

OUTLINE OF A RECOMMENDED PRACTICE FOR THE X-RAY COUNTER DIFFRACTOMETRY OF POLYCRYSTALLINE SUBSTANCES

WILLIAM PARRISH

Philips Laboratories, Irvington-on-Hudson, New York, U.S.A.

Since the end of World War II there has been a very large increase in the application of X-ray powder diffraction analysis to a wide variety of fields. The development of commercial diffractometers with high efficiency counter tubes and associated electronic circuits has greatly enhanced the power of the method. A very important application is the qualitative identification of compounds which is readily accomplished by means of characteristic X-ray powder patterns.

The *X-ray Powder Data File*, a project of the Joint Committee on Chemical Analysis by X-Ray Diffraction Methods, published by the American Society for Testing Materials now contains data for about 6500 substances and is being increased at a considerable rate. Much of the data in the File has been obtained from the literature. Because the methods are not standardized and a large variety of techniques is used to obtain the X-ray patterns, the quality of the data varies over relatively wide limits.

The purpose of this paper is to outline the many factors that contribute to the quality of the patterns obtained with counter diffractometers. It is not possible to list specific experimental conditions that must be used because these are dependent on the nature of the analysis. Nevertheless, it is hoped that this outline will serve as a guide to improve the overall quality of the data published in the literature or contributed directly to the File. Space limitations do not permit a detailed discussion of all the problems, and instead references will be given to the literature for more complete descriptions. A fuller account is being prepared for publication by A.S.T.M. Recommended Practices for film methods and for the use of the File are also being prepared.

X-RAY SPECTRA

X-ray tubes used for powder diffractometry must be operated at a voltage several times greater than the critical excitation potential of the target element to obtain sufficient intensity. Usually 25 to 60 kV is used which

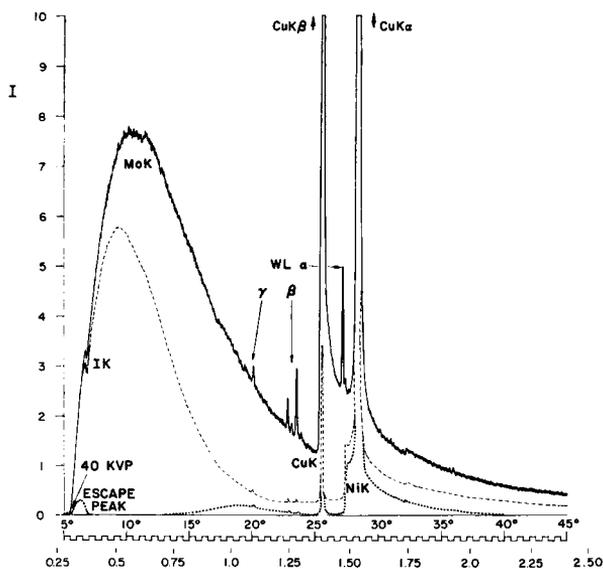


Fig. 1.—Spectrum from a Norelco copper target X-ray tube operated at 40 kvp, full-wave rectification, obtained with a silicon single crystal plate cut parallel to 111, $d = 3.135 \text{ \AA}$, NaI·Tl scintillation counter. The dashed (middle) curve was obtained with 0.014 mm thick nickel filter and dotted (bottom) curve with filter and pulse height analyzer, the latter set to transmit 90 per cent of Cu $K\alpha$. The WL impurity lines are eliminated by the filter. The bottom scales show the reflection angle in $^{\circ}2\theta$ and the wavelengths in \AA .

produces a spectrum consisting of characteristic emission lines superimposed on a continuous band of radiation. The latter contributes to the background making it difficult to measure weak lines. Attempts to avoid the continuum by the use of X-ray fluorescent [18] or radioactive sources [4] have not been successful because the intensities from sources presently available are too low for powder diffractometry. To achieve high statistical accuracy of the intensity measurements it is necessary to optimize the experimental conditions to obtain maximum line intensity and peak-to-background ratio. Various degrees of monochromatization are possible using a beta filter [19], pulse amplitude discrimination [13, 15] and crystal monochromators [8, 12].

