A Coordinate X-ray Diffractometer Based on a Two-Dimensional Proportional Chamber and a Two-Circle Goniometer

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(Received 23 November 1981; accepted 18 June 1982)

Abstract
A coordinate X-ray diffractometer based on a flat two-coordinate multiwire proportional chamber $350 \times 350 \times 10\text{ mm}^3$ and information readout from cathode printed-circuit delay lines is described. The diffractometer is used to study macromolecular single crystals. The chamber is placed on a two-circle goniometer at distances of 300, 500 and 750 mm from the crystal. The diffractometer operates on-line with an SM-2 computer. A diffraction picture is collected in a 64K 16-bit word computer core memory with the maximum count rate of 250 000 events s$^{-1}$. The detection quantum efficiency of Cu K$_\alpha$ radiation is about 70%. The number of spatial resolution elements of a diffraction picture is $\sim 50 \ 000$, the resolution time $\sim 0.5\ \mu$s.

The general case of inclined geometry is used. The diffraction picture is collected during quasi-continuous scanning. Control of the diffractometer, data collection and pre-computing X,Z are performed at the same time. The diffractometer makes it possible to study single crystals having unit cells up to 250 Å at a resolution of 3.5 Å and to 84 Å at a resolution of 1.5 Å.

1. Introduction
Simultaneous measurements of the intensity of diffracted beams occurring synchronously from single crystals having large unit cells allow one to speed up data collection by more than an order of magnitude at an invariable decrease of sample radiation dose (Arndt, 1968; Kheiker, 1978). This makes it possible to investigate unstable objects, to decrease the number of samples to be studied and their size, to examine crystals at a smaller degree of radiation damage and, thus, to speed up the experiment and to increase its accuracy. It should be noted that increasing the intensity of a direct beam or broadening the spectral interval (in energy-dispersion diffractometers) accelerates measurements and does not decrease the dose. Simultaneous measurements of a number of reflections from crystals with large unit cells require a high angular resolution and a large enough solid angle in which a diffraction picture is detected, i.e. the effective experiment acceleration is determined by the number of spatial resolution elements of the detector.

At present, the possibilities of four types of coordinate diffractometers for single crystals are being studied: (1) with a flat multiwire proportional chamber (MWPC) ($128 \times 128$ elements) (Xuong, Freer, Hamlin, Nielsen & Vernon, 1978; Mokulskaya et al., 1980); (2) with a cylindrical mosaic detector ($128 \times 4$ elements) (Vainshtein et al., 1975); (3) with a MWPC having a spherical drift gap ($240 \times 480$ elements) (Kahn et al., 1980); and (4) with a scintillation scan TV detector ($300 \times 300$ elements) (Arndt & Gilmore, 1979). For diffractometers of the first and second types operations have overstepped the stage of preliminary development. The complete data collection from many protein single crystals with high resolution has been obtained with these devices. The collection rate is 10–30 times as fast as that of standard diffractometer (Xuong, Vernon, Nielsen, Hamlin & Cork, 1977; Arutyanyan, Popov, Kheiker, Ageev, Goganov & Shulmeister, 1980). Diffractometers of the second and third types have a fixed angular resolution.

The limiting values of unit cells for Cu K$_\alpha$ are equal to 92 Å (X and Y), 190 Å (Z), $d_{\text{min}} = 2$ Å for the second type and 153 Å (X and Y), 77 Å (Z), $d_{\text{min}} = 2.2$ Å for the third type. Diffractometers of the fourth type have some disadvantages intrinsic to analog systems (Arndt & Gilmore, 1979).

