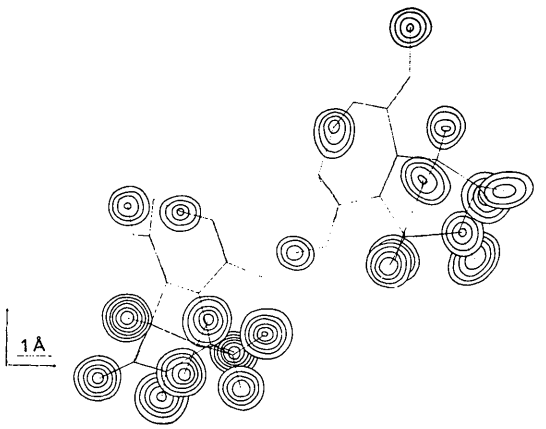

Fig. 1. Hydrogen atoms in the structure of bicyclo[2.2.2]-octadiene-2,5-dicarboxylic acid(2,3). (Two molecules in the asymmetric unit).

The concept of the 'self-checking' diffractometer

A diffractometer installation produces an enormous amount of information in a relatively short time. A Weissenberg camera or a precession camera does so as well. But there is a fundamental difference: after measurement of the spots on the film with a densitometer, the film still remains as a document. If some error is suspected, the spots can be remeasured. Moreover a trained crystallographer can recognize mistakes made by the operator – small misorientations of the crystal, wrong setting of the layer line screen *etc.* Finally he will recognize whether the crystal itself is suited for the measurement; *e.g.* a 'single' crystal, composed of several slightly displaced blocks (a common situation in organic crystal structure analysis) is easily discernible on the film.

Let us now analyze the characteristics of diffractometer measurements: In this case, the paper tape produced by the instrument is the document. Registration of the spots and measurement of their intensity is done simultaneously. Remeasurement is impossible. The output tape should therefore contain the geometrical 'film criteria' and also the criteria for the correction of the intensity measurement, if the documentary value of film methods is to be maintained.

It is customary to check the overall stability of the chain of components in the intensity determination (generator, counter, amplifier, discriminator, scaler) by repeating the measurement of certain reference reflexions. However the 'film criteria' – especially of the orientation of the crystal and the correct θ angles – are only very crudely registered in the output of the usual 3-point measurement (background left, integration, background right), the procedure most frequently used. All that can be said is that the major part of the

reflexion lies somewhere in the scanning range – otherwise the two backgrounds would not be lower than the peak, and that at least a fraction of the reflexion is situated somewhere in the counter aperture – otherwise no reflexion would be measured. This insensitivity to geometrical aberrations led us several years ago to the concept of the self-checking diffractometer. Figs. 2 and 3 demonstrate the principle. The so-called five-point measuring routine in Fig. 2 can determine the peak position within the reflexion curve very accurately, provided that the profile of the reflexion curve is known. If the shape of the crystal is not too irregular, the profile depends mainly on 2θ and can be determined by profile measurements of a small number of reflexions. The idea is to compare the left half-integral L and the right half-integral R of the reflexion curve. If the curve is symmetrical, the peak is in the middle, when

$$\frac{L}{R} = 1 \,. \tag{1}$$

For asymmetric profiles, more general relations can easily be deduced. One can also calculate which deviation of the peaks is acceptable. Something like a lower limit (for $t_1 = t_2$) will be defined by

$$\begin{aligned} U_r + R &\leq U \\ U_l + L &\leq U \,. \end{aligned} \tag{2}$$

(2) excludes intensities with one background measurement in the range of the reflexion profile.

It is true that all this information can be obtained most easily from profile measurements of all reflexions. Such an output tape will contain ample information concerning the correct setting of the θ angles. But it will be extremely long and it is important that a self-checking procedure be economic. The possibilities of profile measurement become interesting again in on-line installations [see Diamond (1969)]. The computer then applies corrections, compresses data, calculates intensities *etc.* But at this stage, I should like to express a very serious warning: There is a tendency today to do all the necessary computations in the computer and to punch out only the final results (*e.g.* structure factors with some statistical measure of accuracy). Such a strategy would be in contradiction with our original aim of creating a document which contains all essential information collected by the instrument. One should never forget that one might like to check the data later for some reason, or to make a new evaluation of the data.

In the case of profile measurement, a compression of data without appreciable loss of information should include the half-width and the separation of the θ_1, θ_2 peaks, their deviation from the calculated position, the background values and their slopes. The 'profile check' can be done in all usual on- and off-line diffractometers, provided that they can be properly programmed. The self-checking scheme according to Fig. 2, however, requires special devices in the instrument. Its aim is to determine the position of the reflexion inside the counter aperture. Figs. 3(*a*) and 3(*b*) show the well-known half shutters (Furnas, 1957), which have been in use in non-automatic diffractometers for a long time. All that we did was to operate them automatically. It is then very easy to program measurements in such a way that any deviation of the spot can be detected. But – in contrast to profile measurements – these checks need additional measuring time. It would be uneconomic (and unnecessary) to do these measurements for every reflexion. A well-selected set of reflexions – reference reflexion included – delivers enough information to check the orientation even in an off-line instrument over periods of one day or so. But we now prefer – especially in on-line installations – automatic slit shutters instead of half shutters [see Fig. 3(*c*)–(*e*)]. Slit shutters allow us to measure the vertical and the horizontal spot profile in the aperture by scanning. Slit shutters are not as convenient for manual operation as half shutters because more measurements are needed to determine, for example, the centre of a spot. This point is not so important in automatic instruments. To some extent, half shutters are analogous to the 'five-point principle' as they also yield half-integrals. The analogy of the slit shutter scanning* to the profile measurement of the reflexion curve is clear.