The spectrum emitted by a copper target X-ray tube operated at 40 kvp is shown in the diffractometer recording (Fig. 1). The dashed line shows how the spectrum is modified by insertion of a nickel foil 0.014 mm thick which reduces the Cu $K\alpha_1$ integrated line intensity by 45 per cent, virtually eliminates the $K\beta$ line ($K\alpha$ is far off the chart) and causes some reduction of the continuum. The dotted line shows that most of the continuous radiation is eliminated when the pulse height analyzer is set to transmit about 90 per cent of the remaining Cu $K\alpha$. The combination of beta filter and pulse height analyzer is thus extremely effective in removing the non-characteristic X-rays, reduces the $K\alpha_1$ line intensity by only about a factor

TABLE I. Data for β -filters.

Element	Target			β -filter	Density (g/cc)	K Abs. Edge (Å)	Thickness ^a			Loss of $K\alpha_1$ (%)
	Wavelength (Å)	$K\alpha_1$	$K\beta_1$				Integ. int. $K\beta_1/K\alpha_1$	mm	mils	
Ag	0.559	0.497	0.290	Pd	12.2	0.509	0.057	2.3	0.070	62
				Rh	12.5	0.534	0.059	2.3	0.073	62
Mo	0.709	0.632	0.279	Zr	6.4	0.689	0.080	3.2	0.051	59
Cu	1.541	1.392	0.200	Ni	8.9	1.487	0.014	0.6	0.013	45
Ni	1.658	1.500	0.189	Co	8.9	1.607	0.012	0.5	0.011	43
Co	1.789	1.621	0.160	Fe	7.9	1.743	0.011	0.4	0.009	38
Fe	1.936	1.940	0.167	Mn	7.2	1.895	0.012	0.5	0.009	43
				Mn ₂ O ₃	4.5		0.028	1.1	0.013	47
				MnO ₂	5.0		0.028	1.1	0.014	49
Cr	2.290	2.085	0.179	V	6.0	2.269	0.013	0.5	0.008	44
				V ₂ O ₅	3.4		0.041	1.6	0.014	57

^a To reduce $K\beta_1/K\alpha_1$ integrated line intensity ratio to 1/100.

of two, and is highly recommended for powder diffractometry. Flat crystal non-focusing monochromators cause a very large loss of line intensity, but curved focusing crystals have been used successfully [2, 12] as described later.

Beta filters

The selection and proper use of filters are very important to achieve the best experimental results. Table I lists the calculated thicknesses of filters for the more common X-ray targets required to reduce the $K\beta_1/K\alpha_1$ integrated line intensity ratio to 1/100. These thicknesses are sufficient for most purposes and greater thicknesses cause greater losses of $K\alpha$ intensity. The integrated intensity ratios $K\beta_1/K\alpha_1$ in the fourth column are those obtained by Williams [25] using a two-crystal spectrometer, and these ratios may be modified by window absorption and other factors. The observed peak intensity ratios are different by amounts depending on the diffractometer geometry, specimen, etc., and hence to calculate the filter thickness required to obtain a specific $K\beta_1/K\alpha_1$ peak ratio it is first necessary to measure the unfiltered peaks using the same experimental conditions.

X-Ray fluorescence background

All X-rays in the primary spectrum having wavelengths shorter than the absorption edges of the elements in the specimen cause X-ray fluorescence. The long wavelength fluorescence ($\lambda > 2.75$ Å) is usually not detected, but shorter wavelengths may add considerably to the recorded background.

When specimen fluorescence is detected the position of the filter may have a marked effect on the intensity of the background. It is easy to check whether the best position is before or after the specimen by setting the counter tube on the background. For example, when using a copper target and a tungsten specimen, the background is five times higher when the nickel filter is placed over the divergence slit than when placed over the receiving slit because the nickel filter absorbs nearly all of the $W L$ fluorescence.

The choice of target element may have a large effect on the background. For example, the continuum and K -lines of a copper target cause intense fluorescence of specimens containing cobalt and iron and the fluorescence is not greatly reduced by the nickel beta filter. For such specimens it is better to use longer wavelengths such as a cobalt target with iron filter. A copper specimen is caused to fluoresce strongly by the continuum from a copper target, but when a cobalt target is used the iron filter absorbs nearly all of the $Cu K$ fluorescence thereby giving a much higher peak-to-background ratio. Thin filters other than the beta filter may also sometimes be helpful in reducing the background without greatly reducing the $K\alpha_1$ target line intensity.