The most important advantage of coordinate diffractometers with a flat MWPC is its flexibility: the possibility of increasing angular resolution $\Delta$ with decreasing resolution of data $1/d_{\text{min}} = 2 \sin \theta_{\text{max}}/\lambda$, and vice versa, as the distance R from sample to detector increases and decreases accordingly. The main disadvantage is the decrease of angular resolution when diffracted beams are inclined. If the chamber is placed so that its central part touches the Ewald sphere, the
angular dispersion of reflection at the chamber edges, where incidence angle $\alpha = \theta_{\text{max}}$ is

$$\Delta \alpha = \frac{t \tan \alpha \cos^2 \alpha}{R} = \frac{t}{2L} \left( \frac{\lambda}{d_{\text{min}}} \right)^2. \quad (1)$$

Here $t$ is the active thickness of the chamber, $L$ is the chamber dimension and $\lambda$ is the X-ray radiation wavelength. It is practically impossible to decrease the effect of an inclined beam by increasing the chamber pressure and, as a consequence, by decreasing $t$, because of the large area of the entrance window; $\lambda$ cannot be decreased because of decreasing the efficiency. Nothing else is left, but to increase the chamber dimensions.

The coordinate diffractometer KARD-3, having a sealed X-ray tube, considered in this paper has been constructed using a flat MWPC $350 \times 350 \times 10 \text{ mm}$ (Anisimov et al., 1981).

2. Diffractometer

A block diagram of the diffractometer KARD-3 is shown in Fig. 1. The diffractometer comprises an automatic X-ray detector ARD-1, a goniometer from the coordinate diffractometer KARD-1 (Vainshtein et al., 1975), a high-voltage stabilized powder supply VIP-50-60 and a control SM-2 computer.

The multichannel automatic X-ray detector ARD-1 (Anisimov et al., 1980) is the basis of the diffractometer KARD-3. It consists of
- a flat two-coordinate MWPC $350 \times 350 \times 10 \text{ mm}$ with a system of gas mixing and HV supply;
- electronics for data readout, recording and analysis from the MWPC, interfaces for program and incremental channels and a TV-monitor display system.

A diffraction picture is collected in the computer core memory having a capacity of $256 \times 256 = 64 \text{ K}$ 16-bit words.

ARD-1 has the following main parameters: the number of spatial resolution elements is $250 \times 200$, the detection quantum efficiency of Cu $K\alpha$ radiation $\sim 70\%$ and the time resolution $\sim 0.5 \mu\text{s}$.

The programmed ALU allows one to choose an area in the MWPC and a field in the computer core memory to determine the number of pixels ($256 \times 256$, $128 \times 128$, etc.) by ordering the corresponding 'compression factor'. The diffraction picture accumulated in the computer core memory can be displayed on the TV monitor with the number of pixels and eight-grey-scale resolution. The fast operation of the computer

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Fig. 1. Block diagram of the coordinate diffractometer. The automatic X-ray detector ARD-1 is denoted by a dotted line.
and standard TV set is coordinated by means of a memory scan unit PEP-500.*

The proportional chamber is placed so that its plane is parallel to the crystal rotation axis $\omega$ and makes an angle $(90^\circ - \theta_{\text{max}})$ with the direct beam at $\mu = 0$. At $\mu = 0$ the direct beam falls in the middle of the right edge of the chamber. The normal $Y$, reconstructed from the chamber centre, lies in an equatorial plane of the goniometer, intersects the goniometer and has angle $\gamma_0$ equal to $\theta_{\text{max}}$ to the direct beam at $\mu = 0$. The chamber has adjustment shifts in two directions in the plane $X$ and $Z$ and adjustment rotations around the axis $X$ and the normal with angle $\omega_0$ equal to $\gamma_0$.

The coordinates $X$ and $Z$ are related to angles $\gamma$ and $\nu$ as follows:

$$
X = R \tan(\gamma - \gamma_0) + X_0 \\
Z = R \frac{\tan \nu}{\cos(\gamma - \gamma_0)} + Z_0.
$$

In their turn $\nu$, $\gamma$ and $\omega$ are determined by indices $hkl$ and orientation matrix $UB$:

$$
\nu = \arcsin(\lambda z + \sin \mu) \\
\gamma = \arccos \left( \cos^2 \nu + \cos^2 \mu - \lambda^2(x^2 + y^2) \right) / 2 \cos \nu \cos \mu \\
\omega = \arcsin \left( \lambda^2(x^2 + y^2) + \cos^2 \mu - \cos^2 \nu \right) / 2 \lambda(x^2 + y^2)^{1/2} \cos \mu + \arctan \frac{y}{x}
$$

$$
\begin{pmatrix}
X \\
Y \\
Z
\end{pmatrix} = UB \begin{pmatrix}
h \\
k \\
l
\end{pmatrix}.
$$