* The scanning itself is done by tilting the crystal and not by moving the slit.

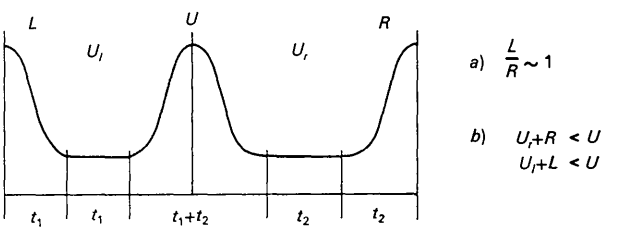

Fig. 2. Five point measurement.

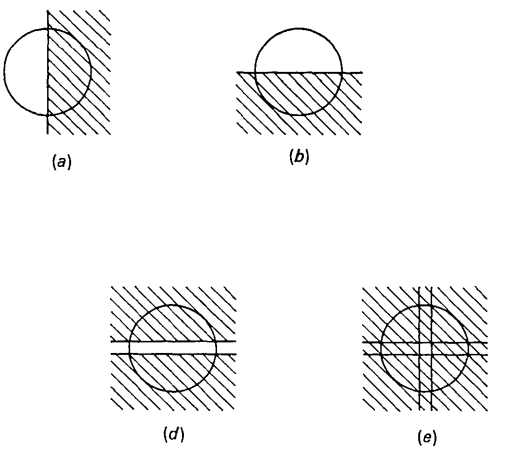

Fig. 3. 'Cross wires' in the counter aperture.

It is obvious that the results of the position-checks inside the counter aperture with these 'automatic cross-wires' should also be registered in some way in the output document, no matter whether an on-line or an off-line instrument is used.

A properly aligned diffractometer with self-check facilities also checks the operator. Small misorientations of the crystal, poor centring of the crystal, and wrong lattice constants can all be detected during a routine run. The same measurements, carried out with a standard crystal, will check the instrument as well. On the other hand, some caution in the exploitation of the data is necessary because of the high sensitivity of the methods described above. A crystal is rarely an ideal optical object because of its shape, mosaicity, absorption *etc.* Only within certain limits do 'errors' have physical sense.

Checks on the orientation of spots in the counter aperture or the shape of the spots can also be made on little photographic films but they cannot be used as permanent checks during routine runs.

It should be borne in mind that even the best 'diffractometer document' will not entirely replace a film taken with the same crystal. One look at the film can show whether the crystal exhibits disorder, substructure, splitting of reflexions *etc.* The testing of a crystal in a film camera before measurement can hardly be replaced by diffractometer methods.

One reason why on-line installations have always been preferred is their check-and-correct characteristics. But the interesting point is that the question – answer facilities of a process control computer are not really utilized. The measurements themselves (which take most of the time) are organized in a rigid frame. Some years ago, certain laboratories tried to optimize the crystal and detector setting. This was necessary mainly because of the limited precision of the first hand-built instruments. Such a process is time-consuming and should not be necessary in a well-designed instrument. The large intensity range makes it useful to choose the measuring time with the aid of an intensity estimate. This can be done by computer, but certain off-line instruments can also determine the measuring time during the measuring routine. An on-line computer will, therefore, send a real 'process control' order only if the crystal and (or) its orientation show appreciable changes. Both changes will be slow. An inspection every day is therefore equally good, especially as the crystallographer has to act in either case. Even measurements of non-oriented crystals can be made on off-line instruments. It is not difficult to write programs for 'off-line' measurements, which can be used *e.g.* for the determination of the misorientation and for the refinement of lattice constants before the starting of the measuring program. Easy access to a computer is obviously extremely important in these cases; it might be worthwhile examining the question of a cheap laboratory computer. The big jump has been from the manual diffractometer to the automatic instrument and not from the off-line instrument to the on-line instrument. The main reason why on-line instruments become more and more common is certainly the low price of small computers and the economical ways of using them with some simple interfaces as control units for diffractometers.

The electronic circuits

X-ray generators of today, which are used as generators for X-ray spectroscopy as well, generally show good properties for X-ray diffraction work. It is well-known that the reproducibility of a measurement is much better than, for example, a comparison of equivalent reflexions would indicate. This means that the counting components also work satisfactorily though semiconductor counters may come into use to improve the peak-to-background ratio. The first elements used in diffractometer control units were tubes and relays (*cf.* Hoppe & Berkl, 1962), the most recent elements are integrated circuits in the so-called TTL-technique. However, experience has shown that well-designed transistor circuits used in conventional units are also very reliable, especially if they are based on a potential technique rather than on a pulse technique. Their replacement by integrated elements facilitates the design (integrated elements are in principle logical elements) and lowers the price. The first small computers built out of these elements are now on the market.

The commonly used simple setting of the circles by pulse motors works very well. If a small digitizer, checking and correcting the last two digits of the setting, is added, then errors due to spurious pulses can be avoided. One minor comment concerns the heat which some types of pulse motor produce. Temperature differences are very unfavourable for the stability of the alignment of the mechanical parts. The motors should, therefore, be cooled, or (better) switched off when not in use. Another pulse principle uses disks with moiré fringes for error-free setting of the dials. Poor performance has been reported for 5-digit digitizers of the contact type. Their life time seems to be too short.

The weakest points – at least in principle – are the input and output devices. Our experience with tape readers and tape punches has shown that there is virtually no error in tape readers, whereas roughly one in a thousand reflexions may be affected by punching errors. Some self-check is therefore advisable to detect them.