Selection of targets

The dispersion increases with increasing wavelength and it is often necessary to use longer wavelengths to measure the more complicated patterns and those with large d -spacings. Copper targets are by far the most widely used and most generally applicable. Although molybdenum K -radiation can now be detected with high efficiency using scintillation counters, its small dispersion causes difficulties in interpreting the patterns of the lower symmetry substances and hence its use is not generally recommended. Cobalt, iron and chromium targets are generally used when higher dispersion is required and to avoid fluorescence, but the intensities are generally considerably lower than those obtained from a copper target. Fig. 2 shows diffractometer recordings of silicon powder using four different targets. In terms of intensity and peak-to-background ratio the copper target is the best [16].

Spectral purity

If the target is impure, or otherwise contaminated, false lines may appear in the diffraction pattern and may not be recognized as such unless the pattern is indexed. It is always advisable to check the spectrum of a tube at periodic intervals. An easy qualitative method is to record in the vicinity of the 111 line of a diamond powder specimen. A quantitative method has also been described [7].

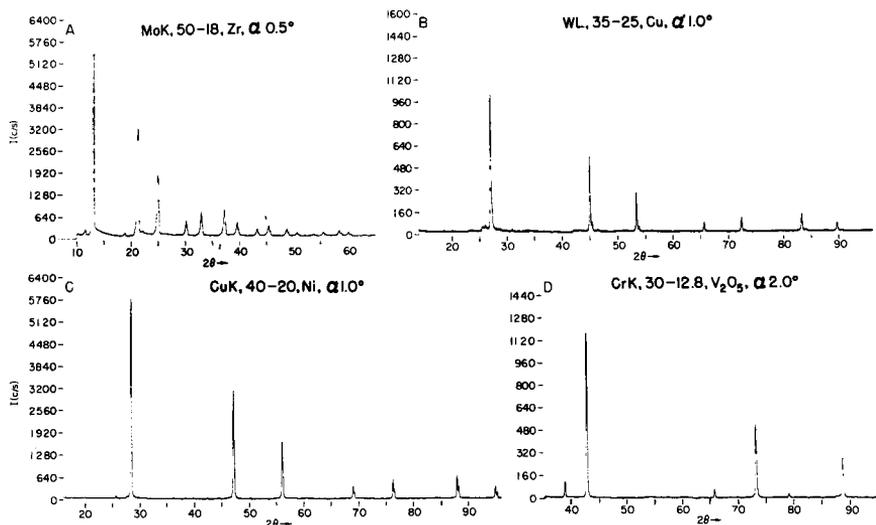


Fig. 2.—Diffractometer recordings of silicon powder using scintillation counter. The target, kv-ma, filter and angular aperture α are shown at the top of each chart. (*J. Appl. Phys.* 27 (1956)).

Stability

Unlike film methods, in which the intensities of all the lines are integrated during the entire exposure, the counter methods accumulate data by scanning. Hence it is essential that the primary X-ray intensity be stable during the entire recording period in order to compare the relative intensities. Stabilization of the voltage and tube current so that short- and long-range stability are better than 1 per cent is essential. Monitoring methods do not conveniently lend themselves to continuous recording.

DIFFRACTOMETER GEOMETRY

The most commonly employed diffractometer geometry is illustrated in Fig. 3. A divergent beam and flat reflecting specimen are used in a focusing arrangement in which the specimen is rotated on the goniometer axis of rotation O at one-half the speed of the counter tube. Each of the components of the geometrical arrangement affects the intensity, peak-to-background ratio, resolution and line shape in a different manner. It is essential to understand the role of each of the components in order to select the experimental conditions best suited for a particular analysis.

