A New Approach to the Determination of Crystallinity of Polymers by X-ray Diffraction

BY FRANK H. CHUNG AND RICHARD W. SCOTT
Sherwin-Williams Research Center, Chicago, Illinois, U.S.A.

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A new X-ray diffraction method for the determination of crystallinity of polymers is reported. A probability function is used to express the intensity distribution of an amorphous halo. The intensity of the halo buried under any crystalline peak can be calculated by this function. An amorphous-standard-addition method was used to determine crystallinity. A linear relationship between intensity and concentration is derived theoretically and applied to polyethylene terephthalate. No previous chemical or structural information about the polymer is necessary for this method. Very good agreement between X-ray data and density measurements were obtained. This method is rapid, practical and suitable for routine analysis.

Introduction

Crystallinity is defined as the weight fraction of the crystalline portion of a polymer. Since the advent of polymer science, two models have been used to correlate the polymer structure and its properties, the earlier fringed-micelle model and the recent folded-chain model. In both models it is assumed that the polymer is composed of crystalline and amorphous regions. The crystallinity of the polymer has a definite effect on its performance and various methods have been used to determine this parameter.

There are five different methods for determining the crystallinity of a polymer: (1) X-ray diffraction, (2) density, (3) infrared, (4) n.m.r. and (5) heat of fusion. The infrared method requires a standard, the crystallinity of which has been determined by other independent methods (Elliott, 1969). Density measurements have been used to give an independent estimate of crystallinity. However, the density method requires the density of the completely crystalline polymer which in turn requires the unit-cell dimensions of the polymer crystals as determined by X-ray diffraction analysis (Meares, 1965). The n.m.r. method is primarily a measurement of motion, not order. The n.m.r. spectrometer classifies the slower-moving protons as the 'rigid' crystalline fraction, the faster-moving protons as the 'mobile' amorphous fraction. The motion of the polymer chains is sensitive to temperature, molecular weight, and crosslinks (Miller, 1966). The calorimetric method has a sound thermodynamic definition of order. It requires the heat of fusion of pure-crystalline polymers derived from other thermodynamic measurements by extrapolation (Du Pont, 1968). The X-ray method provides a sound physical definition of order. It requires a clear separation of the amorphous halo from the crystalline pattern.

Crystals diffract X-rays coherently according to Bragg's law, giving sharp peaks, while amorphous materials scatter X-rays incoherently giving a diffuse halo. The X-ray diffraction pattern of a semicrystalline polymer is the superposition of sharp peaks over a diffuse halo. There are several different procedures to derive the degree of crystallinity from this diffraction pattern. The currently used crystallinity-index methods (Wakelyn & Young, 1966; Statton, 1963; Bosley, 1964) assign an index to a sample by comparing its pattern with that of the least (index = 0) and most (index = 100) crystalline standards obtained by quenching-annealing treatments. The disadvantage of these relative methods is that the indices cannot be compared between different laboratories or for different polymers. The absolute crystallinity methods (Hermans, 1961, 1962; Matthews, Peiser & Richards, 1949; Ruland, 1961) involve many empirical rules, correction factors, and/or abstract functions; hence, they are not convenient for rapid routine analysis.

A new approach to the determination of crystallinity has been applied to polyethylene terephthalate. This approach appears to be sound in theory, and suitable for rapid routine analysis.

Problems and solutions of the X-ray method

There are two major problems involved in all the X-ray methods: (1) the need for quantitative separation of intensity contributions from crystalline peaks, amorphous halo, and background; and (2) the need for near-perfect crystalline polymer standards. Such standards do not exist. These two problems are dealt with in the following manner by this new approach:

(1) Intensity separation

The intensity distribution of the X-ray diffraction pattern is the Fourier transform of the electron-density distribution in the sample. The halo of the diffraction patterns of amorphous polymers is due to the interatomic vectors between adjacent polymer chains (Klug & Alexander, 1954). Hence, the position of this halo is a measure of the interchain separation, and the intensity of this halo is a measure of amorphous material in the sample. For amorphous polymers, the interchain separ-
ation is a continuous variable and completely random within certain limits (James, 1965). This suggests that some kind of probability function might be useful for governing this situation. Naturally, the Gaussian distribution function is the first choice. The Fourier transform of a Gaussian function is another Gaussian function. Hence, the amorphous diffraction halo could be represented by a normal distribution function. It is found that amorphous diffraction halo of many polymers (Hermans et al., 1961, 1962; Klug & Alexander, 1954; Barlow & Young, 1970) can be fitted to a Gaussian function. For practical purposes, any of the following functions can be used to fit the intensity distribution of scattered X-rays by choosing proper scales as shown in Fig. 1.