A more general comment concerns the philosophy behind all diffractometer controls. At least in intensity measuring routines which run for several days, the routine should be self-repetitive. An electronic error of any type within the measurement destroys this measurement, but it should not end the whole series of measurements. Therefore the control should be organized in such a way that the instrument begins again with the next (or in computer-installation even with

the same) reflexion or with the next zero-check. Autostarting schemes of that type make the annoying termination of measurements during the night or over the weekend nearly impossible.

Sources of mechanical error

This paper will be restricted to the most general instrument, *i.e.* to the four-circle diffractometer.

It is a paradox that movement of a crystal with a size of some tenths of a millimeter requires an instrument weighing many pounds. It is, of course, not the stability requirements of the crystal (for this a diffractometer of the size of a wristwatch would be perfectly adequate) but the precision of circles to within one hundredth of a degree and the precise perpendicular orientation of the axes, cutting each other within a very small volume, which makes the instrument bulky. Circles of a certain precision have to be a certain size. Further, the size and weight of the detector and of auxiliary equipment have to be taken into consideration.

What does 'rigidity' or 'stability' mean? External and internal forces (stresses) tend to deform the mechanical parts. Strains can also be produced by temperature gradients. Strains within certain materials can even alter with age. Deformations produced by these forces are highly dependent on the shape. Fig.4 shows a simple example: It is immediately apparent that a force in direction of the arrow tends to bend the support in Fig.4(*a*) but has very little effect on the straight support in Fig.4(*b*). Connecting the two ends (Fig.4(*c*)] again produces high rigidity. An example of a rigid construction is shown in Fig.5. The Eulerian cradle 4, equipped with Φ-circle and motor, transfers its weight to the base 1 directly through the high precision bearing 3. As in Fig.4(*b*) elastic deformations are virtually impossible. Due to the asymmetry of the cradle construction there is a tilting moment, which is neutralized by the spring 5. The same equilibration technique is applied for the very long counter arm 6 in this installation for protein crystal analysis. It is obvious that the wheels 5,7 must not be rigidly mounted, otherwise they would be a part of the bearing

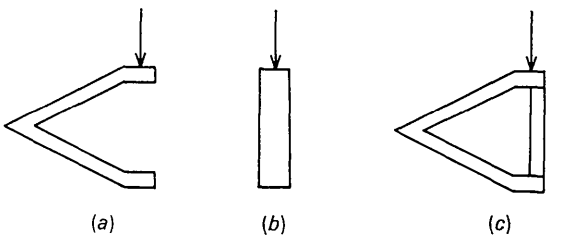

Fig.4. Rigidity and shape of a support.

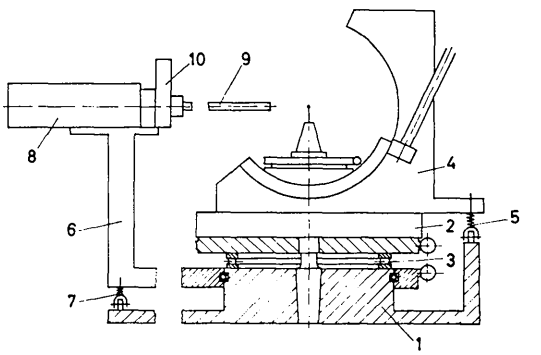

Fig.5. Diffractometer with an extremely long counter arm (reduction of background, protein crystal analysis).

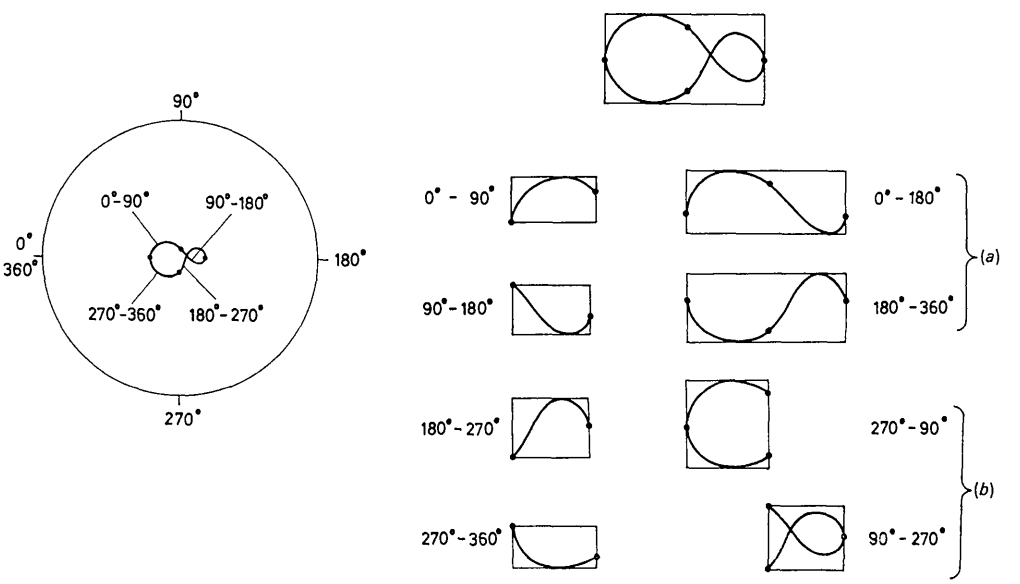

Fig.6. Error figures (schematic) of circular bearings.

which then becomes statically indefinite. The plane on which the wheels run need not be made very precisely, if springs with a flat characteristic are used. It is important that the bearings of the θ-circle and of the 2θ-circle (detector circle) in Fig. 5 be fixed to the base plate. In some early instruments, the θ circle was mounted on the 2θ circle (detector circle). In such a construction the errors of the two circles are added for the important ω, θ movement. For a similar reason, the use of a single circle for the θ and for the ω movement is better (and simpler) than the provision of two separate coaxial circles.

