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Small Molecule Single Crystal Diffractometry *

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In this talk emphasis will be on the use of "standard" diffractometers under the control of "standard computer programs. The factors which affect the various decisions required of an operator will be discussed in general terms but few how-to procedures will be advocated.

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A. The Incident Beam:

(1) Radiation: X-ray tubes with either copper or molybdenum targets are routinely available in many laboratories and so, apart from the interjection that "neutrons really are better" (no Z dependence of f , no radiation damage), this discussion will be limited to these two sources.

Table 1 compares some of the properties on which the choice of radiation is usually made. The factor of 8 in the first line arises because the reflectivity of a sample is proportional to the cube of the wavelength. Over an energy range in which no absorption edges occur the absorption coefficient for a single species also varies as λ^3 . In combination these two effects would result in observed intensities using CuK_α radiation which are larger than those using MoK_α X-rays by a factor which is slightly less than 8 for the same sample crystal and flux of characteristic radiation.

The observed intensity is related to the structure factor by $I \propto F^2 \cdot L_p$ and so the behavior of the L_p term is reflected in the observed count rate. Whenever $2\theta_{\text{Cu}}$ is less than about 127° (ignoring partial polarization of the incident beam) for a given set of diffracting planes the L_p term will favor the datum collected with MoK_α radiation. At higher angles however the L_p factor favors data collected with the longer wavelength and this fact will enhance the weaker data.

For compounds which actually diffract to very high angles the increased resolution (and hence much larger number of data points) available with MoK_α may be important for the analysis contemplated (e.g. charge density studies) and so this would be the radiation of choice. Conversely the "expanded" reciprocal lattice offered by CuK_α implies that the reflections will be better resolved and this may be a determining factor for large unit cells ($d > 20 \text{ \AA}$).

Using CuK_α radiation the effects of anomalous dispersion may be detectable for elements heavier than oxygen but with MoK_α X-rays this effect is small unless $Z \geq 16$. These facts have implications for absolute configuration studies, data averaging procedures, potential coordinate errors and possible phasing techniques which should be weighed before the wavelength is selected.

If the sample contains an element with an absorption edge corresponding to an energy less than that of the incident radiation X-ray fluorescence will occur when electrons fall into the orbital vacancies left by the ejected electrons. This occurs very frequently but is markedly worsened by a close match of incident energy and absorption edge--e.g. a cobalt-containing sample with CuK_α X-rays. For the lighter elements the fluorescent radiation is soft enough to be absorbed in the air path and by the protective window of the detector but high background levels will add noise to the experiment if (for example) elements of the first long period (Ca-Co) are illuminated with CuK_α radiation. The three effects of anomalous dispersion, absorption and fluorescence are intimately related and if, for example, an experiment requires a large Δf this may only be obtained at the expense of increases in the other two effects.

The most energetic (shortest wavelength) radiation produced by an X-ray tube is given by $\lambda_{\min} = 12.4/V_{\text{(kV)}}$. The voltage required to eject a K electron from a given target is obtained by substituting the wavelength of the K absorption edge (not the K_α emission wavelength) into this expression. For Cu and Mo these critical voltages are given in Table 1. The greatest intensity of the characteristic (K_α) line relative to the white radiation occurs when $V/V_c \approx 4$. Normal operating potentials are in the 40-50 kV range and so the spectrum emitted from a molybdenum tube is more contaminated with white radiation than is that from a copper tube. As a corollary of this observation it is worth noting that the K_β line for Mo is nearer the peak of the continuum than in the Cu case and so a β filter will remove a larger fraction of this unwanted radiation. The higher potentials sometimes used for Mo tubes, in order to increase the V/V_c ratio, also result in an increased hardness of the white radiation.

The data on comparative damage to crystals when irradiated with X-rays of different energies is scant but it may be expected that the better absorbed radiation will produce the most damage and this supposition would always favor Mo X-rays. The potentially greater data-collection rate with CuK_α may partially alleviate this problem.