The control computer has two independent processors, a core memory of 96K 16-bit words, two discs (3 Mbytes each), and an input–output device (symbol display, line printer, photoreader, puncher and magnet tape). The computer is interfaced to the electronic apparatus by several channels: a flux of information arrives at the computer core memory through the interfacing unit and processor 1 in the increment mode; the electronics for data recording and the TV monitor are controlled by processor 2 through the duplex register and CAMAC crate controller. The diffraction picture accumulated in the computer core memory is transmitted to the TV monitor in the same manner. The goniometer is also controlled by processor 2 through the code control module, and the value of angular code $\omega$ arrives at the computer through the duplex register and processor 2.

In the fast memory (with a cycle of 300 ns) of processor 1 a special increment command is implemented, by means of which one is added to the memory cell with address $X$, $Z$ corresponding to the coordinates of the event recorded. The operation of processor 1 in the increment mode and of the MWPC electronics is synchronized in the interfacing unit. Data in this mode are transferred asynchronously. Thus, the limiting count rate in the MWPC is 250 000 pulses s$^{-1}$. The use of the fast derandomization memory having a large capacity of 16 events enables one to have a count-rate loss of 25% at the maximum count rate. Count rate losses are mainly determined by the MWPC resolving time.

Data, arriving at the goniometer from the computer, switch on and off a shutter of the direct beam and a step-drive motor, reverse the crystal rotation and change the rotation velocity. A 14-bit cyclic code of the photoelectric angle encoder is supplied to the computer from the goniometer. This encoder is placed directly on the $\omega$ shaft.

3. Method of studying crystals in the diffractometer

The parameters of an elementary crystal cell are determined outside the diffractometer. A crystal can be roughly orientated in the coordinate diffractometer using the optical method or by means of the TV monitor. Pre-alignment along the axis of a goniometer head is performed using the methods applied in diffractometers with inclined geometry: by reflections $00l$ for noncubic crystals and by reflections $hkl$ for triclinic crystals (Kheiker, 1973). The determination of $\omega_0$ is carried out by finding the intensity maximum of a strong reflection with known indices. The counter rotations through angles $\gamma$ and $\nu$ in a standard diffractometer are changed for the program displaying intensities in the region of $9 \times 9$ elements near the point with given $X$ and $Z$. For the pre-aligned crystal a list of indices $hkl$, ordered by intervals $\Delta \omega_i = 0.1–0.3^\circ$, is calculated and transmitted to the magnetic disk memory. When the crystal rotates in the interval $\Delta \omega_i$, a diffraction picture is collected in the computer core memory. Simultaneously, indices $hkl$ are read out from the disks for five intervals $\Delta \omega$ placed symmetrically about $\Delta \omega_{i+2}$. A corrected list of the $hkl$ is formed for the interval $\Delta \omega_{i+2}$ by means of the corrected $UB$ orientation matrix. Coordinates $X_{hkl}$ and $Z_{hkl}$ of the reflection centre are calculated for these $hkl$ from $\Delta \omega_{i+2}$ and corrected $UB$. Addition is per-

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*Lithocon solid state image memory/scan converter. Princeton Electronic Products Inc.