We turn now to the question of the circles – the main elements in a diffractometer. Circular, plane bearings are of course never circular or planar. Fig. 6 shows schematically a possible error characteristic of a bearing. The figure in the middle of the circle can be the movement of a pin or the misorientation of the axis. The rectangles represent crudely the error ranges. We will not discuss the mechanical means for minimizing the error figure. But it can be shown that the size of the error figure depends on the range of the circular motion, simply because of the shorter trace of the specimen if the motion is restricted to a quarter circle or a semicircle. The rectangles again represent schematically the areas of the error figures. It can be seen from the figures for the semicircles that the error depends also on the orientation of the range [compare case(*a*) and case(*b*) in Fig. 6]. The trick of selecting the range of bearing motion showing minimal error

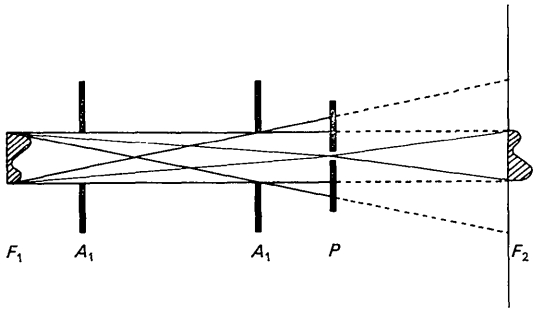

Fig. 7. Determination of the zero position of the counter (2θ circle) using a pin-hole P (replacing a 'standard crystal').

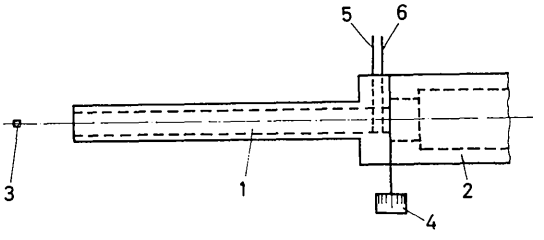

Fig. 8. Alignment of the counter aperture to the image of the focus (Fig. 7). 1 = beam tunnel, 2 = counter, 3 = crystal, 4 = one of the screw-driven slides (schematic), 5,6 = slit shutters (schematic).

for very precise work has been used from the beginning of X-ray spectroscopy.

In diffractometers the Φ-circle must be a full circle. The χ-circle can be a full circle or a quarter circle. An open Eulerian cradle is in principle less rigid than a closed cradle; this can be shown with arguments similar to those in Figs. 4(*a*) and 4(*c*). On the other hand, the error characteristics are more favourable. In addition, an open Eulerian cradle can be made very massive as there is no danger of obstructing the detector support *etc.* This can most efficiently be done if one permits a substantial reduction in the range of negative θ values. Such a restriction means that the favourable error characteristics of partial circular movements again come into effect, because the bulk of the measurements are made with positive θ and 2θ values. The question is only whether there is any particular need for an instrument showing symmetry with respect to the positive and negative θ region. It is true that such symmetry might be required if there were no other way to determine the zero positon of the instrument than by measurements at positive and negative θ values, using their symmetry for the identification of the zero point. With a set of measurements at different θ angles, the influence of absorption and of inhomogeneities of the source can be corrected. But this complicated procedure can be avoided, if the primary beam itself is taken as a reference. First, the primary beam has to be aligned parallel to the (aligned) collimator axis using, for example, a pin-hole collimator, equipped with a fluorescent screen. This adjustment of the focus obviously has to be made after the tube has been changed. The fine adjustment of the zero position is shown in Fig. 7. The crystal is replaced by a small pin-hole P which has been centred in the same way as the crystal. The image F_2 of the focus F_1 at the detector is then equivalent to a reflexion of zero order, produced by an absorption-free crystal with the diameter of the pin-hole. It is obvious that a 'reflexion curve' of this image yields the correct zero point – namely a zero point which is not affected by crystal absorption or crystal shape. Inhomogeneities within the focus will affect the zero-curve and all reflexion curves in the same sense. On the other hand, a homogeneous focus allows the overall alignment of the collimator system to be checked simply by removing the pin hole. Fig. 7 shows that the blurred image of the focus, produced by the collimator aperture near the crystal (dashed lines) has the same centre. Fig. 8 shows that the provision of cross-slides which move the counter aperture allows this aperture to be set into the zero position (using the 'cross-wire facilities' inside the aperture). It is sometimes maintained that the position of the collimator apertures is of secondary importance as only the focus and the crystal determine the geometry of the primary beam. This would be correct if the focus were the only source of radiation in the tube. In order to eliminate stray radiation as efficiently as possible, correctly chosen and aligned collimator apertures near

the crystal and as near as possible to the tube are very important. The tube–crystal distance should be kept low because the intensity is proportional to the reciprocal of the distance from the focus to the crystal.* The crystal–counter distance does not significantly affect intensities (only the background) provided that the air absorption has been effectively reduced or eliminated.