(ii) Collimators: The simple purpose of these devices is to limit the amount of radiation emerging from the source to just that which allows all parts of the crystal to 'see' all parts of the source. To evaluate the parameters which must be set in order to satisfy this requirement the operator must consider the size of the source, the largest dimension of the crystal, the crystal to source distance as well as the diameters and positions of the collimator components. In practice, because the choice is limited to those devices supplied by the manufacturer, the collimator which is reputed to provide a plateau which is slightly larger than the crystal is selected.

(iii) Filters: A thin metal foil (0.0003-0.004" thick) made of an element with atomic number just less than that of the target material will absorb the K_β peak much more strongly than the K_α and, as well, prohibit a substantial fraction of the white radiation from reaching the sample if it is placed on the source side of the crystal. If the filter is placed on the detector side of the sample a "cleaner" experiment may result, because the filter will absorb most of the fluorescent radiation, but the crystal will be subjected to a great deal of unnecessary (and probably harmful) radiation.

In the case of a copper tube the most suitable filter material is nickel with thicknesses in the range 0.0003-0.001" commonly being used. For molybdenum radiation β filters fabricated of either Zirconium ($\lambda_{K \text{ edge}} = 0.68877 \text{ \AA}$) or Niobium ($\lambda_{K \text{ edge}} = 0.65291 \text{ \AA}$) are appropriate. It must be realized, when using β filters, that the background on the low θ side of the peak is intrinsically discontinuous and this may engender serious difficulties in estimating the background for those reflections at sufficiently low angles for the absorption edge to occur within the scan. If this is a problem the low- θ background can be obtained by extrapolation from the high- θ side. Because the Nb edge is further from the MoK_α peak than is that for a Zr filter this problem will occur less frequently and Nb is preferred for this reason.

(iv) Monochromators: In the current context this term has come to imply a small slab of some material (usually Pyrolytic graphite) which, when appropriately oriented in an X-ray beam, will eliminate all except the desired radiation and will pass this characteristic with good efficiency. To a first approximation this is correct, but not all aspects of the experiment are made better by the use of a graphite monochromator (for example).

(a) The intensity profile of the beam is highly direction dependent. If the diffraction vector of the monochromator is in the equatorial plane of the instrument (Syntex P2₁ geometry) then a horizontal traverse of the beam may reveal a plateau of only a few tenths of a millimeter in extent. A vertical profile will indicate a much longer region of constant intensity. For the geometries of the Picker and Enraf-Nonius CAD4 diffractometers (diffraction vector of monochromator in a plane perpendicular to the equatorial plane) the vertical direction through the beam will show the narrow profile.

The fact that the beam is so narrow in one direction places a stringent upper limit on the size of crystal which may be used.

The intensity profile of the beam may be examined either by taking a pinhole photograph or by translating a small probe crystal through the beam and measuring the diffracted intensity. If significant fluctuations are noted, over that portion of the beam intercepted by the sample crystal, these are probably due to local conditions over small regions of the monochromator and may be alleviated by translating the crystal in its plane.

(b) It has been shown that graphite crystals behave neither as if they were ideally perfect nor as if they were ideally mosaic and this introduces an uncertainty in the form of the polarization correction. For molybdenum radiation the error introduced by assuming the wrong form of the correction factor is about 1% (maximum at $2\theta = 90^\circ$) but this may be as high as 5% for CuK_α . Again this effect may be due to the fine structure of the monochromator. Ideally the degree of perfection should be determined whenever the experimental set-up changes significantly but in practice the assumption of something between zero and 50% perfection seems to be common.

Both β filters and graphite monochromators will allow a significant fraction of the $\lambda/2$ component in the spectrum to be passed. If the energy discrimination of the detector circuitry is weak this may have important consequences for the data analysis.