X-ray tube focus

In modern diffractometers, the line focus of the X-ray tube is parallel to the goniometer axis of rotation and is viewed at a small angle. The focus itself

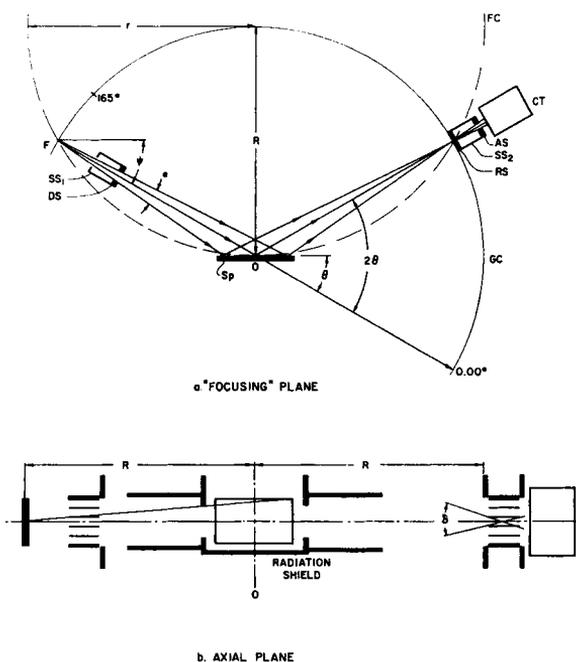


Fig. 3.—Geometry of the Norelco diffractometer in the focusing (vertical) plane and axial (horizontal plane). F line focus of X-ray tube, SS_1 divergence Soller slit assembly, DS divergence slit, ψ angle-of-view of target to central ray, α full angular aperture, O goniometer axis of rotation, Sp specimen, GC goniometer circle of radius R , FC focusing circle of radius r , RS receiving slit, SS_2 receiving Soller slit assembly, AS anti-scatter slit, CT counter tube, δ angular aperture of Soller slits. (*Am. Mineral.* **44** (1959).)

acts as the source slit and its projected width in the direction normal to O must be narrow to obtain sharp reflections since the finite width of the focus adds a symmetrical broadening to each line independent of the diffraction angle. For example, the projected size of a focus 1.6 by 10 mm viewed at an angle of 6° is 0.16 by 10 mm and is sufficiently narrow for most diffractometer analyses. It is also feasible to use a much wider focus, 3×10 mm, which increases the line intensities by a factor of two with little broadening or loss of resolution [12]. This is possible because other instrumental factors also contribute to the line breadths and mask the small increase arising from the wider projected focus.

Angular aperture in focusing plane

The angular aperture α in the focusing plane is determined by the width of the divergence slit. A flat specimen is used and the irradiated specimen length $l = \alpha R / \sin \theta$ (α in radians). Thus l increases rapidly with decreasing glancing angle θ and sets a lower limit to the angle that can be scanned with a given α and specimen length without exceeding the specimen length.

TABLE II. *Data for divergence slit in focusing plane.*^{a, b}

Angular aperture α	$2\theta_{\min}$	Maximum d -spacing		
		Mo $K\alpha$	Cu $K\alpha$	Cr $K\alpha$
5'	1.45°	28 Å	62 Å	92 Å
30'	8.50	4.8	10.4	15.5
1°	17.0	2.4	5.2	7.8
2°	34.5	1.2	2.6	3.9
4°	72.8	0.6	1.3	1.9

^a From Parrish [12]. ^b For $R = 170$ mm, specimen length = 20 mm.

When l exceeds the actual specimen length the background may increase because of scattering from the ends of the specimen holder and it will not be possible to compare the relative intensities of all the lines. Table II gives some representative values of α , the minimum 2θ angle for $R = 170$ mm and specimen length 20 mm, and the corresponding maximum d -spacings for three common radiations.

Flat specimen aberration

Ideally the specimen should be curved to fit the focusing circle whose radius of curvature $r = R/2 \sin \theta$. This is impractical since it would require a flexible specimen whose curvature varied continually with θ during scanning. The use of a flat rather than a curved specimen causes a defocusing and the line profiles are asymmetrically broadened and shifted toward smaller θ by an amount that increases with α and decreases with θ [20, 26]. In routine practice no corrections of intensity and peak position are normally made to correct for this aberration and the peak shift is usually $< 0.01^\circ (2\theta)$.