In discussing the general principles, it is important to note that a definition of the zero beam direction along these lines is possible only if the geometric positions of the primary beam and of reflected beams can be accurately determined. Thus, the 'cross wires' (half shutters, slits, small openings) which have been introduced in order to enable self-checking, can now provide new procedures for setting and orienting the crystal and for determining lattice constants. In principle all these possibilities are well-known from photographic work. The relation between the position of the spot on a film and the camera geometry is so relevant for every crystallographer that it is a little surprising that these points have been neglected (at least partially) in automatic single-crystal diffractometers.

As one further example, Fig. 9 shows a θ, Φ plot which we use to separate these two variables for an equatorial reflexion. If a wide counter aperture is used, the 2θ value is not well defined. The θ setting for the middle of the reflexion curve is, however, very accurate; but it is not known how it is influenced by deviations in the position of the Φ circle. If one uses a small hole (or a vertical slit in order to minimize small errors in orientation) in the middle of the aperture, the 2θ position now becomes sharply defined. Scans with small variations in Φ (shown as a Φ, θ plot in Fig. 9) provide the correct Φ and θ values. The generalization of this principle to more than two variables is obvious. Fig. 10 shows schematically the two possibilities for the determination of the peak (for two variables). The integral scanning corresponding to Fig. 10(*a*) determines the peak integrating along lines, scanning along other lines. Fig. 10(*b*) shows how a point scanning along a zigzag line leads to the determination of the peak.

I now wish to return to the question of the open or the closed Eulerian cradle, this time to discuss their properties for the organization of the measurements. First, it is interesting to note that – as in the case of the θ, 2θ movement – there is a redundancy here as well in the movements in the Eulerian cradle. Fig. 11 shows the range of the cradle divided into four quadrants. It can easily be shown that movements within either the shaded or the unshaded quadrants suffice for the measurement of the whole reciprocal sphere. In Fig. 10(*a*) the two quadrants are adjacent; an open cradle can, therefore, be constructed, which exhibits the same properties as a full circle cradle. A movement of χ from 0 to 90° and from 0 to −90° must then be provided. Such a cradle, properly designed, avoids the inconveniences of the full circle instrument, namely

* In an open cradle instrument this distance can be made extremely small, as the tube does not obstruct the movement.

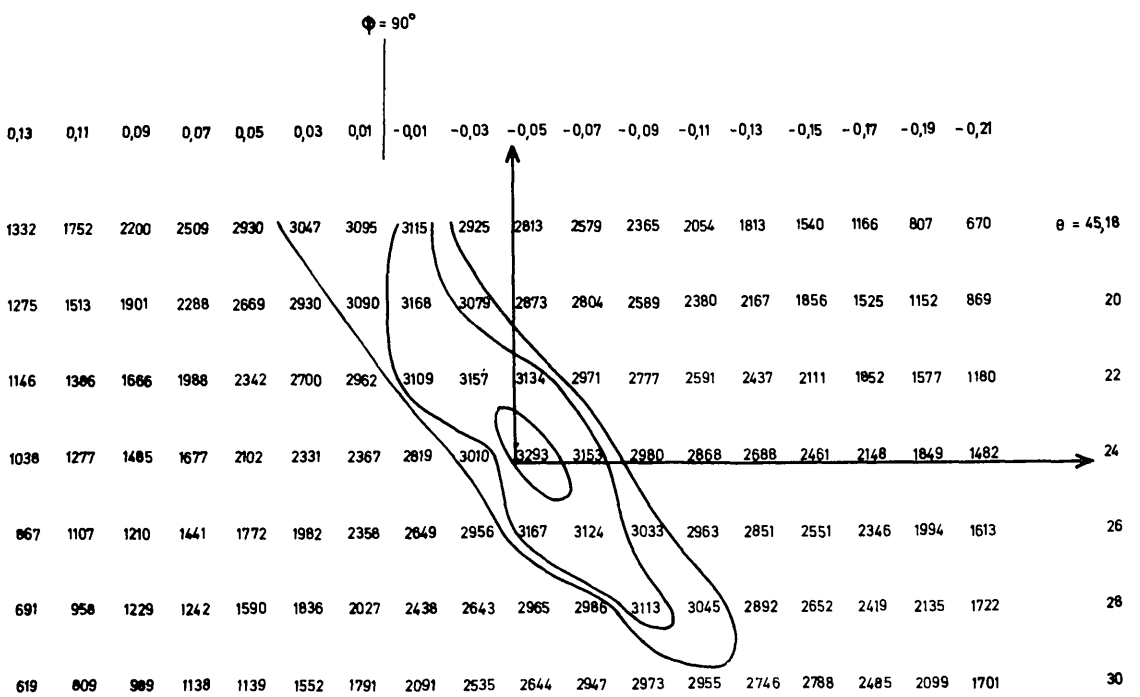

Fig. 9. θ, Φ plot for the separation of these two variables.

limitation of the 2θ range and obstruction by the beam tunnel in changing from the bisecting position of the cradle to the parallel position.