Table 1. A comparison of some properties of CuK_α and MoK_α X-rays

	Copper $\bar{\lambda} = 1.5418 \text{ \AA}$	Molybdenum $\bar{\lambda} = 0.7107 \text{ \AA}$
Reflectivity	1	1/8
Absorption coefficient	1	1/8
Resolution (d min)	$0.77 \text{ \AA}$	$0.35 \text{ \AA}$
Anomalous dispersion f'' detectable	$Z \geq 8$	$Z \geq 16$
Fluorescence OK	$Z < \text{Ca}, Z > \text{Co}$	$\text{Ca} \leq Z \leq \text{Co}$
Radiation damage	Related to absorption	
Detection efficiency NaI(Tl)	0.95	1.0
V crit	8.98	20.0

B. The Crystal

(i) Selection: The eventual outcome of the experiment is probably more sensitively dependent upon this step than upon any other. The chosen crystal should have an appropriate, size ($t_{\text{opt}} = 2/\mu$), shape (consider the plateau region of the beam at the crystal) physical perfection (no cracks, inclusions or vacancies) and singularity. Careful photographic and microscopic examination of the sample crystal is very strongly recommended.

(ii) Mounting: For air-stable materials (or those that can be stabilized by a thin film of oil, plastic, etc.) the normal mount on a glass fibre is quite satisfactory if both the adhesive and the fibre are unobtrusive. This requires that the crystal be mounted on the END of a THIN fibre with a SMALL amount of an X-ray TRANSPARENT adhesive with good mechanical STABILITY. The rigidity of thin fibres may be greatly enhanced by glueing a thick support fibre to the thin one and embedding this assembly in a brass nib with molten wax. A little foresight in choosing the height of the mount will often obviate remounting the crystal when it is found to be too high (or low) for the diffractometer. A simple homemade height jig is of great assistance in this. Materials or experiments which require that the sample be enclosed within capillaries, cold gas stream, cryostats, ovens, etc. pose much more difficult problems which often must be solved on an individual basis.

(iii) Centering: The only requirement here is that the position of the crystal be invariant as the various setting angles of the goniometer range through their motions. For fibre-mounted crystals on diffractometers equipped with microscopes this requirement is relatively easy to satisfy. If the crystal is obscured from view however substantial difficulty may be experienced in achieving the above requirement.

At Brookhaven, where neutron diffraction data is routinely collected with the crystal inside a closed cycle helium refrigerator, a simple procedure has been developed which permits this centering. The procedure has its basis in the W. C. Hamilton's analysis in the International Tables Vol IV. Briefly it is as follows

For a reflection near $\chi = 90^\circ$ two reflecting positions are chosen for which the "x" and "y" motions which control the crystal's translation are each in the plane of the χ circle. These two positions then differ in ϕ by 90° e.g.

	2θ	ω	χ	ϕ
1.	20.00	6.00	89.43	-30.0
2.	19.90	10.76	86.23	-120.0

From these two positions two more are generated by changing the sign of χ and adding 180° to ϕ . These positions will permit the Friedel pair of the first reflection to be detected

3.	20.00	6.00	-89.43	150.00
4.	19.90	10.76	-86.23	60.00

Using tight collimation, each of these four positions is then centered. The following results were obtained in this example

1.	19.89	5.95	89.68	- 30.00
2.	19.91	10.69	86.52	-120.00
3.	19.98	5.95	-88.72	150.00
4.	19.98	10.68	-85.64	60.00

Now $2\theta_1 - 2\theta_3 = -0.09^\circ$ and $2\theta_2 - 2\theta_4 = -0.07^\circ$ and so $\Delta 2\theta_{\text{mean}} = -0.08^\circ$. This number represents a 'Z' error (at $\chi = 90^\circ$ 'Z' is along the diffraction vector) which can be translated into an actual translation if the parity of the diffractometer and the source/crystal and crystal/detector distances are known. Experimentally it is better to learn the angle/distance correspondence by experience and to discern the direction of motion from the fact that an erroneous positioning of the crystal in the positive direction of the diffraction vector will produce 2θ value which is apparently too large.

