Determination of Crystallite Size with the XRay Spectrometer

Leroy Alexander and Harold P. Klug

Re-register for Table of Content Alerts

Create a profile.   Sign up today!

Determination of Crystallite Size with the X-Ray Spectrometer*

Leroy Alexander and Harold P. Klug

Department of Research in Chemical Physics, Mellon Institute, Pittsburgh, Pennsylvania

(Received July 25, 1949)

The accuracy of the Scherrer crystallite size equation is limited in part by the uncertainty in β, the experimentally deduced pure diffraction broadening. Currently used procedures for estimating β from the observed breadth of a Debye-Scherrer line are not, in general, applicable to the x-ray spectrometer.

By making use of a scheme of convolution analysis for analyzing the effect of geometrical factors in broadening the pure diffraction contour, a correction curve is developed for determining β from the experimentally measured line breadths b and B (Jones' notation). The degree of reliability of this correction procedure is ascertained by applying Stokes' direct Fourier transform procedure for determining the form of the pure diffraction contour free of instrumental effects.

Suggestive procedures are given for crystallite size determination with the x-ray spectrometer in different size ranges, and several examples are described.

I. INTRODUCTION

THE accuracy of the familiar Scherrer equation,

$$D = (K\lambda)/(\beta \cos\theta), \qquad (1)$$

is limited by the uncertainties in K, the crystallite shape factor, and β, the pure diffraction broadening. Theoretical work by Stokes and Wilson[1] has elucidated the relationship between K and the crystal shape to a degree not previously attained. However, for the usual applications to crystallite size measurement a large degree of indeterminancy in K, as much as 20 percent or even more, remains, and it is customary to let $K=1$. To gain optimum accuracy it remains to reduce the uncertainty in β as much as possible, preferably to a value much less than 20 percent.

Considerable effort has been expended by a number of investigators in evolving expressions for readily deducing β from B, the observed breadth, for the case of Debye-Scherrer lines. The most widely applied are the procedures due to Warren[2] and Jones.[3] These published correction curves have also been applied to the analysis of spectrometer maxima, although no one has specifically demonstrated their applicability to the particular conditions governing the generation of spectrometer contours. The formula of Warren,

$$\beta^2 = B^2 - b^2, \qquad (2)$$

where b is the observed breadth of a line produced by crystallites of sufficient size to give no diffraction broadening, applies only to the case in which the β and b contours are both true "error" curves of the form $e^{-k^2x^2}$. Similarly Jones' two correction curves (a) and (b) apply only to the cases where the β contour has the respective forms $e^{-k^2x^2}$ and $1/(1+k^2x^2)$. The form of the b contour assumed by Jones was experimentally obtained by microphotometering a Debye-Scherrer line

at a Bragg angle large enough to clearly resolve the $K\alpha$ doublet.

Recently Shull[4] and Stokes[5] have developed Fourier transform procedures for deducing the β contour from observed b and B contours. The method of Stokes is the more generally applicable but it requires a means for the rapid summation of Fourier series. More recently one of the present authors[6] has shown how the convolution, or *Faltung*, theorem can be used to synthesize the form of a b or B contour generated by an x-ray spectrometer starting with a pure diffraction contour of known dimensions. In the light of these developments it seemed that this was a propitious time to examine the problem of crystallite size determination with the x-ray spectrometer with a view to improving the accuracy with which the width of the pure diffraction contour can be deduced free of the various instrumental broadening effects.

Since most of the commercial spectrometers in use today are of the older Norelco design which is limited to the θ range from 0° to 45°, it is felt desirable to concentrate the present analysis on crystallite size determinations which can be carried out in this angular range. Hence, we shall consider size measurements mainly in the range 0 to 500A and particularly those between about 250 and 500A, where the errors due to improper correction of the instrumental contributions may be very large. With the older type of spectrometer, having a wide x-ray source contour and limited to angles below $\theta = 45°$, it is futile to attempt size measurements for crystallites much larger than 500A because the mandatory precision of the experimental measurements becomes too great for practical work.

II. COMPUTATION OF A CORRECTION CURVE FOR CRYSTALLITE SIZE DETERMINATION WITH THE X-RAY SPECTROMETER

In reference 6 the broadening effects of the five significant instrumental factors, or weight functions,

---

* Presented in part before the American Society for X-Ray and Electron Diffraction at Cornell University, Ithaca, New York, on June 25, 1949.

[1] A. R. Stokes and A. J. C. Wilson, Proc. Camb. Phil. Soc. 38, 313 (1942); *ibid.* 40, 197 (1944).

[2] B. E. Warren, J. App. Phys. 12, 375 (1941).

[3] F. W. Jones, Proc. Roy. Soc. A166, 16 (1938).

[4] C. G. Shull, Phys. Rev. 70, 679 (1946).