1. Gaussian function
   \[ y = ae^{-x^2} \]

2. The Witch of Agnesi
   \[ y = \frac{a}{x^2 + 1} \]

3. Hyperbolic function
   \[ y = a \text{sech} x \]

4. Trigonometric function
   \[ y = \frac{a \sin^2 x}{x^2} \]

The feature of this treatment is that only one observable point of the curve is needed to trace out the whole curve. Of course, more points can be used to improve the precision.

The fitting is slightly off for values of \( x > 1 \) and therefore, the observable point should be chosen not too far away from the maximum. In very unusual cases where the only observable point is at \( x > 1 \), then a correction term should be added, such as

\[ y = \frac{a}{x^2 + 1} + bx \]

to obtain a best fit for the whole curve.

In the X-ray diffraction pattern of a polymer, Fig. 2, the minimum between well separated peaks, e.g. at \( x = 20^\circ (2\theta \) value), minus the background, should be solely due to the amorphous portion of the polymer. This experimental point can be used to calculate the constant \( a \), which is the maximum intensity of the amorphous halo, in the intensity distribution functions. Once the scale and the constant are determined, the intensity of the amorphous halo buried under the crystalline peaks can be easily calculated, thus achieving the desired intensity separation.

Because of improved modern instrumentation, the background due to electronic noise and white radiation is suppressed to the minimum. This can be seen from the diffraction patterns of rutile TiO\(_2\) (Swanson & Tatge, 1953) and toluidine red (Chung, 1971), Fig. 3, an inorganic and an organic pigment. The air scattering is significant only below the 15° (2\( \theta \)) value. Since these crystals have near-perfect lattices, the very low background can be totally attributed to electronic noise and white radiation. Any background higher than this is due to amorphous materials and lattice imperfections. By comparing Figs. 2 and 3, it is apparent that when the observable point is between two peaks separated by about 2° or more, its intensity would not be affected by the tails of the crystalline peaks.

The diffraction patterns were obtained by use of a Norelco X-ray diffractometer equipped with a full-wave rectifier, high-intensity copper tube, curved graphite-crystal monochromator, solid-state scintillation counter and an electronic-circuit panel containing a pulse-height analyzer. All subsequent data were obtained with this diffractometer under the same instrumental conditions. The same background (32 c.p.s.) was also used for all subsequent calculations.
Amorphous-standard addition

Although the perfect crystalline polymer does not exist, a completely amorphous polymer of the same chemical composition is usually available with a few exceptions such as polyethylene and Teflon, etc. These completely amorphous polymers can be used as standards to determine the crystallinity.

Consider the polymer as a mixture of two components, the crystalline and the noncrystalline. The crystalline component is defined as the one which diffracts X-rays coherently according to Bragg's law. The noncrystalline component is defined as the one which scatters X-rays incoherently, forming a halo. Thus a polymer is a simple two-phase system. According to a mathematical relationship derived by Klug & Alexander, (1954), the intensity of X-rays diffracted by component a of a mixture is:

$$I_a = \frac{K_a x_a}{\rho_a(x_a(\mu_a - \mu_m) + \mu_m)}$$

where:

- $K_a$ = a constant dependent on nature of component a,
- $x_a$ = weight fraction of component a,
- $\rho_a$ = density of component a,
- $\mu_a$ = mass absorption coefficient of component a,
- $\mu_m$ = mass absorption coefficient of the matrix.

It is obvious that when $\mu_a \neq \mu_m$ the intensity–concentration ($I - x$) relationship is not linear. However, in the case of a polymer its two components, the crystalline and the noncrystalline, are polymorphic (or allotropic) forms in the sense they are the same compound in two different forms, hence $\mu_a = \mu_m$, and a linear relationship between intensity and concentration should exist.

