Development of a New Imaging-Plate Diffractometer (IPD-WAS) for Time-Resolved Crystallography with a Laboratory X-ray Source

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Abstract

A new imaging-plate diffractometer of the Weissenberg-camera type with an adjustable multilayer-line screen system (IPD-WAS) has been developed. Prior to data collection, the IPD-WAS automatically aligns the axis of a sample crystal and sets the multilayer-line (MLL) screens. The MLL-screen system is adaptable to a wide range of cell parameters of the sample crystals, and is advantageous for taking photographs in a wide rotation angle with a low background level. For Weissenberg photography, the IPD-WAS system uses two cylindrical imaging plates (IPs). The IPs are read two-dimensionally by rotary and transverse mechanisms. The rotary readout system has nonuniformity of response less than 1.4%, efficiency near 100% for Cu Kα radiation, a dynamic range of 1:10⁶ and spatial resolutions of 220 and 200 μm in the two directions. Owing to the good performance of the adjustable MLL screen system and the rotary readout system, the IPD-WAS achieves a data acquisition time of about 1 h with reflection data of sufficient quality (R_merge = 2.3% for a standard sample crystal), which is suitable for time-resolved X-ray crystallography. The IPD-WAS also enables faster crystal structure determinations of small molecules, including unstable crystals.

Introduction

In recent years, much interest has been focused on ‘crystalline state reactions’ (Ohashi, 1993). These reactions occur while the single-crystal form is retained.

Ohashi, Yanagi, Kurihara, Sasada & Ohgo (1981) have found that in a cobaloxime complex, [(R)-1-cyanoethyl] [(S)(-)-2-methyl-benzylamine] bis(dimethylglyoximato) cobalt (III) crystals, the cyanoethyl ligands undergo the ‘crystalline state reactions’. Since the reaction time is over two weeks, the reaction pathway can be elucidated stroboscopically by time-resolved X-ray crystallography using a conventional four-circle diffractometer. Use of the diffractometer was adequate for the study of slow reactions, even though it took one day to collect one set of intensity data.

For faster reactions such as of the dimethoxy carbonylethylcobaloxime, where the reaction time is about one day (Ohashi et al., 1995), the four-circle diffractometer is unsuitable and another type of diffractometer must be used. In this case, it is essential to use X-ray detectors that hasten data collection and improve performance compared with those of the scintillation counter of the four-circle diffractometers.

The imaging plate (IP) is a two-dimensional detector developed by Fuji Photo Film Company for X-ray radiography (Sonoda, Takano, Miyahara & Kato, 1983; Takahashi et al., 1984; Takahashi, Miyahara & Shibahara, 1985), the efficiency of which is comparable to those of photon-counting detectors such as the scintillation counter and the multiwire proportional counter (Miyahara, Takahashi, Amemiya, Kamiya & Satow, 1986). Furthermore, IPs are reusable. Their two-dimensional nature, high efficiency and reusability make them highly advantageous for the development of an automatic camera-type diffractometer for time-resolved crystallography of small molecules.

Some automatic rotation-camera-type diffractometers using IPs have already been developed to study macromolecular crystallography and are available commercially, as DIP100 of MAC Science Company, Ltd (Tanaka et al., 1990; Fujii et al., 1991), R-AXISIIc of RIGAKU Company, Ltd (Sato et al., 1992), and MAR Research Imaging-Plate Detector System of X-ray Research Company Ltd. Since macromolecular crystals require a small angular range of observable reflections, these cameras use flat IPs. For crystals of small molecules, which diffract X-rays in a much larger angular range, a Weissenberg-camera-type diffractometer with cylindrical IPs is preferable.

Sakabe (1983) developed the Weissenberg camera with a multilayer-line (MLL) screen and a cylindrical cassette for conventional X-ray films, for macromolecular crystallography. The Weissenberg mechanism allows a wide rotation of the φ axis and reduces the number of photographs necessary for full data collection. However, wide rotation of the φ axis increases the background level. The role of the MLL screen is to shade the X-ray film from the background emissions.