The χ_1 & χ_3 values of the centered measurements should sum to zero (as should χ_2 & χ_4). The fact that they sum to 0.96 indicates a significant error in the translation which is perpendicular to the diffraction plane at ϕ_1 and ϕ_3 . The magnitude of the error is given by

$$|\Delta X| = \Delta \chi \cdot 2 \sin \theta \left(\frac{1}{R_s} + \frac{1}{R_c} \right)$$

Where R_s and R_c are the distances from the crystal to the source and the counter. In practice, notice is taken of the fact that the apparent χ offset is dependent upon the diffraction angle and the adjustment is made empirically. Note that in this method if the crystal is offset above the equatorial plane for one setting (e.g. χ_1) then it is also above the plane for the derived setting (χ_3). In this example numerically larger values of χ imply increasingly larger displacements of the ϕ axis from the bottom of the χ circle and so the direction of the translation adjustment required is such as to lower the position of the crystal.

This procedure is iterative because the error offsets do not lead to simple one-parameter equations in the setting angles. It must therefore be repeated until tolerably low errors are detected.

(iv) Defining the orientation: There are two components to this operation. Firstly optimum setting angles must be carefully measured for a group of reflections and then a set of cell and orientation parameters must be derived from the setting angles.

The methods used by diffractometer operators for determining optimum setting angles are usually just those provided by the manufacturer. The parameters which are adjustable may be limited to only:

(i) The maximum size of limiting apertures. (The minimum size may be computer controlled as part of the centering process.) These should be set as small as possible while still ensuring that sufficient intensity is seen by the detector to allow the centering procedure to work.

(ii) Limiting the amount of cross-fire in the incident beam. In X-ray diffraction the horizontal divergence is diminished by decreasing the take-off angle to $2-3^\circ$. In the neutron case both vertical and horizontal soller slits are used to provide better definition both in and perpendicular to the diffraction plane.

The best definition of the relationship between the crystal lattice and the axial system of the goniometer will be obtained when intense high-angle reflections which are well distributed in reciprocal space

are used for centering. Often, of course, it is not known a priori which high angle reflections are sufficiently intense to use and so one must resort to either the hunt-and-peck method or bootstrap ones way out in reciprocal space in shells, or better yet TAKE PHOTOS!

In the former case it is worth noting that symmetry equivalent reflections are quite acceptable here and so, in all except the triclinic case, it is usually only necessary to find three or four suitable reflections.

If one is constrained to use low angle reflections on which to base a data collection at higher angles then it may be necessary to remove some of the inherent χ insensitivity at low angles by performing an auxiliary scan. The comparative insensitivity to χ arises of course because in a χ scan the reciprocal lattice point moves on an arc which is tangential to the sphere whereas in an ω scan the reciprocal lattice point moves through the sphere. By choosing a second position which is rotated 90° around the diffraction vector from the first, centering at this second position as well, and adding this second determination to the list the direction of the diffraction vector is thereby better defined (see figure). This procedure was first pointed out to me by Dr. L. C. Andrews who described it at a workshop meeting in 1977. An earlier development of a similar method has been presented by Dr. R. A. Sparks and the necessary software for its implementation has become available from Syntex. The Enraf-Nonius CAD4 instrument does not have a χ circle and so cannot perform these inherently imprecise χ scans. The rather neat trick of using a horizontal scan of the detector to define a vertical displacement is accomplished with a pair of slant slits. By inserting a slant slit in front of the detector, driving this assembly through the diffracted beam and examining the resultant profile for the early or late appearance of the peak, height errors can be detected and corrected for. The insensitivity to χ error is not eliminated by this procedure of course.

Once a list of angular coordinates for centered reflections has been obtained some optimization procedure must be invoked in order to obtain the 'best' cell parameters and orientation matrix from the data.

If the operator has the option of assigning weights to the various data points this should be done here in a realistic manner (e.g. by giving high σ_ϕ 's to the reflections measured near $\chi = 90^\circ$ and high σ_χ for reflections measured at low θ).

Some software systems permit the operator to constrain some unit cell parameters to have special values or to be equal to functions of other parameters. The least-squares methods programmed for the CAD4 and P2₁ instruments however treat all crystal systems as triclinic and this same procedure has been programmed for the neutron diffractometers at BNL. The advantage of this method is that it is without prejudice and does yield an independent estimate of the standard deviation in the cell parameters, in all except the triclinic case, by noting how close the angles (for example) come to their required values.