If subscript a is used for the noncrystalline component, and subscript c is used for the crystalline component, we have

$$\begin{align*}
I_a &= \frac{K_a}{\rho_a(x_a(\mu_a - \mu_m) + \mu_m)} x_a = k_a x_a \\
I_c &= \frac{K_c}{\rho_c(\mu_c - \mu_m)} x_c = k_c x_c
\end{align*}$$

Linear relation

$$x_c = \frac{k_a I_a}{1 + k_c I_c}$$

Note that $x_c$ is the weight fraction of the crystalline phase which is also the crystallinity of the polymer by definition, and $k$ is the slope of the straight line when $x_a/x_c$ is plotted against $I_a/I_c$. Incidentally, the linear relationship between intensity and concentration was assumed in the method of Hermans et al. (1961, 1962). $I_a$ and $I_c$ are experimental data, $k$ and $x_c$ are two unknowns. One more equation is required to solve for $k$ (slope) and $x_c$ (crystallinity). The completely amorphous polymer rather than the perfectly crystalline polymer (which does not exist) can be used as a standard. If a mixture of resin powders of 80% unknown and 20% amorphous standard is made, then

$$for \ unknown: x_c = \frac{1}{1 + k \frac{I_a}{I_c}} \text{solve for } k \text{ and } x_c.$$  

$$for \ 80/20 \ mixture: 0.80 x_c = \frac{1}{1 + k \frac{I_a}{I_c}} \text{solve for } k \text{ and } x_c.$$  

In order to increase the precision, mixtures of different proportions can be made and run. We can have $n (n > 2)$ equations for 2 unknowns which can be easily solved by the least-square method to obtain the best possible value of slope ($k$) and crystallinity ($x_c$).

This amorphous standard may be (a) the quenched melt of the same polymer, (b) a polymer made from the same monomer by a different process (Sweeting, 1971), or (c) a polymer made from isomeric monomers such as polyethylene terephthalate and polyethylene isophthalate. The scattering factor and absorption coefficient of these standards should be the same.

**Experimental**

A crystalline PET powder SWPET (Sherwin–Williams Company) was used for this study. Three amorphous standards were used: VPE (Goodyear PET), polyethylene isophthalate SWPEI (Sherwin–Williams Company), and a quenched melt made from SWPET. Three series of experiments were run by using these three amorphous standards respectively. All the four resin powders were passed through a Fisher 150 mesh sieve. The amorphous-standard powder was added into the unknown sample in various proportions. The mixtures were thoroughly blended by putting them on a roller mill for about two hours. The X-ray diffraction patterns

![Fig. 3. The X-ray diffraction patterns of (a) rutile TiO$_2$ and (b) toluidine red.](image)
of these mixtures were obtained. The three series of data are listed in Table 1. The intensity data are in chart units. One chart unit is equivalent to 32 c.p.s.

Sample No 1 is the polymer SWPET whose crystallinity is to be determined. Sample No. 10 is the completely amorphous standard. The X-ray diffraction patterns of the three amorphous standards are nearly the same, as shown in Fig. 4. The experimental intensity distribution of the halo is fitted to one of the previously mentioned functions. For the sake of simplicity, the Witch of Agnesi is picked

\[ y = \frac{a}{x^2 + 1} \]

where \( y \) is the intensity, \( x \) is the 2θ value, and \( a \) is the maximum intensity. In our case, Fig. 1, \( x=0 \) at \( 2θ=21.6^° \), \( y=a=33.2 \) chart units (maximum intensity). When an interval of 6.8° in \( 2θ \) is taken as the unit of \( x \), the amorphous halo can be well represented by the above equation.

The 100 crystalline PET peak is at \( 2θ=26^° \), (Fig. 2) which is equivalent to \( x = 22/34 \). The observable amorphous intensity is chosen at \( 2θ = 20^° \) which is equivalent to \( x = -8/34 \). The background is one chart unit (equivalent to 32 c.p.s.) based on the X-ray diffraction patterns of near-perfect crystals under the same instrumental conditions.

The result obtained for sample No. 9 is too far from the average. This sample was prepared with 92.32 % of standard and 7.68 % of the unknown. Further, the determined crystallinity of this mixture is only \( 7.68 \times 66.0 \% = 5.0 \% \) which is close to the detection limit of the X-ray method.

The average crystallinity of the polymer SWPET is 66.0 % (samples Nos. 6 and 9 are excluded). The standard deviation is 0.5%. At the 95% confidence level, according to Student statistics, the crystallinity of this polymer is 66.0 ± 0.3 %.

Using the determined crystallinity of polymer SWPET of 66.0%, the crystallinity of all 20 samples was calculated. Their intensity ratios and concentration ratios are listed in Table 2. The data in Tables 1 and 2 are plotted in Fig. 5 and 6. A linear relationship between intensity and concentration does exist as expected from theoretical considerations even with different amorphous standards. Note that in Fig. 5, the \( I_c \) line passes through the origin, while the \( I_c \) line by extrapolation passes through the point of 100 % crystallinity.