Angular aperture in axial plane

The angular aperture δ in the plane normal to the focusing plane is limited by the Soller or parallel slit assemblies which consist of thin metal foils of length l and spacing s , and $\delta = 2 \tan^{-1} s/l$. With $\delta = 4.5^\circ$ each set reduces the intensity by a factor of two, but they are required to obtain good line shapes particularly at small θ . When intensity is of greater importance than line shape the receiving Soller slit assembly may be removed. Axial plane divergence causes asymmetric broadening and a shift of the line toward smaller angles in the front-reflection region and toward larger angles in the back-reflection region, the effects being greatest at very small and very large 2θ [20–22]. Normally no corrections are made for this aberration, but if reflection angles $< 10^\circ (2\theta)$ are to be measured, it may be desirable to decrease δ .

2:1 Setting

To obtain proper focusing conditions, it is necessary that the receiving slit be at 2θ when the specimen surface is at θ . This 2:1 relationship must be accurately set and maintained by the goniometer at all reflection angles. If it deviates by as little as 1° , it will cause asymmetrical line broadening and a large decrease in peak intensity. The effect decreases with increasing θ causing a systematic error in the observed intensities [12]. The 2:1 setting should be carefully checked [17].

Receiving slit

The receiving slit width is usually the major factor in determining the intensity and breadth of line profiles of well-crystallized substances [11, 12]. Increasing the receiving slit width increases the integrated line intensity and the breadth. The peak intensity also increases up to a receiving slit width of about 0.2° (2θ) and the peak-to-background ratio decreases. When the $K\alpha$ doublet is partially resolved with a narrow slit, increasing the width causes a marked change in line profile and shifts the peak to some angle between each of the doublet components. For good resolution a receiving slit of 0.05° (2θ) may be used, but in routine analysis when intensity is of importance the width may be increased by a factor of two or three.

Alignment and angular calibration

Optimum performance of the diffractometer can be achieved only when it is correctly aligned and calibrated. Unless these are properly done, the intensity, peak-to-background ratio, resolution and line shape will deteriorate and also make it difficult to compare data with other workers. A full description of a mechanical method for alignment and calibration has recently been published [17].

Anti-scatter slits

Anti-scatter slits as shown in Fig. 3 are desirable to minimize the background and to make certain the counter tube will receive radiation only from the specimen area. These slits must be carefully aligned to obtain the maximum peak-to-background ratio and to avoid extraneous scattering [17].

Monochromator

A diffractometer geometry which supplements the normal diffractometer described above may be useful for many purposes [8, 12]. The specimen is made into a thin mount and used in transmission instead of reflection. The divergent beam after passing through the specimen strikes a focusing crystal monochromator which reflects the beam to the counter tube. The resolution is determined by the crystal rather than the receiving slit. The

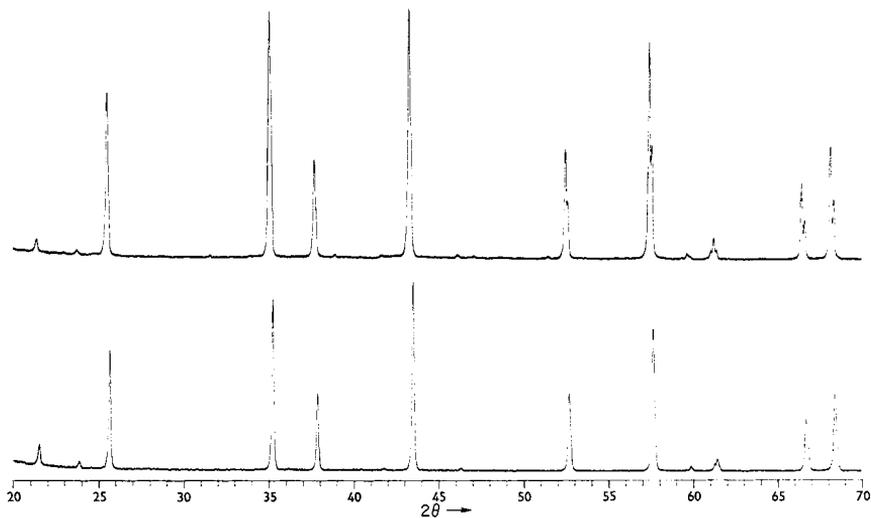


Fig. 4.—Recordings of $\alpha = \text{Al}_2\text{O}_3$ powder specimen in reflection (above) using a standard diffractometer, and in transmission (below) using a focusing monochromator after the specimen. $\text{Cu } K\alpha$ radiation.