Our aim is to develop a fully automatic diffractometer with a time resolution of about 1 h. In order to achieve this purpose, we have developed an imaging-plate...
New Imaging-Plate Diffractometer (IPD-WAS)

The Weissenberg-camera type with an adjustable MLL screen system (abbreviated as IPD-WAS).

The main differences between our Weissenberg chamber and that of Sakabe are the MLL screen system and the fully automatic operation of IPs (Sakabe, 1991). Sakabe's MLL screen has a fixed number of fixed intervals of slits and, hence, cannot be used to study sample crystals with a wide range of unit-cell dimensions. During the crystalline state reactions, a sample crystal may change its cell parameters. We therefore developed a new MLL screen system that is automatically adaptable to any cell dimensions. In addition, our equipment includes a mechanism for fully automatic alignment of a sample crystal, which is required prior to data collection. For the cylindrical IPs, a rotary readout mechanism from MAC Science (1989) is adopted and optimized for time-resolved X-ray crystallography of small molecules.

In this paper, we describe the IPD-WAS system in detail, and report on the good performance of the rotary readout system. Some practical measurements with this new system are also described.

System Description

The IPD-WAS consists of four parts: a Weissenberg chamber including an X-ray optical system, an adjustable MLL screen system, a rotary readout mechanism for cylindrical IPs, shown in Fig. 1, and a control system. It is a relatively large piece of equipment of 140 cm length × 75 cm width × 50 cm height.

Weissenberg Chamber

The X-ray optical system of IPD-WAS consists of a rotating-anode X-ray generator with a maximum power of 18 kW and a focusing monochromator of graphite or lithium fluoride (LiF). Three rotating anodes (Mo, Ag and Cu) are provided. A singly bent graphite monochromator is designed for Mo Kα and Ag Kα radiation, and a doubly bent LiF monochromator (Sakabe, 1983) is designed for Cu Kα radiation. These monochromators are placed in vacuum, as are the collimator and the beam tunnel.

The IPD-WAS has two IPs: IP1 and IP2 (Fuji-type BA) of 314 × 300 mm. They are glued to the inner side of the cylindrical bases, which have radius 200 mm. The detection limits for the reflections at the equator layer line have resolutions of 0.93, 0.73 and 2.0 Å for Mo Kα, Ag Kα and Cu Kα radiation, respectively. IP1 moves on a transverse mechanism synchronized with the ϕ-axis rotation during Weissenberg photography. IP2 also moves on a transverse mechanism, as well as back and forth on another mechanism to avoid collision during the replacement of the two IPs.

The automatic axial alignment of a sample crystal, required prior to Weissenberg photography, is carried out by a three-axis goniometer. Two arcs perpendicular to each other adjust the crystal axis in a range of ±10° for the ϕ axis. The system is mounted in such a way that the ϕ axis of the goniometer coincides with the cylindrical axis of the IPs and the MLL screen system. The distance between the ϕ axis and the focusing monochromator in the X-ray optics is 200 mm and the X-ray path length between the monochromator and the IPs is 400 mm.

Adjustable Multilayer-Plane (MLL) Screen System

The position $z_n$ of the nth layer line from the central position of incident X-rays is given by

$$z_n = r_s/[(a/n\lambda)^2 - 1]^{1/2},$$

where $r_s$ is the screen radius, $\lambda$ is the wavelength and $a$ is the spacing of the crystal rotation axis.

The adjustable MLL screen system of IPD-WAS was composed of 18 screens, $Am$ and $Bm$ ($-4 \leq m \leq 4$), each one positioned independently along the ϕ axis by a corresponding pulse motor, as shown in Fig. 2. Each screen is composed of a pair of arcs (180 mm radius) that form a slit. The minimum distance between the two slits of $A0$ and $A1/A_{-1}$ or between those of $B0$ and $B1/B_{-1}$ is 18.4 mm. Three distinct setting modes can be selected.
In setting mode I, the number of layer lines on each screen, \( n \), is equal to the screen number \( m \). The available spacing of the crystal rotation axis is limited from 3.3 to 6.6 Å for Mo K\( \alpha \) radiation. In setting modes II and III, the number \( n \) for the \( Am \) and \( Bm \) screens is determined from