### Table 1. Crystallinity of PET from amorphous-standard-addition method

<table>
<thead>
<tr>
<th>Sample</th>
<th>% SWPET</th>
<th>( I_{obs} ) at 20°</th>
<th>( I_c ) at 20°</th>
<th>( I_{obs} ) at 26°</th>
<th>( I_c ) at 26°</th>
<th>( I_{obs}/I_c )</th>
<th>Crystallinity k %</th>
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<tr>
<td>SWPET + VPE</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>1</td>
<td>100</td>
<td>12.6</td>
<td>11.6</td>
<td>75.5</td>
<td>65.9</td>
<td>0.176</td>
<td>66.8</td>
</tr>
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<td>2</td>
<td>88.76</td>
<td>15.0</td>
<td>14.0</td>
<td>68.8</td>
<td>57.4</td>
<td>0.243</td>
<td>66.4</td>
</tr>
<tr>
<td>3</td>
<td>74.74</td>
<td>17.5</td>
<td>16.5</td>
<td>60.0</td>
<td>46.7</td>
<td>0.353</td>
<td>66.4</td>
</tr>
<tr>
<td>4</td>
<td>60.71</td>
<td>21.0</td>
<td>20.0</td>
<td>54.4</td>
<td>38.5</td>
<td>0.519</td>
<td>66.8</td>
</tr>
<tr>
<td>5</td>
<td>50.68</td>
<td>22.8</td>
<td>21.8</td>
<td>49.5</td>
<td>32.3</td>
<td>0.675</td>
<td>65.7</td>
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<td>6</td>
<td>39.08</td>
<td>25.0</td>
<td>24.0</td>
<td>44.5</td>
<td>25.6</td>
<td>0.938</td>
<td>64.1</td>
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<td>28.5</td>
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<td>37.6</td>
<td>16.1</td>
<td>1.708</td>
<td>66.2</td>
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<td>8</td>
<td>19.57</td>
<td>30.0</td>
<td>29.0</td>
<td>35.2</td>
<td>12.6</td>
<td>2.302</td>
<td>66.0</td>
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<td>9</td>
<td>7.68</td>
<td>31.1</td>
<td>30.1</td>
<td>29.5</td>
<td>6.1</td>
<td>4.934</td>
<td>55.5</td>
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<td>10</td>
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<td>32.2</td>
<td>24.8</td>
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<td>∞</td>
<td></td>
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<tr>
<td>SWPET + SWPEI</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>11</td>
<td>83.73</td>
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<tr>
<td>12</td>
<td>68.16</td>
<td>19.5</td>
<td>18.5</td>
<td>58.8</td>
<td>44.0</td>
<td>0.421</td>
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<td>59.70</td>
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<td>37.1</td>
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<td>14</td>
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<td>63.3</td>
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<td>15</td>
<td>35.15</td>
<td>25.2</td>
<td>24.2</td>
<td>41.8</td>
<td>21.8</td>
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<td>SWPET + Quenched melt of SWPET</td>
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<td>16</td>
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<td>15.4</td>
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<td>18</td>
<td>70.83</td>
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<tr>
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<td>0.619</td>
<td>65.8</td>
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<td>23.3</td>
<td>43.3</td>
<td>25.0</td>
<td>0.952</td>
<td>66.3</td>
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### Table 2. Intensity ratios and concentration ratios of PET

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<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
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<tbody>
<tr>
<td>( L_c/I_c )</td>
<td>0.176</td>
<td>0.243</td>
<td>0.353</td>
<td>0.519</td>
<td>0.675</td>
<td>0.938</td>
<td>1.708</td>
<td>2.302</td>
<td>4.934</td>
<td>∞</td>
</tr>
<tr>
<td>( x_c/x_e )</td>
<td>0.515</td>
<td>0.707</td>
<td>1.027</td>
<td>1.496</td>
<td>1.990</td>
<td>2.879</td>
<td>4.967</td>
<td>6.740</td>
<td>18.72</td>
<td>∞</td>
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</table>

<table>
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<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
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<tbody>
<tr>
<td>( L_c/I_c )</td>
<td>0.275</td>
<td>0.421</td>
<td>0.520</td>
<td>0.686</td>
<td>1.110</td>
<td>0.267</td>
<td>0.332</td>
<td>0.391</td>
<td>0.619</td>
<td>0.932</td>
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<tr>
<td>( x_c/x_e )</td>
<td>0.810</td>
<td>1.223</td>
<td>1.538</td>
<td>2.041</td>
<td>3.191</td>
<td>0.786</td>
<td>0.978</td>
<td>1.139</td>
<td>1.822</td>
<td>2.711</td>
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</table>
Discussion

For X-ray diffraction work, the integrated intensity should be preferred rather than simply the peak height. However, because of serious overlapping, it is difficult to obtain the integrated intensities with reasonable confidence. The difference between the integrated intensity and peak height will be regulated by the empirical constant $k$ which also takes care of the absorption factor and the Lorentz-polarization factor automatically.