$\omega$, $\gamma$, $\mu$, $\nu$ are standard designations of angles for inclined geometry.
formed in the regions of n × m elements in proximity to the centre of each reflection (n and m vary from 3 to 7 depending on the distance to the chamber centre along X and Z). Thus, the background on the left of J_{b1} is measured for these reflections in the interval Δω_{1}. The corrected list of hkl for Δω_{1} goes sequentially through four tables which, in addition to hkl, include successively the sums of J_{b1}, when measuring in Δω_{2}, J_{b1}, J_{p1} for Δω_{3}, J_{b1}, J_{p1}+J_{p2} for Δω_{4} and J_{b1}, J_{p1}+J_{p2} for Δω_{5}. After the fifth sum of J_{b2} has been obtained, the background skew J_{b1}−J_{b2}<n(J_{b1}+J_{b2})^{1/2} is controlled. Integral intensities J_{m}=J_{p1}+J_{p2}+J_{p3} and background skew J_{b1}−J_{b2} are calculated and the statistical error σ=[J_{p1}+J_{p2}+J_{p3}+\frac{2}{3}(J_{b1}+J_{b2})]^{1/2}, together with indices hkl and background skew marker τ are introduced into the fifth table. As the cycle of measurements in the five intervals is completed, hkl, J_{int}, σ, τ of the corresponding reflections are stored on the disk. Using the technique described, the integral intensity is measured in 27–147 elements of Aγ × Δv × Δω reciprocal space with dimensions approximately equal to 2×0.2×0.2° placed in the vicinity of the calculated position of the knot centre of a reciprocal lattice. The first two dimensions are determined from a compromise between the needed resolution of neighbouring orders and resolution of data 1/d_{min}. The value of Δω_{1} is set so that the number of reflections with Δω_{hkl}>3Δω_{1} may be small. The background is measured in 18–98 elements displaced in ω to the left and right of the pack (Fig. 2). The technique resembles the procedure of measuring the integral intensity in the 512-channel diffractometer KARD-1 (Vainshtein et al., 1975). To make a correction for drift once an hour, the number of anode pulses is stored in the counter over the time of passage of given intervals of Δω.

After completing data collection for the crystal, an initial processing of the data obtained is carried out. The analysis includes making a correction for drift, introduction of correction factors for Lorentz polarization, absorption, averaging of equivalent reflections, massive collection, calculation of structure amplitude and weight modules, sorting and ordering by hkl and statistical analysis (Shulmeister, 1981). The results of the initial analysis are stored on magnetic tape and used to determine and correct the structure in a host computer.

In order to correct for drift, the ordered intervals are investigated preliminarily over a short period of time. The intensity of reflections is also measured in these intervals to monitor the crystal decay. To make an absorption correction (Phillips), transmission curves are preliminarily obtained.

The orientation matrix is corrected by finding X, Z, ω for the maxima of 10–15 reflections placed in two regions of ω different by approximately 90°. With this aim, diffraction pictures from the stationary crystal with a step of 0.05° are recorded (Xuong et al., 1973).

4. Main parameters of the coordinate diffractometer

The possibility of separate measurement of the integral intensity for neighbouring reflections recorded in the proportional chamber is determined by the distance between the reflections λR/a cos^2 z and spot dimensions depending on the chamber space resolution A_N, diffracted beam deviation from the normal at angle x, divergence of diffracted beams γ and sample dimensions P. The total value of A_N, can be obtained from the resolution curves of inclined beams (Anisimov et al., 1980). A_N, is mainly determined by dispersion of the inclined beams (1). Setting equal the distance between the spots and their dimensions at the chamber edges x=θ_{max} we get the limiting value of the cell parameter of the crystal studied a_{max} for a given sample–chamber distance:

\[ a_{max} = \frac{\lambda R}{A_{N,x,z,p} \cos^2 \theta_{max}} = \frac{\lambda R}{A_{N,z} \cos^2 \theta_{max} + R_N + P \cos \theta_{max}}. \]  

A rise of experimental collection rate in the coordinate diffractometer is proportional to a_{max} and to the data resolution squared (1/d_{min})^2 = (2 sin θ_{max}/λ)^2. With increasing R, a_{max} increases and 1/d_{min} decreases as θ_{max} = arctan L/2R. Table 1 presents the values of d_{min} and a_{max} for different sample–detector distances and values of γ (P = 0.4 mm).