focusing is adjusted by changing the curvature of the crystal and usually the $K\alpha_1$ and $K\alpha_2$ lines are focused together at about 30° (2θ). Fig. 4 shows the reflection pattern of alpha aluminum oxide ($\alpha = \text{Al}_2\text{O}_3$) obtained with the usual diffractometer arrangement and the transmission pattern obtained with the monochromator diffractometer. The line breadths of the monochromator pattern are sharper because of the absence of resolved $K\alpha_2$ lines which begin to appear only at the higher angles. Since the specimen is nearly normal to the primary beam the angular aperture may be two or three times larger than for the reflection specimen. However, loss of intensity caused by reflection from the crystal results in a lower intensity by about a factor of two compared with the normal diffractometer set up for maximum resolution. The background obtained using the monochromator consists almost entirely of $\text{Cu } K\alpha$ and all fluorescent radiation is eliminated. The peak-to-background ratio with non-fluorescent specimens is about the same as that achieved with pulse amplitude discrimination.

There are several important uses for the monochromator arrangement. The method is ideally suited for the measurement of large d -spacings because the specimen surface displacement error is proportional to $\sin \theta$, whereas in reflection the error is proportional to $\cos \theta$. If the *same* specimen is measured in reflection and transmission, differences in the relative intensities of the lines in the two patterns caused by preferred orientation become immediately apparent. In addition the method lends itself to the use of very small specimens which can be coated onto a thin substrate.

SPECIMEN FACTORS

One of the most important factors limiting the precision of the data is the specimen preparation. Poor specimen preparation may cause large errors in the intensity and angle measurements. Space limitations make it impossible to describe fully the various factors, but it will be clear that much more attention will have to be given to preparation techniques.

Specimen preparation

The specimen must be prepared with a flat surface of sufficient area to intercept the entire incident X-ray beam at all required diffraction angles. For many diffractometers this requires an area 10×20 mm. The specimen may be a flat solid such as used for metallography, a sintered briquette or a powder which has been coated onto a flat mounting with a binder or packed into a holder either dry or with a binder. One volume of collodion diluted with 10 volumes of amyl acetate is frequently used as a binder for inorganic substances. Vaseline or other binders are sometimes used for organic substances. The surface should be examined with a binocular microscope prior to use.

Homogeneity

It is essential that the surface be characteristic of the bulk specimen and that it be homogeneous across its entire area. This is particularly important in diffractometry because the irradiated specimen length changes with diffraction angle.

Displacement

If the specimen surface is displaced from the goniometer axis of rotation by an amount x , the observed reflection angle is shifted [17, 26] from the correct value by an amount $\Delta(^{\circ}2\theta) = 114.6 x \cos \theta/R$. The shift may be to larger or smaller angles depending on whether the surface is above or below O . This is the source of the most common systematic angular error and may be caused by incorrect specimen preparation, incorrectly machined goniometer specimen holder or both. If $x = 0.1$ mm, $\Delta 2\theta = 0.061^{\circ}$ at 50° and 0.034° at 120° for $R = 170$ mm.

Transparency

Unlike the Debye-Scherrer case where it is necessary to use specimens with low absorption to avoid line shifts, a high absorption specimen is desirable for reflection diffractometry [20, 26]. Penetration of the beam into the specimen gives rise to reflections from various depths which shift and asymmetrically broaden the lines. This causes a systematic error which is maxi-

mum at 90° (2θ) and zero at 0° and 180° . The relative intensities may also be in error [10]. To avoid these difficulties it is usually necessary to use very thin smears of low absorption substances mounted on a low reflecting substrate even though the intensities may be lower than those of a thick specimen.

Preferred orientation

In powder diffractometry it is assumed that the specimen consists of randomly oriented crystallites. Unfortunately the crystallites of some substances with good cleavage or a particular morphology, such as the clay and mica minerals, tend to orient themselves in some special manner when prepared as X-ray specimens. Consequently certain reflections are enhanced and others reduced by amounts dependent on the degree and type of preferred orientation in a given preparation. The non-reproducible character of the specimen preparation makes it difficult to obtain reliable relative intensities for identification purposes.