[5] A. R. Stokes, Proc. Phys. Soc. 61, 382 (1948).

[6] L. Alexander, J. App. Phys. 21, 126 (1950).

TABLE I. Data utilized in the preparation of the spectrometer correction curve. $\theta = 30°$, $w_I = 0.20°$, $w_s = 0.088°$. By convolution analysis $b = 0.210°$.

$D(A)$	$\beta(°)$ (from Scherrer formula)	$B(°)$ (from convolution theory)	b/B	β/B
∞	0	$0.210(b)$	—	—
1000	0.102	0.272	0.773	0.375
700	0.1455	0.300	0.700	0.485
500	0.204	0.341	0.616	0.598
300	0.341	0.444	0.473	0.769
200	0.510	0.596	0.352	0.856
100	1.020	1.061	0.198	0.962
50	2.040	2.040	0.103	1.000

upon a pure diffraction contour were investigated. A scheme of convolution analysis was employed to develop generalized broadening curves for each of the factors, and it was shown that by successively employing each of these curves the width of the diffraction contour generated by the spectrometer could be predicted, starting with a pure diffraction contour of any assumed width.

In reference 6 it was pointed out that with a proper choice of the experimental conditions three of the five instrumental factors causing contour broadening become negligible and only the effects of (I) the x-ray source width and (V) the receiving slit width need be considered. The requisite conditions are that the linear absorption coefficient of the powder for the x-ray beam be not too small ($\mu \geqq 40$) and that the diffraction angle 2θ be 20° or greater. The first condition is met in the case of CuKα radiation for nearly all materials except organic and metal-organic compounds, and the second condition can nearly always be satisfied by the proper choice of a diffraction line. It will accordingly be assumed in the development to follow that these simplifying conditions obtain.

The results of the convolution analysis can be easily plotted as a correction curve in the manner given by Jones[3] wherein β/B is plotted as a function of b/B. In order to simplify the terminology the notation of Jones will be used as far as possible. However, as it will prove necessary to refer to the different symbols of reference 6 occasionally, it will be helpful at the outset to compare the two notations:

Function	Jones	Reference 6
Pure diffraction breadth	β	w
Observed breadth for large crystallites (uncorrected for Kα doublet)	b_0	w_6
Same (corrected for Kα doublet)	b	w_5
Observed breadth for small crystallites (uncorrected for Kα doublet)	B_0	w_6
Same (corrected for Kα doublet)	B	w_5

It will be noticed that the contour breadths for small and large crystallites have not been distinguished in the notation of reference 6. This is because the analysis of reference 6 was of a general nature, applicable to contours of any breadth. Unless otherwise indicated the term *width*, or *breadth*, of a contour in the present

paper denotes the width at half maximum intensity. Jones' analysis and correction curves apply to the integral breadth, which is defined by $\beta_x = (\int I_x dx)/(I_x)_{max}$.

The present analysis will deal mainly with the case of a relatively wide x-ray source (appropriate for the older Norelco spectrometer). For materials with crystallite size larger than 1000A the observed contour breadth b_0 will be due largely to the x-ray source and to a lesser extent to the receiving slit (unless an abnormally wide slit is employed). For materials smaller than 1000A the observed contour breadth B_0 will also be widened because of the width of the pure diffraction contour, β. If the crystallite size is very small the pure diffraction broadening becomes the dominant factor in determining the breadth of the observed contour. In addition to these effects, if the Kα doublet is not resolved, the observed contour will in all cases be widened as a result of the superposition of the overlapping contours produced by the α_1 and α_2 components of the radiation.

It will be assumed in the present paper that all observed contours have been corrected for Kα doublet broadening before the crystallite size correction curve is to be employed. The curve of Jones[3] for correcting for Kα doublet broadening is satisfactory for use with x-ray spectrometers having wide sources (of the order of 0.20° 2θ).
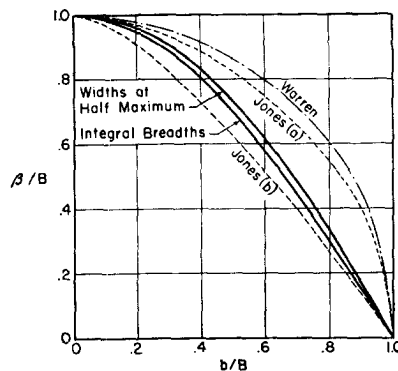

FIG. 1. X-ray spectrometer curves for correcting the breadths of diffraction contours for instrumental broadening. Also shown are the curves of Jones and Warren for Debye-Scherrer photographs.

Our procedure will now be as follows: (a) Using Eq. (1) compute the pure diffraction breadth, β, of the contour produced by a material of crystallite dimension D. (b) Using the convolution method of reference 6 compute the breadth B of the contour generated by the instrument without the added effect of the Kα doublet. (c) Similarly compute the breadth b of the contour generated for materials of large crystallite size (for which $\beta \rightarrow 0$). (d) Following the appropriate scheme of Jones, plot β/B as a function of b/B.