Modern X-ray diffractometers allow the operator to mount a crystal for which even the unit cell is unknown and after executing a few simple commands eventually determine both the dimensions and orientation of the unit cell. This may be considered a third component to the operation of defining the orientation which precedes the first two. This facility is a significant advance in the art of diffractometry and is a considerable convenience to the operator. The indiscriminate acceptance of the results of an auto-indexing routine is very unwise however for three reasons

(a) Entirely plausible but incorrect results will be obtained if, by accident, certain classes of reflections (e.g. $hk\ell$ with ℓ odd) were not present in the list of reflections.

(b) Only the dimensional properties of the lattice are considered. The symmetry must be guessed from the lattice dimensions or determined by examining lists of reflection intensities.

(c) The software is (almost) guaranteed to produce a primitive cell. The symmetry of the primitive lattice will be lower than that of the "true" lattice.

The ability to execute a simple command and thereby set up the diffractometer to take a limited oscillation photograph has been provided in the Syntex system. Examination of the three axial oscillation (not rotation) photographs will quickly indicate both the true lattice repeat and the diffraction symmetry. The Enraf-Nonius system does not provide

the facility in a simple way but does offer an array of geometry translation commands which may be used to manipulate the goniometer appropriately. The required condition is for a real crystallographic axis to be oriented vertically so that omega may be oscillated to take the picture. Diffractometers operate exclusively in reciprocal space and the orienting of a real axis must be accomplished by subterfuge. If we wish to oscillate around c then the commands HC 1,0,0 and HC 0,1,0 are typed. The output of these commands are the coordinates in an orthogonal system of the a^* and b^* axes. Now the c axis is in the direction of $a^* \times b^*$ and so the operator must (by hand) form the cross product of the above two vectors. These three quantities are then entered with the CB command. The angles output will be θ , χ and ϕ which will place the c axis in the equatorial plane and in the plane of the notional χ circle at the bisecting position. The operator must then add (or subtract) 90° to χ and enter these new values with a BP command. The goniometer should then be positioned with c-vertical and the photograph may be taken.

These photographs will determine the primitivity (or otherwise) of the chosen lattice but they offer no information on whether or not the highest symmetry Bravais lattice has been found. This question is addressed either by examining the Niggli matrix of the dot products of the lattice vectors or by repeatedly transforming the chosen cell according to an algorithm designed to detect higher symmetry lattices. Some diffractometer systems provide assistance in detecting the 'true' lattice.

C. The Diffracted Beam:

(1) Aperture sizes: Just as the size of the incident beam collimator if chosen to allow the sample to interact with X-rays emerging from all parts of the source but minimize the volume of irradiated air surrounding the crystal the diffracted-beam-limiting devices should be set to accomplish a similar purpose.

In the vertical direction the experimental components which define the minimum angle subtended at the crystal by the edges of the aperture are--the height of the source, the height of the crystal and the crystal mosaicity. It is to be noted that the last two of these components are very likely to be dependent upon the orientation of the crystal. The aperture size, which will almost always remain invariant throughout the data collection, must therefore be set for the worst case. As always some allowance must be made for errors and so the height of the aperture must be set somewhat larger than that which just fails to dip into the peak of the profile of the tallest reflection.

In the horizontal direction, the width of the source, the largest width and the largest mosaic spread of the crystal are joined by the spectral dispersion as components of the width of a reflection. In addition the required width of the horizontal aperture may depend the kind of scan made. Again because of the anisotropy of the mosaic spread and crystal size the best method for determining the basic width is by experiment. A plot of net intensity vs aperture width should rise smoothly and plateau out at large aperture sizes. Curvature in the background can complicate these simple plots and any unusual features should be investigated.

The final hardware component of the diffraction experiment is the detector crystal and its associated circuitry. Apart from the simple purpose of counting the X-ray quanta this assemblage is usually charged with the responsibility of ensuring that only pulses of the appropriate energy (wavelength) are detected.