Drifting the powder onto a holder covered with adhesive, using a side-loading holder [24], mixing the powder with a plastic to coat the particles [5], cutting a fine saw-tooth pattern on the surface [23], mixing with Lindemann glass, Canada balsam, etc., have all been used with varying degrees of success. Rotating the specimen in its own plane is helpful to reduce second-order effects, but has little effect on the orientations parallel to the specimen plane.

The use of the monochromator-transmission specimen technique described on p. 347 in conjunction with the standard reflection method may often be very useful. The specimen preparation can then be modified until substantially the same relative intensities are obtained by both methods. If a monochromator diffractometer is not available, comparison of the reflection diffractometer pattern with that obtained using a Debye-Scherrer film or Guinier type of monochromator camera, both of which use transmission methods, may be helpful in estimating the degree of preferred orientation.

Strain and plastic deformation

Strain and plastic deformation caused by grinding and lapping may cause line broadening and loss of resolution and peak-to-background ratio. Annealing may be required in some cases and care must be exercised to avoid possible phase transformations, selective volatilization of one of the constituents or excessive grain growth.

Crystallite sizes

The crystallites should preferably be approximately 1 to 10μ . Line broadening is caused by smaller crystallites and variations of the relative and ab-

solute intensities by larger crystallites. Rotating the specimen rapidly in its own plane during the scanning eliminates fluctuations in the relative intensities caused by the larger crystallites [3, 12].

X-RAY COUNTERS

Counter tubes make possible the direct, rapid and precise quantitative measurement of X-ray intensities. For a given experimental arrangement the measured intensity is determined by the quantum counting efficiency of the counter tube, and the peak-to-background ratio by the spectral response of the counter tube-discriminator system.

Geiger, proportional and scintillation counters are the most widely used detectors (aside from film) for powder diffractometry [13]. The Geiger counter is the simplest to use and requires the least circuitry [1, 6]. The principal disadvantages are its limited range of linearity and the fact that the pulse amplitudes are independent of the X-ray quantum energy, which makes it impossible to use electronic discrimination methods.

Proportional counters and scintillation counters with NaI·Tl scintillators have greatly extended the power of the counter tube method [15]. They are linear over the intensity range normally encountered, and with them it is possible to use a single channel pulse height analyzer to increase greatly the peak-to-background ratio. The scintillation counter has nearly 100 per cent quantum counting efficiency for the wavelengths generally used in powder diffractometry.

A full description of counter tubes, electronic circuits, counting statistics, etc., is beyond the scope of this paper. For a detailed account the reader may refer to the literature references [1, 6, 13, 15, 16]. There are several factors that must be considered in selection of the counter tube system. The most important are: (a) linearity; (b) quantum counting efficiency; (c) energy resolution; and (d) stability.

Statistical factors

Although the average X-ray intensity may be constant to, say, 1 per cent during a measurement, the quanta arrive at a random rate and hence it is necessary to take into account the statistical factors which are associated with random counting [9, 11].

The most common and generally useful method for powder diffractometry is to drive the counter tube automatically at a constant angular velocity and to record the ratemeter output on a strip chart recorder. There is always a certain time constant associated with the ratemeter circuit and the output lags behind the input. Consequently the recorded pattern is distorted by an

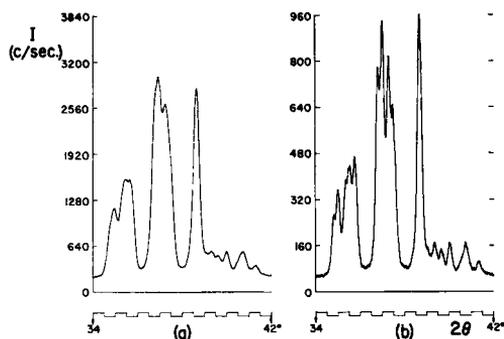


Fig. 5.—Recordings of a portion of the dickite pattern showing effects of scan speed, time constant and receiving slit width on the resolution and intensity. Cu $K\alpha$. (Proc. 7th Nat. Conf. on Clays and Clay Minerals.)