The success of this method of arriving at the correction curve will be contingent upon our correct choice of mathematical functions to describe the pure dif-

138

fraction contour and the x-ray source contour. A careful appraisal of these functions will be found in Parts III and IV of reference 6, so that it is necessary here only to repeat the final results, viz., that a typical crystallite size distribution tends to generate a pure diffraction contour which is closely approximated by $1/(1+k^2\phi^2)$, whereas an x-ray source contour is more nearly described by $e^{-k^2\phi^2}$. Accordingly, the derivation of the correction curve which follows will be based on the premise that these simple mathematical functions accurately describe the pure diffraction and x-ray source contours.

The method of determining the curve of β/B as a function of b/B will be illustrated in detail by the calculation of one selected point, after which the complete data required for locating the entire curve will be tabulated. We shall select the case $\theta=30°$ and a crystallite size of $D=500A$. The spectrometer is assumed to be of the older design with an x-ray source width (w_I) of $0.200°$, and a relatively narrow receiving slit width, $w_s=0.088°$, is employed. The radiation is CuKα, for which $\lambda=1.542A$.

Using the standard crystallite size equation with K set equal to unity, we find for the theoretical breadth of the pure diffraction contour

$$\beta=w=\frac{K\lambda}{D\cos\theta}=\frac{1.542\times57.3}{500\times.866}=0.204°.$$

The ratio of the width of the contour to that of the source is $w/w_I=0.204°/0.200°=1.02$. Referring to Fig. 4(I) of reference 6, we find for the broadening ratio $w_1/w=1.62$. Then the width of the resulting contour is

$$w_1=w\times(w_1/w)=0.204°\times1.62=0.330°.$$

This contour will be intermediate between $e^{-k^2\phi^2}$ and $1/(1+k^2\phi^2)$ in form because it is the convolution of two functions which are of these two pure forms and of approximately equal width.

We turn next to the action of the receiving slit in broadening this contour. The ratio of its width to that of the slit is $w_1/w_s=0.330°/0.088°=3.75$. Since we are neglecting the instrumental weight functions II, III, and IV, this ratio becomes the abscissa, w_4/w_s, of Fig. 4(V) of reference 6. The initial contour will be broadened by an amount which is approximately the mean of the values given by curves (a) and (b), hence $w_5/w_4=(1.030+1.036)/2=1.033$. This leads to a resulting contour width of

$$B=w_5=w_4\times(w_5/w_4)=0.330°\times1.033=0.341°.$$

For the reference material of large crystallite size the pure diffraction breadth β is zero. Hence, we start with the source contour and determine the broadening ratio due to the action of the receiving slit upon it. We have then

$$w_I/w_s=0.200°/0.088°=2.27,$$

TABLE II. Calculation of the crystallite sizes of four materials from spectrometer measurements after determining β (A) by Stokes' Fourier method and (B) from the correction curve of Fig. 1 (widths at half maximum).

	CaF$_2$	MgO	Cristo-balite	Basic calcium phosphate
Observed breadths				
B_0	0.500°	0.700°	0.470°	0.468°
b_0 (quartz powder)	0.330°	0.330°	0.320°	0.330°
Breadths after correcting for K$\alpha_1\alpha_2$				
B	0.460°	0.674°	0.462°	0.456°
b	0.276°	0.284°	0.307°	0.314°
Correction ratios				
b/B	0.600	0.421	0.665	0.689
β/B (Fig. 1)	0.620	0.810	0.533	0.500
Pure diffraction breadths				
β (Stokes' method)	0.335°	0.530°	0.260°	0.215°
β (Fig. 1)	0.285°	0.546°	0.246°	0.228°
Calculated crystallite sizes				
D(A.) (Stokes' method)	290	179	346	422
D(A.) (Fig. 1)	342	174	366	398

and from Fig. 4(V), curve (a), of reference (6), $w_5/w_4=1.05$, and consequently

$$b=w_5=w_4\times(w_5/w_4)=0.200°\times1.05=0.210°.$$

From these calculated values of β, b, and B we obtain

$$b/B=0.616 \quad \text{and} \quad \beta/B=0.598.$$

By proceeding in a similar manner for a number of crystallite sizes ranging from 50 to 1000A the remaining data of Table I of the present paper were obtained. When plotted with β/B as a function of b/B, the solid curve marked "Widths at Half Maximum" of Fig. 1 is obtained. Although deduced specifically for the case of $\theta=30°$ and a receiving slit width of $0.088°$, this curve is found to be perfectly general for all values of θ in the range 0-45° and for receiving slit widths ranging from 0 to about 0.20°. When the slit width exceeds the angular width of the source by an appreciable amount, the correction curve shifts to the right. The most satisfactory policy in this regard is to always employ the narrowest receiving slit that is compatible with the diffracted energy available.