By the standards of today's technology these X-ray counting chains are quite unsophisticated (and therefore highly reliable?) but operators often do not feel inclined to undertake the periodic routine performance checking that is required. Failures of this system range from catastrophic through insidious to trivial with the second category being the most harmful.

The hour or so invested in checking the energy discrimination (i.e. resetting the window) will often indicate the beginnings of any degradation in performance. A system in good working order should have a resolution ($\text{FWHM} \div \text{Peak position}$) of ~ 0.5 . If a statistic significantly larger than this is discerned this may indicate that the analyzer is not completely removing the $\lambda/2$ components from the diffracted beam. A simple check on this function is to scan a portion of reciprocal space which would be expected to produce a diffracted ray only from the $\lambda/2$ component. In this regard systematic absences are not appropriate because of the possibility of multiple scattering. However, if, for example, the $1.1.1(\lambda)$ reflection is strong then the $1.1.1(\lambda/2)$ may be detectable and a scan of the $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}(\lambda)$ reflection should reveal if any $\lambda/2$ contributions are being passed. A short-term cure for this occurrence is simply to narrow the acceptance window.

Detector circuits sometimes spontaneously generate high-intensity spikes of pulses with clearly deleterious effects on an experiment. Spikes of modest intensity are more dangerous however because they are less obvious. By leaving the shutter closed and feeding the analyzer output into a strip-chart recorder overnight it is possible to detect the occurrence of such pulses.

For several reasons, e.g. age, being partially blinded by too many photons or because of holes developing in the protective covering

of the detector crystal the system may gradually lose efficiency. Advanced warning of this may be given by a decline in energy resolution but a simple check with a standard source (e.g. ^{55}Fe) is a more valid test if the source can be positioned reproducibly.

At high count rates all detector systems lose efficiency due to coincidence of pulses. The correction for this effect may be--

(a) experimental: attenuators or lowered voltage/current on the tube (both of these will change the spectrum seen by the detector but no serious error should result) or (b) electronic: circuits exist which examine the pulse shape for overlapping trigger pulses and add-in an appropriate number of counts or (c) computational: a parabolic approximation to the observed/actual count rate curve is made which accommodates some of the non-linearity.

Coincidence losses may be expected to occur if more than about 25000 cps reach the detector and the need to correct for them is therefore quite common.

D. Choice of Scan

The objective of the experiment is to obtain an estimate of the integrated intensity for each one of the unique and accessible reciprocal lattice points. Burbank has defined this integrated intensity for the case of a small crystal fully bathed in a beam as "a measurement of all the Bragg reflected radiation that is produced when a crystal is rotated sufficiently through the reflecting position, at a uniform angular velocity, for all the mosaic blocks in all parts of the crystal to have the opportunity to diffract some specified spectral distribution from all parts of the source".

Three methods have been generally used in diffractometry to estimate the integrated intensity --

(i) The fixed position measurement. This technique does not in principle violate the definitions requirement for a rotation because this can be simulated with a convergent primary beam. The speed with which data can be collected with this method makes it attractive and it has been used for this reason. Unfortunately peak widths, α_1/α_2 separations and rocking range increase as the scattering angle is increased according to the formula

$$\Delta 2\theta = \frac{360}{\pi} \cdot \frac{\Delta \lambda}{\lambda} \cdot \tan \theta$$

For CuK_α and MoK_α the quantity $\frac{360}{\pi} \left(\frac{\lambda_{\alpha_1} - \lambda_{\alpha_2}}{\lambda_{\alpha_2}} \right)$ has the values 0.00247 and 0.00603 respectively. These figures imply that the necessary source widths to just barely allow the full peak-to-peak valley between the α_1 and α_2 components to be collected are 0.087, 0.461 and 1.176 mm for $2\theta_{\alpha_1} = 10^\circ, 50^\circ$ and 100° respectively using the Copper K_α doublet. In the Molybdenum case the corresponding widths are 0.209, 1.124 and 2.873 mm. The knowledge that (i) one wants to use a wavelength range which is several times that between the α_1 and α_2 maxima, and (ii) a line source 10 mm long when viewed end on at a take-off angle of 6° appears only 1.05 mm long, clearly indicates that impractically large source sizes are required at even modest scattering angles. This difficulty may be partially alleviated by the use of calibration curves but for accurate work the stationary crystal-stationary counter technique is not recommended.