In Fig. 3(a) is shown the separation of reflections from a leghaemoglobin protein single crystal for x = 27°, R = 275 mm. The second profile is obtained when the chamber is shifted by five elements, which is equivalent to the distance between neighbouring orders for a_{max} = 84 Å. This is in agreement with Table 1 for R = 300 mm, γ = 0.15°, P = 0.4 mm. The distance between the reflections and spot dimensions decreases with the decrease of the distance from the centre of the chamber. In order to keep the resolution of neighbouring reflections, the number of elements in

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Fig. 2. Measurement of the integral intensity in the diffractometer.
A COORDINATE X-RAY DIFFRACTOMETER

Table 1. Resolution of data \(1/d_{\text{min}} = 2 \sin \theta_{\text{max}}/\lambda\), spot sizes \(\Delta_{N,z,x,p}\) in pixels and limiting value of cell parameters \(a_{\text{max}}\) versus sample–detector distance \(R\) and diffracted beam divergence \(\chi\)

<table>
<thead>
<tr>
<th>(R) (mm)</th>
<th>300</th>
<th>500</th>
<th>750</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2 \theta_{\text{max}}) (°)</td>
<td>58</td>
<td>38</td>
<td>25</td>
</tr>
<tr>
<td>(a_{\text{min}}) (Å)</td>
<td>1.6</td>
<td>2.5</td>
<td>3.5</td>
</tr>
<tr>
<td>(\Delta_{N,z,x,p}) ((P = 0.4) mm)</td>
<td>(\chi = 0.08)</td>
<td>–</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>(\chi = 0.15)</td>
<td>5.4</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>(\chi = 0.3)</td>
<td>6.0</td>
<td>5.3</td>
</tr>
<tr>
<td></td>
<td>(\chi = 0.5)</td>
<td>6.8</td>
<td>6.6</td>
</tr>
<tr>
<td>(a_{\text{max}}) (Å) ((P = 0.4) mm)</td>
<td>(\chi = 0.08)</td>
<td>–</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>(\chi = 0.15)</td>
<td>84</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>(\chi = 0.3)</td>
<td>76</td>
<td>122</td>
</tr>
<tr>
<td></td>
<td>(\chi = 0.5)</td>
<td>67</td>
<td>98</td>
</tr>
</tbody>
</table>

which the intensity is added up should be reduced versus the distance to the chamber centre. Fig. 3(b) shows the separation of reflections near the centre of the chamber, \(\chi = 5°\), when the chamber is shifted by three elements, \(a_{\text{max}} = 103\) Å.

The accuracy in measuring integral intensities is determined by detector efficiency, uniformity and stability in time. When the direct beam is displaced along the chamber by \(\mu\) and its intensity is measured in a group of \(3 \times 3\) elements, the same value of intensity is obtained with a deviation of \(\pm 1\%\). The efficiency fall at the chamber edges, owing to a large absorption in air, is compensated for by a large absorption of inclined beams in the effective volume. The absorption in input cathode wires, \(\varnothing 50\) μm, placed behind a 2 mm drift gap, can be neglected for beams with a diameter larger than \(0.5\) mm (Anisimov et al., 1981). The non-uniformity of the channel width (relative root-mean-square deviation), measured by radioisotope \(^{55}\)Fe, is \(\delta_x = 2\%, \delta_y = 4\%\). The non-uniformity of the channel width in a group of \(3 \times 3\) elements is small \((<2\%)\), but its effect is excluded when measuring peak and background in the same elements.

The total instability defined by the instabilities of the chamber efficiency and direct beam is swamped by a larger instability of the X-ray apparatus and does not exceed \(0.5\%\) when making a correction for drift. The region of \(n \times m\) elements is shifted along \(X\) and \(Z\) in a coordinate diffractometer instead of rotating a standard counter through angles \(\gamma\) and \(\nu\) in an inclined diffractometer [see (2)]. When a correction depending on \(\nu\) and \((\gamma - \gamma_0)\) is made, the position of the reflection centre of gravity can be calculated with a deviation not exceeding the measured one by \(\pm 0.25\) pixel \((\pm 0.35\) mm\) independently of the reflection position in the chamber (Table 2). Such an error in the prediction of the reflection centre of gravity does not result in an error larger than \(\pm 2\%\) in measuring integral intensities for \(3 \times 3\) elements.