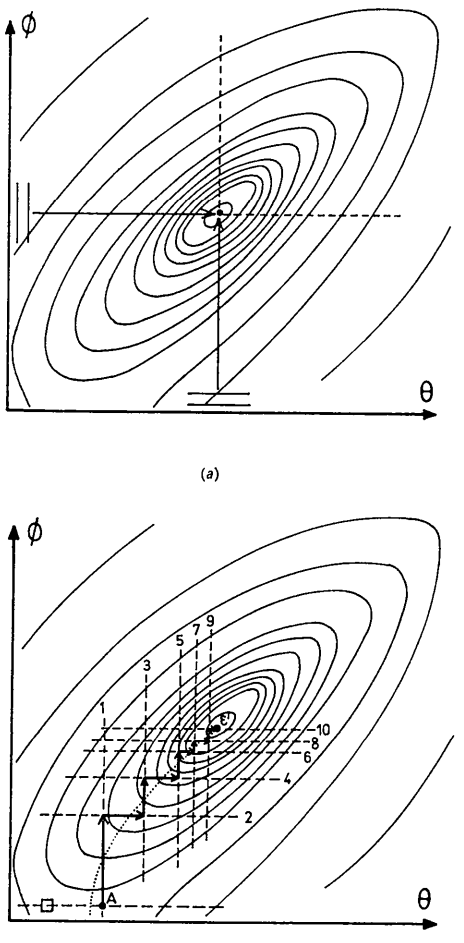

Fig. 10. The two schemes to determine maxima in the orientation functions of a reflexion. (*a*) Integral scheme. Two scans. (*b*) Point scheme. Scanning along a zigzag line.

It should be mentioned that the two χ ranges (0 to $+90°$, 0 to $-90°$ or $180°$ to $270°$) are not of the same value for practical work. At higher χ values, the goniometer head and the Φ circle itself cause shadowing in the range 0 to $-90°$. This limitation in χ is quite substantial. But even if one reduces this limitation by using special crystal supports, the absorption in the fibre below the crystal remains. On the other hand, it is important that all data including all anomalous pairs fall within the advantageous χ-range of 0 to $+90°$, if the orientation of the crystal is properly chosen. The only exception is the space group $P1$. In this case, there are no symmetry-related reflexions and, therefore, the data must be measured over the whole reciprocal sphere. As a deliberately chosen crystal orientation is possible in most cases, this scheme is also recommended for users of a full circle instrument. There is no better way of obtaining not only all data, but also with minimal absorption errors. The shadowing at higher χ values makes it unnecessary to cover the whole χ range 0 to $-90°$, which facilitates the construction of the cradle.

Another way of extending the χ range for measurements over the whole reciprocal sphere is shown in Fig. 12. It is in principle a 'crystal inverter', which orients the crystal in the opposite direction. The attachment works as shown schematically in Fig. 11(*b*). Fig. 13 shows the construction in greater detail. The change in direction is performed by a small motor. One advantage of this design is that the error figure of the cradle is that for a $90°$ motion, provided that the crystal lies within this error figure in both positions. Another advantage is that the mechanical shadowing for high χ values is quite small, as there is no obstruction by the Φ circle. On the other hand there is additional shadowing by the two L-shaped supports. This means that two sets of measurements have to be made. For the second set of measurements, the crystal has to be rotated through $90°$ and the angles at the goniometer arcs have to be reversed in order to keep the crystal in the same orientation. This means that the

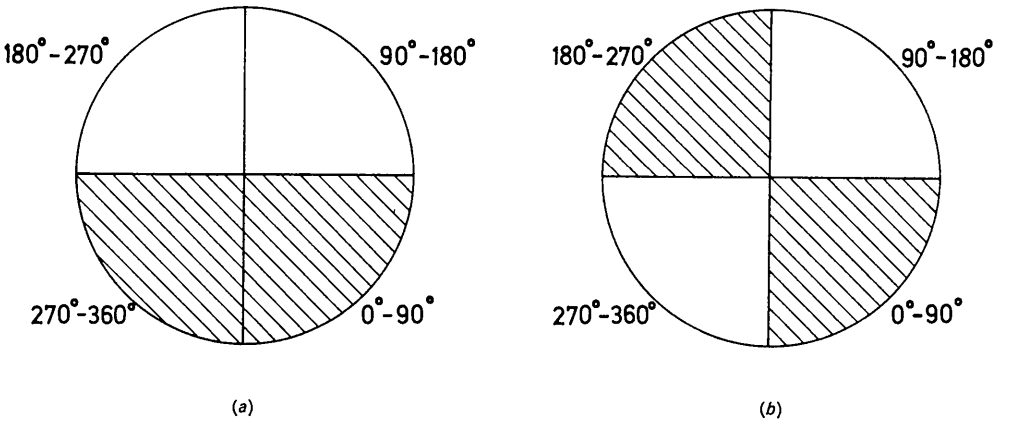

Fig. 11. Redundant regions for Eulerian cradle movements.

fine adjustment of the crystal has to be performed twice. (In an on-line instrument the small misorientation from a given position has to be determined twice.)

For the measurement of unoriented crystals it is important that as much as possible of the reciprocal sphere can be covered, as the position of the independent reflexion regions on the sphere is general and unknown. In these cases special adaptions of the crystal inverter in Fig. 13 may have certain advantages, as the goniometer head shown in this figure can be replaced by a simple and very small crystal support. As there is no shadowing by the Φ-circle, the χ range can indeed be made very large, provided that the above mentioned absorption errors caused by the fibre *etc.* are corrected experimentally (see Kopfmann & Huber, 1968).

Summarizing, one can say that there are no severe restrictions which make either the open or the closed design of the Eulerian cradle preferable from an objective viewpoint. It is to some extent a question of personal preference whether the inconvenience of having no free access to all 2θ angles without obstruction in a full circle instrument is considered more important than, for example, the inconvenience of reversing the crystal for the second half set of measurements in instruments of the type shown in Fig. 12. In addition it may be of interest to the users of existing installations with 90° Eulerian cradles that accessories of the type shown in Figs. 12 and 13 can cope with the well-known restriction to a hemisphere in reciprocal space.