\[
\begin{align*}
n(\text{Am}) &= mM \\
n(\text{Bm}) &= mM - 1
\end{align*}
\]  

where \( M \) is the number of screen setting modes. In mode II, reflections on the even and odd layer lines are recorded on the upper and lower halves of the IP, respectively. In mode III, the symmetrically related reflections are recorded only once on the IP, except the reflections on the layer lines of \( \pm 3, \pm 6, \pm 9 \) and \( \pm 12 \), which are recorded twice on the upper half of the IP. Although setting modes II and III eliminate one-half and two-thirds of the reflections, the available spacings for Mo K\( \alpha \) radiation are expanded to 6.6–13.2 Å for mode II and to 9.9–19.8 Å for mode III.

The flexibility of the screen system yields the possibility of a wider range of spacing than 19.8 Å, as explained below. Here, we define a number, \( j \), which is the required number of photographs for a certain rotation range to observe all unique reflections. Again, for screen setting modes II and III, the layer-line number \( n \) for the \( Am \) and \( Bm \) screens at the \( k \)th photography (\( 1 \leq k \leq j \)) is determined as

\[
\begin{align*}
n(\text{Am}) &= mMj - 2(k - 1) \\
n(\text{Bm}) &= mMj - 2(k - 1) - 1.
\end{align*}
\]

Here, \( j = 2 \) or \( 3 \). If \( j = 3 \), the available spacing becomes three times larger and the screen system of IPD-WAS is adaptable to any spacing within 3.3–59 Å for Mo K\( \alpha \) radiation, coupled with the selections of the screen setting modes and the number \( j \). The corresponding ranges of screen adaptation for Ag K\( \alpha \) and Cu K\( \alpha \) radiation are 2.6–47 Å and 7.2–130 Å, respectively.

Very recently, Tanaka, Yao, Kamiya & Iwasaki (1994) have developed a new technique for crystal orientation using the flexibility of the adjustable MLL screen system. They used a different setting of screens (denoted as mode 0). The 18 screens are divided into four groups of \( A4-A1 \), \( A0-A4 \), \( B4-B0 \) and \( B1-B4 \), and the slits of each group are closed by neighboring arcs. Every other group of screens is separated in the upper and the lower halves of the system and acts as a window with the moderate width. The setting of 130 mm width could be used for the fully automatic axial alignment of a sample crystal in order that two photographs might be taken on one IP.

**Rotary readout mechanism for IPs**

We developed an IP reader with a larger acceptance of the photostimulated luminescence (PSL) because of the importance of high efficiency (Amemiya et al., 1988). In the original readout optics (MAC Science, 1989), the PSL was collected only by an aspherical lens with an acceptance of about 0.5\( \times \)sr in solid angle.

The present readout optics of the IPD-WAS system have an additional pathway to expand the PSL acceptance, as illustrated schematically in Fig. 3. We placed a window with a conical mirror in the optical path; hence, the PSL, reflected by the conical mirror, which does not directly reach the aspherical lens, can be collected through the aspherical lens and a cylindrical mirror. With this improvement, the acceptance of PSL is twice that of the original readout optics.

With this new readout scheme, the X-ray diffraction patterns recorded on the cylindrical IPs are read out by a

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**Fig. 2. Screen-setting modes of adjustable multilayer-line-screen system.** Layer lines are indicated by thick lines. Reflections in the layer lines are recorded in shaded areas by Weissenberg photography. The two dots are fiducial marks. The screen names are indicated at the top and bottom of mode I. The layer-line numbers are indicated at the top and bottom of modes II and III. The cylindrical IP is represented by a flat square for clarity.
rotary mechanism. The He–Ne layer light is converged to 120 μm in diameter by the aspherical lens. The IP surface is scanned by the focused laser beam accompanied by the rotation of the optical pipe at a speed of 4 rev s⁻¹. This rotation is synchronized by the transfer movement of the IP at a speed of 0.5 mm s⁻¹, and the intensity distribution of the PSL from the IP phosphor is again measured two-dimensionally through the optical pipe. The pixel size is 125 × 125 μm, and the readout time for each pixel is 25 μs. This rotary mechanism requires a total readout time of 10 min for one cylindrical IP.