The total count rate of the chamber smoothly varies within \(\pm 15\%\) owing to changing absorption factor as the plate leghaemoglobin crystal rotates. Count-rate oscillations are not larger than \(\pm 4\%\) as a result of varying the number and intensity of reflections within \(\Delta \omega = 0.5\). Thus, the error due to count losses does not exceed 1% when making a correction for the number of pulses recorded in the interval \(\Delta \omega\) by a counter in a chain of the anode plane.

Fig. 4 presents the diffraction picture from the oriented leghaemoglobin crystal obtained when the crystal is rotated in the interval \(\Delta \omega = 2°\). The flat MWPC diffractometer KARD-3 has a large number of resolution elements, a high recording efficiency of X-ray radiation and is fast in operation. The given parameters allow the readout time of protein single crystals to be decreased significantly. Owing to the method of information readout from MWPC, the diffractometer is simple and reliable in operation. In the future, the MWPC time resolution

\[ \sum \sigma_{hkl} = 4\%, \quad R_{\text{sym}} = \frac{\left( \sum |J_{hkl} - J_{hkl}| \right)}{\sum J_{hkl}} = 5\%. \]

*To test the diffractometer experimentally a set of 12 000 reflections \((\text{resolution} 2.9\) Å, \(\phi = 0.6\) mm) was obtained from a single leghaemoglobin crystal \((a = 92.25, \ b = 38.31, \ c = 52.15\) Å, \(\gamma = 99°, \ B2\)).
Table 2. Comparison of the calculated and measured centroid coordinates for the beam traversing the goniometer centre (in number of pixels)

<table>
<thead>
<tr>
<th>v (°)</th>
<th>-20</th>
<th>-15</th>
<th>-10</th>
<th>-5</th>
<th>-4</th>
<th>-2</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>29</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Z_{	ext{exp}}$</td>
<td>-74.42</td>
<td>-54.52</td>
<td>-35.73</td>
<td>-17.37</td>
<td>-13.78</td>
<td>-6.89</td>
<td>0</td>
<td>7.01</td>
<td>14.20</td>
<td>17.76</td>
<td>35.61</td>
<td>54.53</td>
<td>74.22</td>
<td>95.22</td>
<td>113.43</td>
</tr>
<tr>
<td>$Z_{	ext{calc}}$</td>
<td>-74.25</td>
<td>-54.44</td>
<td>-35.61</td>
<td>-17.55</td>
<td>-13.95</td>
<td>-6.90</td>
<td>0</td>
<td>6.90</td>
<td>13.95</td>
<td>17.55</td>
<td>35.61</td>
<td>54.44</td>
<td>74.25</td>
<td>95.40</td>
<td>113.66</td>
</tr>
<tr>
<td>$\Delta Z$</td>
<td>0.17</td>
<td>0.08</td>
<td>0.12</td>
<td>-0.18</td>
<td>-0.17</td>
<td>-0.01</td>
<td>0</td>
<td>-0.11</td>
<td>-0.25</td>
<td>-0.21</td>
<td>0</td>
<td>-0.09</td>
<td>0.03</td>
<td>0.18</td>
<td>0.23</td>
</tr>
<tr>
<td>$\Delta V$ (°)</td>
<td>0.04</td>
<td>0.02</td>
<td>0.03</td>
<td>-0.04</td>
<td>-0.04</td>
<td>0</td>
<td>0</td>
<td>-0.02</td>
<td>-0.05</td>
<td>-0.05</td>
<td>0</td>
<td>-0.02</td>
<td>0.01</td>
<td>0.03</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Fig. 4. Photograph of the leghaemoglobin crystal diffraction picture from the TV-monitor screen.

will be reduced by a factor of a few units, which will make it possible to perform studies by means of synchrotron radiation.

The authors would like to express their deep gratitude to Professors B. K. Vainshtein and A. M. Baldin for their attention and interest in the work, and L. G. Makarov for his support in constructing the automatic X-ray detector ARD-1.

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