The diffuse scattering need not come only from amorphous materials in the sample but can also arise from crystal-lattice distortions and crystallite-size effect. This is surmounted by defining the polymer as a system of crystalline and noncrystalline components. The weight fraction of the crystalline component, hence the crystallinity, is a measure of order, and the order is represented by that portion of the structure which diffracts X-rays coherently according to Bragg's law. Then the paracrystalline state, the lattice imperfections, the crystallite-size effect, the thermal vibrations, and the noncrystalline structure are merely different kinds of disorder.

The crystal structure of PET has been determined by use of X-ray diffraction analysis (Daubeny, Bunn & Brown, 1954) the density of completely crystalline PET is $1.455 \text{ g cm}^{-3}$, and the density of completely amorphous PET is $1.335 \text{ g cm}^{-3}$. The density and the crystallinity are related by the following equation (Alexander, 1969):

$$x = \frac{q_c (q - q_a)}{q (q_c - q_a)},$$

where $x =$ crystallinity

$q_c =$ crystalline density

$q_a =$ amorphous density

$q =$ density of partially crystalline sample.

Given $x = 66.0\%$, the calculated density of SWPET should be $q = 1.412 \text{ g cm}^{-3}$. The density of the SWPET powder measured by ASTM method D153-B which should give accurate density for powder samples is $1.415 \text{ g cm}^{-3}$. The agreement is remarkably close in this case, even though the agreement between X-ray and density crystallinity is still controversial in the literature (Miller, 1966; Dumbleton & Bowles, 1966).

The features of this new approach are: (a) the intensity-separation and standard-addition procedures are not subject to human error. Hence the data should be comparable between different laboratories or for different polymers, (b) previous chemical or structural information about the polymer sample is not required for this method, and (c) it is simple, rapid and suitable for routine analysis.

The SWPET and SWPEI were prepared by Dr Thomas Plaisance of the Sherwin-Williams Resin Research Department. The quenched melt of SWPET and the X-ray diffraction patterns were obtained by Mr August Lentz. To them we express our sincere thanks.
Note on the Aberrations of a Fixed-Angle Energy-Dispersive Powder Diffractometer

BY A. J. C. WILSON

Institute for Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo, Japan

and

Department of Physics, University of Birmingham, Birmingham B15 2TT, England*

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The geometrical and physical aberrations affecting the positions and breadths of diffraction maxima as determined by the energy distribution of photons diffracted through a fixed angle and analysed by a solid-state detector differ in many points of detail from those determined by the angular distribution of photons of fixed energy analysed by a conventional diffractometer. The main differences are investigated and the accuracy of spacing measurements is discussed. There is no simple analogue of the extrapolation method of reducing errors in spacing measurements.

1. Introduction

By use of a solid-state detector and pulse-height analysis it is possible to produce a diffraction pattern in which the various diffraction maxima are distinguished by the different energies of the scattered photons rather than by the different Bragg angles of photons of the same energy. Various arrangements and applications of this principle have been described by Geissen & Gordon (1968), Cole (1970) and Lauriat & Pério (1972). The angle between the incident and diffracted rays is fixed, and the energy distribution of the diffracted photons is displayed by a multichannel analyser. In the arrangement used by Fukamachi, Hosoya & Terasaki (1973), the equatorial divergence of the radiation is limited to a few tenths of a degree by two sets of Soller slits, the diffraction angle being determined by the angle between the lamellae of the two sets. The powder specimen is a slab of uniform thickness situated between the sets of Soller slits. The plane of the slab may be perpendicular to the incident beam or it may be placed symmetrically, so as to bisect the angle between the incident and diffracted rays, or it may be used in reflexion instead of in transmission. These three possibilities are sketched in Fig. 1.

Each interplanar spacing $d$ in the specimen selects the appropriate wavelength from the continuous radiation for diffraction through the fixed angle; the process is somewhat analogous to the production of a Laue photograph. If the angle between the lamellae of the Soller