The IPD-WAS system measures PSL intensities by means of photomultiplier tubes (PMTs). The dynamic range of the PMT is usually less than 10⁴, while that of the IP itself is over 10⁶. To cover the wide range, the IPD-WAS uses two PMTs: PMT1 and PMT2. The sensitivity of PMT1 is selected to be one-eighth that of PMT2. The PSL is divided into two PMTs by a prism mirror. The position of the prism mirror can be varied in the vertical direction to optimize the ratio of PSL intensities. The PSL ratio is, in practice, selected as 1:6. The two PSL intensities are amplified independently by readout electronics. The amplification factor for the PMT1 is adjusted to be one-third that for the PMT2. The total sensitivities between the two PMTs differ by a factor of about 100.

After a logarithmic transformation of the amplified analog value of PSL, the value is changed to a corresponding digital one by a 16-bit analog-to-digital converter (2 bytes). Each pixel has two digital values of 2 bytes from the two PMTs. The 314 × 300 mm IP includes 6 × 10⁶ pixels of a pixel size of 125 × 125 μm, and the total volume of image data for one frame is 24 Mbytes. The digital values are sent in parallel with the IP readout to a computer workstation through an EtherNet board of the IPD-WAS control system.

Control system

All IPD-WAS mechanisms are operated by an electronic controller and a computer system. The controller includes stepping-motor drivers and power supplies for all elements of IPD-WAS. The computer system consists of a main computer workstation, Sun SPARC 1+, and a subcomputer, NEC PC9801, for displaying Weissenberg photographs.

The software system developed for the IPD-WAS on the workstation consists of two parts. One is a group of software programs to control the IPD-WAS hardware, written in C by T. Mori of MAC Science Company, Ltd. The other is for data acquisition from the Weissenberg photographs, written in Fortran. First, the raw data from the two PMTs of IPD-WAS were merged into a single image with a dynamic range of 10⁶. Then, nonuniformity of IP response is corrected. The magnification factor for the PMT1 signals, the magnitude of the fading effect and the nonuniformity of IP response are determined experimentally from the performance tests of the rotary readout mechanism, as is described in the next section. After the merging procedure and correction of the image, the integrated intensities of reflections are calculated by the data-acquisition software system. Detailed descriptions of the data-acquisition software programs will be presented in a forthcoming paper (Yao, Tanaka, Suzuki, Kamiya & Iwasaki, 1995).

Performance of rotary readout mechanism

Experimental set-up

Fig. 4 shows the experimental set-up of IPD-WAS to expose cylindrical IPs with the line-shaped 333 reflection of a germanium crystal (Cu Kα radiation) as a function of the φ-axis rotation. By coupling of this geometry with the transverse movement of IPs, a rectangular area exposed by X-rays of uniform level can be formed at any position on the IP surface. By the use of PSL values from these areas, averages and root-mean-square (r.m.s.) errors of IP response are calculated simultaneously (Miyahara et al., 1986).

Using the set-up shown in Fig. 4, we first measured the intensity distribution of X-rays along the line direction using an NaI scintillation counter on the cylindrical base of IP1. Measurements were carried out at five angles of the φ axis between 38 and −24°. We obtained similar results for all measurements, and a uniform distribution within 3σ fluctuation was achieved near the center of line-shaped X-rays with a length of about 3.5 mm on the IP surface. To determine the absolute number of X-ray photons incident on an area of one pixel, the scintillation counter was scanned back and forth across the line-shaped X-rays with a uniform velocity of 0.1 mm s⁻¹. From the integrated intensities, we obtained the absolute values for the five φ angles that were in the range of

Fig. 3. Rotary readout optics for He–Ne laser and photostimulated luminescence. A dichroic mirror, B rotary mirror, C aspherical lens, D cylindrical IP, E blue filter, F prism mirror, G photomultiplier tube 1 (PMT1), H PMT2, I window with conical mirror, J cylindrical mirror. The straight and curved arrows indicate the laser light and the direction of rotation, respectively.
1813–1845 photons (pixel)$^{-1}$ for an X-ray generator current of 10 mA. The acceleration voltage of the generator was fixed at 20 kV to avoid contaminations of higher-harmonic X-rays.