(ii) The Omega Scan. Because the detector does not move to a position where it can accept photons attributable to a reciprocal lattice point adjacent to the one under consideration this type of scan is preferred for closely spaced reciprocal lattices.

An important use of the ω scan is, in conjunction with a narrow detector aperture and diminished beam crossfire, to detect orientation faults in the sample crystal and to evaluate the mosaic spread of the specimen. The careful examination of a few reflections, each at several ψ values, should reveal something about the quality of the crystal which may impact upon the data collection.

The usual conception of an ω scan is that it is "orthogonal to the direction of the reciprocal lattice vector" and so cannot yield an estimate of any white radiation streak which may lie under the peak (along the direction of the r.l. vector). This is not strictly true and it may be fairly easily demonstrated that, if a large aperture is used, an ω scan may contain separate estimates of the "background" and "white radiation" levels. As a corollary it must be noted that the increasing width of reflections employing the "specified spectral distribution" as θ is increased must be accommodated in the ω scan case by an increasing width of the detector aperture. This dispersion factor varies as noted above and in practice means that, for the δ filter or balanced filter cases, prohibitively large apertures (tens of degrees) are required at large scattering angles. For this reason the ω scan technique has been discouraged for high resolution data collection if the primary beam is monochromatized by filtration.

For the case of radiation which has been monochromated by reflection from a graphite crystal this argument is partially vitiated by the narrower band pass of the device. For the purpose of a concrete example the wavelength range $4(\lambda_{\alpha_2} - \lambda_{\alpha_1})$ was chosen to calculate the aperture widths required. For the CuK_{α} and MoK_{α} cases the assumed wavelength ranges imply $\Delta\lambda/\lambda$ values of 0.00986 and 0.02403 respectively. The corresponding values for Ni/Co and Zr/Y filter pairs are 0.0779 and 0.05466. Using the former numbers minimum aperture widths of $0.3_{2\theta=10}^{\circ}$, $1.8_{2\theta=50}^{\circ}$, $4.7_{2\theta=100}^{\circ}$ and $8.5_{2\theta=130}^{\circ}$ mm are required for CuK_{α} X-rays. In the MoK_{α} case the

widths are 0.8, 4.5 and 8.1 mm for $2\theta = 10, 50, 80^\circ$ respectively. In the ω scan case the mosaic width of a reflection influences the scan width but not the aperture width and so this technique is appropriate for highly mosaic samples at low scattering angles.

(iii) The $\omega/2\theta$ scan. In this technique the dispersion-related increase in the peak width at high scattering angles may be accommodated (in principle) by simply increasing the scan width. This fact, together with the greater ease with which the characteristic peak may be extracted from the scan profile has made the $\omega/2\theta$ technique the most popular for routine work.

The problem of dispersion remains however. The increasing divergence of the α_1 and α_2 reflections at increasing scattering angles is usually allowed for by a $\Delta 2\theta$ increment of $(360/\pi)(\Delta\lambda/\lambda)\tan\theta$. This term however does not allow for the fact that the "specified spectral distribution" also covers an increasing range of 2θ as the scattering angle increases. For filter-monochromated radiation this increased range of 2θ may be much greater than a usual scan width. For example, using the Zr and Y absorption edges to define the $\Delta\lambda$ range in the MoK_α case necessitates a scan width of over 6° at $2\theta = 80^\circ$. For a Ni-Co filter pair the scan widths are over 6° if $2\theta > 55^\circ$. For graphite monochromated radiation the required 2θ scan ranges are significantly smaller. For the assumed $4(\alpha_2 - \alpha_1)$ range of wavelengths the required $\Delta 2\theta$ will be less than about 3° except at very high angles.