The alignment of an instrument which has a precision of the order of ten times higher than that of a camera cannot be done properly with 'standard crystals' and X-rays. 500-mm auto-collimators, microscopes *etc.* have to be used. This should, therefore, be left as far as possible to the manufacturer. It must be a relic of the old pioneering days of diffractometry that many users like to turn the screws and to adjust the slides of an instrument themselves. The manufacturer, equipped with special tools and special optical procedures, can do the alignment much better. No user of an UV-spectrometer, for example, would dare to change the alignment of prisms, lenses or mirrors in his instrument. On the other hand, diffractometry is quite a new field and sometimes one has the impression that some manufacturers have the tendency to provide a basic instrument with all facilities for the user to play with. I think it is now time for the manufacturers to recognize that most users need a tool for measurements not an apparatus for alignment experiments. Of course, this makes life harder for the manufacturers. It means that they must have confidence in the rigidity of the construction and in the stability of the alignment over long periods. The simple statement 'realign it yourself, if something is wrong' is then no more valid. But, as comparison with other optical instruments shows, there is no other way out if diffractometry is really to be used on a larger scale. An excellent paper on the principles of alignment is available (Samson & Schuelke, 1967) and it therefore appears unnecessary to go into further detail here.

My final remark concerns the goniometer head. It is true that procedures to determine misorientations in an on-line instrument make goniometer heads with a setting accuracy of one hundredth of a degree unnecessary. But on the other hand it is also true that an instrument of that precision is to some extent incomplete, if it does not include the possibility of bringing the crystal into a given orientation. This is vital in off-line instruments but even in an on-line installation the small effort required for adjusting the crystal may well be repaid by the easier computation of the control routine at least in special cases. An 'angle fine adjustment instrument' with arcs which can be conveniently set within the precision of the diffractometer is, therefore, in my opinion a worthwhile accessory.

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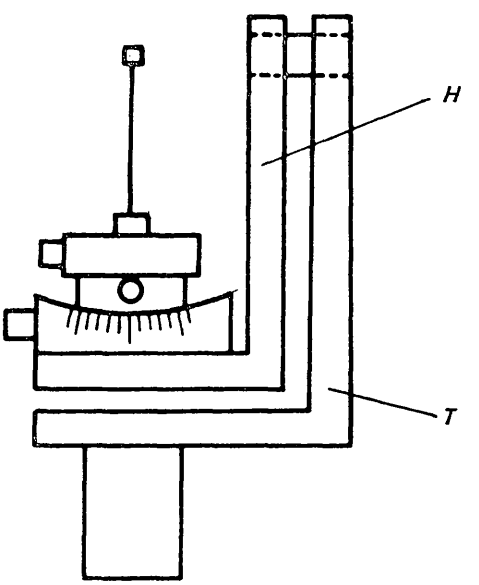

Fig. 12. Principle of the crystal inverter. The *L*-shaped support *H* can rotate 180° about the support *T*.

DISCUSSION

ROGERS: It is of considerable importance that straightforward procedures should be available for checking the alignment of diffractometers and even more particularly checking the homogeneity of the flux density at the specimen crystal position.

JEFFERY: The beam uniformity can be checked readily by taking a photograph.

HOPPE: One can also use a pin hole for scanning the beam.

LADELL: Parrish has described a method of producing very small apertures defined by cylinders (Parrish, 1966).

ROGERS: A small probe crystal is preferable, but it assumes a uniformity of response across the detector area.

FURNAS: The problems of using a pinhole to check the zero of 2θ and to map the uniformity of the beam differs from those associated with the use of a very small crystal since different wavelength regions are involved. For the latter technique, it is almost imperative to use a very small, nearly perfect, crystal and use this to study the distribution in the region to be occupied by the larger specimen crystal. Only with this procedure, is the operational wavelength distribution reproduced. Using a pinhole, the radiation detected includes scatter from the edges of the pinhole. While the Parrish design reduced this effect, it probably does not wholly remove it.

HOPPE: Scattering from the edges of a pinhole does not influence the position of the profile maximum. Of course, cylinders are better. By lowering the voltage of the tube it is easy to adjust the maximum of the white radiation of any tube to the wavelength of the characteristic radiation. Experiments have, however, shown that alteration of the spectral distribution hardly offects the profile at all.

ROGERS: The question of uniform sensitivity of detector area is of importance. We have had evidence of relatively slow 'recovery' effects evident after the scintillation detector