Other experiments were carried out to evaluate the performance of the rotary readout mechanism in terms of the following four items: fading effect at 298 K, uniformity of response, dynamic range including uncertainty and spatial resolution.

**Fading effect**

The fading effect is a fundamental characteristic of phosphor materials which exhibit PSL phenomena (Takahashi et al., 1984). Fig. 5 shows the large fading effect of IPD-WAS. After a delay time of 80 min, the relative PSL intensity decreases to about 85% of the standard one (the PSL intensity obtained after a delay of 3 min). Furthermore, the decay rate changes with delay time. These characteristics require the use of IPD-WAS at a standardized X-ray exposure time.

Fortunately, the exposure time of IPD-WAS is determined by the adjustable MLL screen system and the width of the Weissenberg pattern for each layer line is limited in the region between 20 and 40 mm (see Fig. 2) which favors the standardization of exposure time.

For some experiments of data collection, which will be discussed later, the standard exposure time is selected to be 30 min. Based on the results in Fig. 5, we adopt a fading factor of 2.5% for the readout time of 10 min after the 30-min exposure to correct the raw images obtained from the IPD-WAS. With this correction, we reduce the error from the fading effect to less than 1% for X-ray exposure time between 20 and 40 min.

**Uniformity of response**

The cylindrical IPs and the rotary readout mechanism of IPD-WAS cause two difficulties in equipment fabrication. The first is concerned with the cylindrical surface of the IP and the second is related to the optical setting of the rotary readout mechanism.

![Schematic drawing of experimental set-up for performance tests of rotary readout mechanism](image)

Fig. 4. Schematic drawing of experimental set-up for performance tests of rotary readout mechanism. A source point of X-ray generator, B filter, C base (on the three-axis goniometer of IPD-WAS), D monochromator, E slit holder, F layer-line screen (A0/B0), G window (2.4 mm diameter), H scintillation counter. The distance between $A$ and $D$ is 550 mm and $E$ is at the center of $D$ and $G$.

The IPD-WAS makes use of an aspherical lens to converge the He–Ne laser beam, as discussed earlier. The focal length of the lens is 12 mm, and the depth of focus is only 150 μm. Therefore, the IPs must have a cylindrical surface with high precision.

As shown in Fig. 3, the optical axes of both He–Ne laser light and PSL must be coincident on the rotation axis of the rotary readout mechanism. When this criterion cannot be achieved, the PSL axis moves up and down with the rotation, causing a serious variation of the PSL ratio divided by the prism mirror.

In order to check whether these difficulties have been overcome, we measured the PSL intensities at a uniform X-ray exposure level of 3650 photons (pixel)$^{-1}$. The PSL intensities were captured by the PMT2 on 36 rectangular areas over the whole IP surface.

On IP1, the values averaged over 1000 pixels fluctuate within a r.m.s. deviation of 0.8%. There we performed a linear correction of 0.7% that increased from the bottom to the top of the IP in the laser scanning direction.

For IP2, we applied the same procedure as for IP1 and found the fluctuation to be slightly larger, 1.4%, after the linear correction of 1.2%. No correction was required in the transverse direction for both IP1 and IP2 since the fading effect was already corrected.

We also performed similar experiments for PMT1 and obtained similar results with no significant correction factor. Errors of the order of 1.4% for the uniformity of response are sufficiently small compared with the $R$ values expected for the ordinary structural analyses of small molecules.