It is to be noted that the aperture widths and scan ranges given above are just those which are necessary to accommodate the dispersion-related broadening. Effects related to the size of the sample crystal and the source as well as any mosaic spread broadening are in addition to that of dispersion.

(iv) Crystal/Detector scans with a variable coupling. Opinions on this subject will be solicited from the audience.

E. Data Validation.

Because of the substantial amounts of time and money spend in analyzing crystallographic data sets it is very advisable to have both on-line quality control of the experiment and the ability a posteriori to detect and (possibly) correct for experimental inadequacies. Several methods are commonly used to provide input into these validation procedures.

(i) Periodic checking of a small number of designated monitor reflections. Although often reported as the use of "standard reflections to check the stability of the crystal" this procedure is more properly one of using monitor (reference) reflections to check the stability of the experiment. For the purposes of monitoring the stability of the crystal a commission of The International Union of Crystallography has recommended that "at least three strong, three medium and three weak reflections distributed throughout reciprocal space should be measured periodically in the course of the data collection". The frequency of these measurements was not discussed in the Commission's report but it would seem reasonable to propose that, for the purpose of monitoring the stability of both the sample crystal and the experimental equipment, the reference reflections should be measured sufficiently often to detect the highest frequency perturbation likely to be encountered. The presence of intermittently active machinery and different day/night electrical loads are factors which could affect the experiment if the stabilizing circuits are weak. In practice this regime could well mean that too large a fraction of the diffractometer time is spent measuring monitors and not enough on "data". Decreasing the frequency of collecting the monitor reflections should be done only if short-term fluctuations (minutes-hours time scale) are shown to be absent by the periodic performance of a suitable test--e.g. repeated measurements of a single reflection from a stable crystal over a time span of several hours. The number of monitor reflections may be reduced on the (facetious) premise that "any more than one will probably provide conflicting data on which to base a correction curve" but in reality the (probably different) time dependencies of the several monitor reflections should be determined. Any time-dependent scale factor applied

to the data to account for decomposition should be based on all of the information gathered and a variance contribution appropriate to the spread of the monitor reflections should be added to σ_I^2 .

(ii) In the two moving-crystal methods (i.e. ω or $\omega/2\theta$ scans) it is possible to record the intensity profile of the scan and this is to be recommended over the cumulative-peak/fixed-position-background method for (at least) four reasons:

(a) The minimum-variance estimate of the net intensity is obtained when the least number of background points are counted as lying under the peak.

(b) Corrections for intrusion of other reflections and/or the β -filter-edge effect are possible if the profiles are available.

(c) Counter dead-time correction by software should be made on a point by point basis and this also can only be done if the counts at each step are known.

(d) Some history of the experiment is available and this may prove invaluable if some doubt is cast on the validity of a data point.

(iii) Multiple diffraction effects can be detected and eliminated if each reflection is measured at several azimuthal rotations around the scattering vector. For this purpose only very limited ψ scans are usually necessary, e.g. at ψ values of -5° , 0 and $+5^\circ$, but for the purposes of validating an absorption correction several full ψ scans should be performed on low-angle reflections.

(iv) The deliberate introduction of redundancy into the experiment can provide an important check on the experimental results. This can be done by (a) collecting more than one asymmetric unit of reciprocal space, (b) collecting the same asymmetric unit twice (in the same order as the first time?) or (c) mounting a new crystal and repeating the experiment. Of these procedures option a is the most frequently exercised and, although it does not provide as comprehensive check as procedures b and c, is, at least, a good first step.

(v) The performance of peripheral equipment (heaters, coolers, etc.) should be both well calibrated and, at least, spot checked. Continual monitoring is preferable but this may not be practicable.

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X X-AXIS OF DIFFRACTOMETER
 Y Y-AXIS OF DIFFRACTOMETER
 S DIFFRACTION VECTOR
 D DIFFRACTED BEAM

FIGURE 1

Courtesy Dr. L. C. Andrews
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