Scan speed ($^{\circ}/\text{min}$)	a	b	Receiving slit (2θ)	a	b
Time constant (sec)	1	$\frac{1}{4}$	Chart speed (in/hr)	0.2	0.05
Product (sec \times $^{\circ}/\text{min}$)	4	1		30	$7\frac{1}{2}$

amount dependent on the product of the scanning speed of the goniometer and the time constant of the ratemeter. If the product is small, say $\frac{1}{2}^{\circ}$ (2θ) per minute with a 2-sec time constant, the distortion is negligible for the usual identification analyses. If the product is large, say 2° (2θ) per min and 8-sec time constant, the peaks will be shifted toward the scanning direction and the line profiles distorted. At intermediate values the products are proportionally smaller. For good results the product should not exceed about 1 sec \times $^{\circ}/\text{min}$, which may be obtained with a $\frac{1}{2}^{\circ}$ (2θ) scan speed and 2-sec time constant, or preferably with $\frac{1}{4}^{\circ}$ (2θ) and 4-sec time constant. The effect of this product and the receiving slit width on a portion of the dickite pattern is shown in Fig. 5. The large differences in the resolution and intensities of the two patterns vividly illustrate the importance of these factors in powder diffractometry.

REFERENCES

1. CURTISS, L. F., *U.S. Natl. Bur. Stand. Circ.* 490 (1950).
2. DE WOLFF, P. M., *Acta Cryst.* 1, 207 (1948).
3. DE WOLFF, P. M., TAYLOR, J. M. and PARRISH, W., *J. Appl. Phys.* 30, 63 (1959).
4. FINE, S. and HENDIE, C. F., *Philips Tech. Rev.* 18, 229 (1956/57).
5. FLÖRKE, D. W. and SAALFELD, H., *Z. Krist.* 106, 460 (1955).
6. FRIEDMAN, H., *Proc. Inst. Radio Eng.* 37, 791 (1949).
7. LADELL, J. and PARRISH, W., *Philips Res. Repts.* 14, 401 (1959).
8. LANG, A. R., *Rev. Sci. Instr.* 26, 680 (1950).
9. MACK, M. and SPIELBERG, N., *Spectrochim. Acta* 12, 169 (1958).
10. MILBERG, M. E., *J. Appl. Phys.* 29, 64 (1958).
11. PARRISH, W., *Philips Tech. Rev.* 17, 206 (1955/56).
12. — Proc. Seventh Nat. Conf. on Clays & Clay Minerals, p. 230. Pergamon Press, New York, 1960.
13. PARRISH, W., *Int. Tables for X-Ray Cryst.* 3 (1961). In press.

14. PARRISH, W., HAMACHER, E. A. and LOWITZSCH, K., *Philips Tech. Rev.* **16**, 123 (1954/55).
15. PARRISH, W. and KOHLER, T. R., *Rev. Sci. Instr.* **27**, 795 (1956).
16. ——— *J. Appl. Phys.* **27**, 1215 (1956).
17. PARRISH, W. and LOWITZSCH, K., *Am. Mineral.* **44**, 765 (1959).
18. PARRISH, W., LOWITZSCH, K. and SPIELBERG, N., *Acta Cryst.* **11**, 400 (1958).
19. PARRISH, W. and TAYLOR, J., *Norelco Reporter* **3**, 105 (1956); see also *Int. Tables for X-Ray Cryst.* **3** (1961). In press.
20. PARRISH, W. and WILSON, A. J. C., *Int. Tables for X-Ray Cryst.* **2**, 154, (1959).
21. PIKE, E. R., *J. Sci. Instr.* **34**, 355 (1957).
22. ——— *ibid.* **36**, 52 (1959).
23. PORRENGA, D. H., *Am. Mineral.* **43**, 770 (1958).
24. SMALLMAN, C. R., *Rev. Sci. Instr.* **23**, 135 (1952).
25. WILLIAMS, J. H., *Phys. Rev.* **44**, 146 (1933).
26. WILSON, A. J. C., *J. Sci. Instr.* **27**, 321 (1950).