**Dynamic range and uncertainty**

To cover a wide dynamic range of the IP, the DIP100 of MAC Science (Katayama, personal communication) and the drum scanner of the Photon Factory (Amemiya et al., 1988) have already been developed. In both cases, the PSL ratio of the two PMTs was selected to be a large value of about 100. However, a greater amount of PSL is
preferred to produce a higher efficiency for the lower dynamic range, whereas a smaller amount of PSL may cause a larger uncertainty for the higher dynamic range. The prism mirror of IPD-WAS optimizes the PSL ratio to achieve a continuous uncertainty as smooth as possible over the wide dynamic range of $10^6$.

Fig. 6 shows the linearity and the relative uncertainty for IP1. Similar results were obtained for IP2. The magnification factor for the PMT1 signals was determined from Fig. 6(a) as 137 for both IPs. These results were obtained after changing the PSL ratio from 1 to 100. The PSL ratio was varied and this was accompanied by variations of the PMT sensitivities and the amplification factors, maintaining the total sensitivity difference between the two PMTs at about 100. We selected the PSL ratio of 1:6 where the two uncertainty curves can be regarded as approximately continuous at $10^4$ incident X-ray photons (pixel)$^{-1}$, where the PMT2 is saturated.

We also found that the uncertainty curves shift easily on changing of time constants in smoothing circuits of amplifiers. Each of the two PMTs of IPD-WAS has a preamplifier near the PMT itself and a main amplifier in the control system. We tested several sets of the two time constants between 2 and 22 μs, and finally selected the value of 9 μs for all amplifiers. With this value, the uncertainty curve of PMT2 was in agreement with the line expected for an ideal photon-counting detector. However, this does not imply that the detective quantum efficiency (DQE) of IPD-WAS is exactly 100%. According to Dainty & Show (1974), the DQE can be determined by inclusion of a modulation transfer function (MTF), but the MTF was not observed in our experiments. The results in Fig. 6 only indicate that the DQE of IPD-WAS is near 100% in the range of absolute photon number from 1 to $10^4$ photons (pixel)$^{-1}$.

Although strict discussions in terms of the well defined DQE cannot be made, it is judged that the efficiency of the rotary readout mechanism is sufficiently high to fulfill the requirements for studying the time-resolved X-ray crystallography of small molecules.

**Spatial resolution**

One example of the line-spread function (LSF) along the laser scanning direction, measured with a 50 μm slit, is shown in Fig. 7. From consideration of the full width at half-maximum (FWHM) of incident X-rays, the spatial resolution in this direction is estimated as 220 μm (FWHM) for PMT2. The spatial resolution for PMT1 seems to be slightly lower. This can be caused by the nature of the logarithmic amplifier used for logarithmic transformation after the linear amplification of the PSL signals.

The spatial resolution along the transverse direction of the IP was estimated as 200 μm (data not shown), which is slightly lower than that along the laser scanning direction. This may indicate that the time constant of amplifiers, 9 μs, is slightly larger than the optimal one. We have observed that the spatial resolution along the laser scanning direction is identical to that along the IP transverse direction when the time constant is selected as 2 μs, but we do not expect identical spatial resolutions.
along both directions \textit{a priori} because the PSL signals are smoothed through the electric circuit of the control system only in the laser scanning direction. The most suitable time constant can be determined from where the fluctuations of PSL intensities are identical in both directions. However, this type of experiment requires a wider area of the uniform exposure level of over 10 x 10 cm (Ito & Amemiya, 1991).

\textbf{Practical measurements}

In order to estimate the overall performance of the IPD-WAS (e.g. data-collection time and quality of observed reflection intensity), an experiment using a ruthenium complex, C$_{41}$H$_{21}$O$_{16}$PRu$_{6}$ (Chihara & Yamazaki, 1992), was carried out in a total rotation of 181°. The total time required was 2 h, including six Weissenberg photographs. The photograph shown in Fig. 8 is one of the Weissenberg photographs taken at the $\varphi$-axis rotation of 31°.