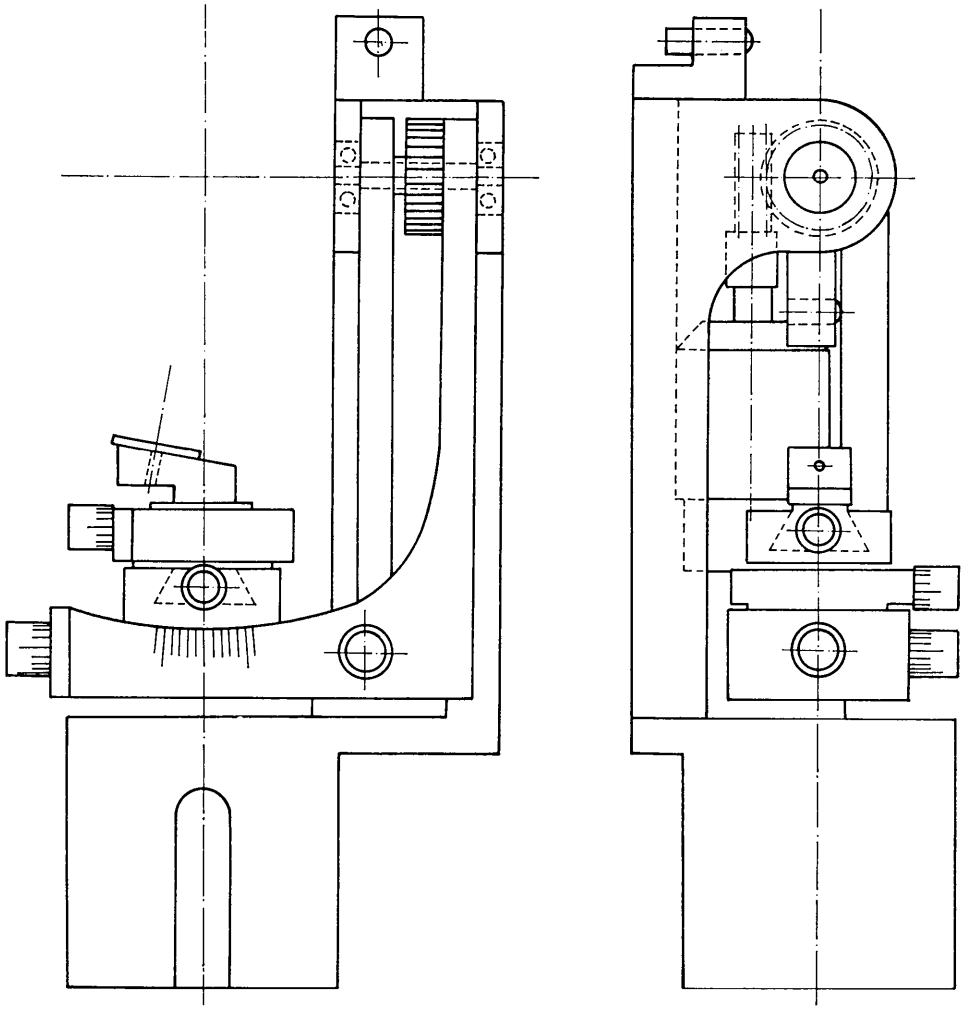

Fig. 13. Motor-driven crystal inverter equipped with a goniometer head.

has been 'swamped' by a very strong reflexion. The 5-point check system referred to by W. Hoppe has proved most valuable in detecting drifts, *e.g.* in goniometer heads due to thermal gradients. Since the operational region has been thermostatted these effects have been greatly reduced.

FURNAS: Particularly with instruments which have a long path length it is necessary to consider not only changes of temperature, but also of barometric pressure which occur during the experiment and alter the air absorption.

LADDELL: With a crystal monochromator, the high intensities referred to by Rogers do not occur and hence the probability of photomultiplier 'fatigue' occurring is correspondingly less.

JENNINGS: Our experience with photomultiplier tubes may shed some light on the point raised by Professor Rogers in connexion with changes in detector sensitivity after exposure to high count rates. We have found that such exposure can change the gain of the photomultiplier for many minutes. Such gain change can cause an appreciable fraction of the pulses to lie outside of the acceptance of the pulse height analyzer. There are similar changes in gain across the face of the photocathode and it is necessary to take cognizance of these for the most accurate work. It is our experience that the more recently designed photomultipliers minimize these effects, but do not completely eliminate them.

ROGERS: There are important restrictions in mounting triclinic crystals if there is only a quarter circle. On the other hand, the obscuration produced by the goniometer head can be quite large and may nullify the advantages of a full circle.

WOOSTER: It may be an advantage to construct the χ-circle as a full circle, even though one only uses part of it. We have constructed a small goniometer head which produces minimal obscuration.

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Error Evaluation *versus* 'On Line' Correction

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Crystallographers have enjoyed a freedom of access to computers that cannot continue. In spite of widespread pressures to automate experiments, computers are not a substitute for proper experimental technique. As a group, crystallographers are remarkably naive not only regarding the evaluation or comparison of the experimental and computational techniques which they employ, but also regarding the actual cost and value of their efforts. Some concerted thought, effort and self-education must be undertaken soon lest extravagance endanger future support.

Introduction

The art of crystal structure determination has and seems always to be of interest to at least two widely divergent groups of people. The first and far more numerous is composed of those whose interests are primarily chemical in nature, who for many years have been delighted with the ability to write structural formulae on a flat paper and for whom three-dimensional structural information is and will be a great and appreciated improvement often containing far more information than can be used, explained, or even comprehended by their majority. The second group is composed of those whose interests concern details such as bonding electrons, anisotropic or anharmonic motions of atoms, interatomic distances and angles with high precision and accuracy towards a better understanding of molecular structure and the solid state. Yet, there are a growing number of persons whose interests oscillate between these extremes and it is good that through them, we may be better able to assess the needs of each and the role to be played by this assembly of 'experts in the field' toward realistic solutions.

The convenience of large computers and the ingenuity of mathematicians and programmers have in many instances far overworked the experimental data available in an ever tightening spiral toward a 'better R factor'. There has been dangerously little attention given to the actual cost of the overall operation and the value of the result obtained beyond the intellectual and status satisfaction of 'having gotten an R factor below 5 or 3%', *etc.*

It is unfortunate, but true, as many of our colleagues are telling us at this very meeting, that our understanding of many of the experimental parameters that enter into and affect the data are so far out of our grasp that we are genuinely unprepared to do an honest job of 'on-line correction'. We are unable to describe in concise, reproducible, and understandable terms all the criteria for performing a valid experiment whose resulting data will have the meaning intended and be the object of worthwhile expenditure of effort to any specified precision or accuracy. By this it is implied, as stated before, that much expenditure of time, effort and money in the past has *not* been worthwhile. It is also implied that we are essentially unable to point a finger