Here, we can see the ability of the IPD-WAS to record reflections over a wide rotation range due to its adjustable MLL-screen system. In the case of the ruthenium complex, the width of the Weissenberg pattern for each layer line was 31 mm, that is, three times wider than that without the screen system. The wider rotation range or the longer exposure time of X-rays causes an increase of the background level in the Weissenberg patterns. However, the adjustable MLL-screen system has an advantage in this respect; since only one-ninth of background emissions from a sample crystal pass through the slit of 3 mm width, the background level is equal to that of a 3.5° $\varphi$-axis rotation on a screenless Weissenberg chamber. The unique data set obtained for this ruthenium complex proved to be of satisfactory quality. A total of 8415 reflections were observed, of which 6265 were independent. The merging $R$ value ($\sum (I_{h} - \langle I_{h} \rangle) / \sum I_{h}$, suffixes $h$ and $i$ indicate independent and symmetrically related reflections, respectively) was very small at 2.3%. The quality of the IPD-WAS data will be reported in more detail in a forthcoming paper (Yao et al., 1995).

When the parameters required for time-resolved crystallography are set beforehand, the IPD-WAS continues the data collection after waiting for the designated intervals. Such a measurement of 20 data sets was performed for dimethoxycarboxylcetylcobaloxime (Ohashi et al., 1995). Six photographs were taken for each data collection, and the time resolution of this experiment was 2.5 h.

The shortest time resolution attained so far on the IPD-WAS was 20 min, by Murakami (1990). He carried out sequential data collections for a cyclic trithioether with the chemical formula, C$_{16}$H$_{14}$S$_{3}$ (Iwasaki, Toyoda, Yamazaki, Fujihara & Furukawa, 1990). This crystal is unstable in air when removed from the mother solvent, trichloromethane. The well established diffraction patterns changed completely within 15 h, from that of a single crystal to that of crystalline powder. Four sets of reflection data were collected within 7 h after the extraction of the crystal from the mother solvent. Owing to the relatively small cell parameters, each reflection data set was collected from only one Weissenberg photograph at 120° of rotation. However, this experiment yielded no chemically significant results (no difference could be observed in the crystal structures analyzed using the four data sets) but it confirmed that the IPD-WAS has the capability of time-resolved X-ray crystallography with the time resolution of 20 min.

Compared with the four-circle diffractometer, the IPD-WAS is limited in observable reflections. It has a blind region in which reflections around the $\varphi$ axis are never recorded on the IPs. Furthermore, since the IPD-WAS has a limited number of layer-line screens and a limited size of the IP, the number of observable reflections on the IPD-WAS may be insufficient for the determination of unknown organic structures. In spite of these disadvantages, the IPD-WAS has been proven to be an excellent tool for routine structural analyses of two organic compounds (Iwasaki et al., 1996).

The short measurement time of the IPD-WAS allows collection of a full data set of unstable crystals before any changes appear on a sample. By utilizing the IPD-WAS, Iwasaki et al. (1995) succeeded in determining the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{weissenberg.png}
\caption{Typical Weissenberg photograph taken by IPD-WAS. The $b$ axis of a sample crystal (see text) was aligned along the $\varphi$ axis, and the screen setting at mode III and the number $j = 1$ were selected for Mo $K\alpha$ radiation. The exposure time was 19 min (X-ray generator, 48 kV, 200 mA). Two solid arrows indicate fiducial marks.}
\end{figure}
crystal structure of an unstable bismuth compound with the chemical formula, \((\text{CH}_3\text{C}_6\text{H}_4)_3\text{BiCl}_2\).

Considering the future aspects of the IPD-WAS, we would like to mention the need for improvement in the free mounting of the sample crystals. The present IPD-WAS requires an axis of a sample crystal to be mounted on a goniometer head within \(\pm 20^\circ\) around the \(\varphi\) axis. To eliminate this inconvenience, the present three-axis goniometer should be replaced by an unrestricted goniometer, such as the Eulerian type or the \(\kappa\) type used in four-circle diffractometers. Developments of new IP diffractometers with the \(\kappa\)-type goniometer have already been started independently by F. Iwasaki of the University of Electro-Communications (personal communication), and by Y. Ohashi of Tokyo Institute of Technology (personal communication).

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