By a parallel set of calculations it can be shown, or by direct comparison of the geometrical conditions it can be inferred, that this same correction curve applies, within limits, to spectrometers with narrower sources. However, when the source width becomes much smaller than 0.10°, the several minor broadening factors become relatively significant, so that the premises upon which the present curve is based are no longer correct.

III. EXPERIMENTAL SUBSTANTIATION OF THE CORRECTION CURVE

In Part III of reference 6 the pure diffraction contours of six miscellaneous materials were investigated, five of them by the Fourier transform method of Stokes.[5] Four of these materials made excellent subjects

TABLE III. Comparison of the crystallite sizes of four materials as deduced by different correction curves. The figures are calculated crystallite sizes in A.

Method of correction	CaF_2	MgO	Cristobalite	Basic calcium phosphate
Stokes (Fourier)	290	179	346	422
Curve of Fig. 1, widths at half maximum	342	174	366	398
Jones' curve (a)	285	162	284	301
Jones' curve (b)	414	201	448	491
Warren's curve $[\beta/B = (1 - b^2/B^2)^{\frac{1}{2}}]$	265	156	260	274

for a test of the spectrometer correction curve of Fig. 1. The widths of the pure contours deduced by the Fourier method can be considered to be the best obtainable and hence to also lead to the most reliable values of the crystallite sizes. In Table II the crystallite sizes are calculated using the curve of Fig. 1 marked "Widths at Half Maximum," and the resulting values are compared with the presumably best values from the Stokes procedure.

In every case an appropriate quartz maximum was measured in order to obtain the required value of b_0 for a material of large crystallite size. The contours were measured with a Norelco Geiger-Counter Spectrometer, Type No. 12021 (with wide x-ray source), the spectrometer arm being set manually at appropriate intervals and the counting rates being recorded directly. In every instance except that of basic calcium phosphate it was possible to reduce the probable statistical counting error in the peak height above background to 1 percent or less. It is seen that in three out of four cases the agreement is highly satisfactory, and, furthermore, that in the single case of less satisfactory agreement (CaF_2) a greater deviation from the presumably best value (by Stokes' method) is to be expected because the pure diffraction contour is intermediate in nature between the forms $1/(1+k^2\phi^2)$ and $e^{-k^2\phi^2}$ rather than resembling more closely the first function (refer to Table I of reference 6).

Table III compares the crystallite sizes of these same materials as calculated using various correction curves with the values arrived at by Stokes' Fourier method. For the sake of ready comparison these correction curves are also plotted in Fig. 1. An examination of Table III shows that on the average the present curve gives much better agreement with the Fourier results than any of the other curves. Only in the case of the somewhat anomalous contour of CaF_2 would somewhat better results have been obtained by using other curves, e.g., by employing either Warren's curve or Jones' curve (a). It is interesting to note from Fig. 1 that the new spectrometer curve agrees more nearly with Jones' curve (b) at large values of b/B (large crystallite sizes), while it approaches both Jones' curve (a) and Warren's curve more closely at small values of b/B (small crystallite sizes). However, as is well-known, the choice of correction curve is unimportant for small crystallite sizes.

IV. DISCUSSION OF THE CORRECTION CURVE

In Part II it was emphasized that the derivation of the present correction curve is based on the premise that the functions $1/(1+k^2\phi^2)$ and $e^{-k^2\phi^2}$ accurately describe the pure diffraction contour and x-ray source contour respectively. These formulas should be regarded realistically as being only limiting functions which are approached only more or less imperfectly in any experimental situation. Consequently the most that should be claimed for the present correction curve is that the probability of its yielding an accurate value of β is good and also much better than that of curves based on other pairs of simple mathematical functions.

In particular, it is suggested that each investigator test the focal spot of the particular x-ray tube employed for agreement with the function $e^{-k^2\phi^2}$. A simple but sufficiently accurate method for accomplishing this is described in Part IV of reference 6. If reasonably good agreement is found he may then use the present correction curve with confidence.

For a spectrometer with a wide source the correction curve of Fig. 1 will have rather general reliability provided that the following experimental requirements are satisfied: (a) The linear absorption coefficient of the powder (including solid and interstices) should be approximately 40 or larger. (b) The diffraction angle, 2θ, should be greater than 20°. (c) The receiving slit width should not exceed the width at half maximum intensity of the x-ray source contour (both expressed in terms of 2θ units). (d) By proper adjustment of the x-ray slit the horizontal and vertical divergence of the x-ray beam should preferably be limited to moderate values, say, 1° and 2° respectively. Under these circumstances, if we disregard the usual remaining uncertainty in K of Eq. (1), satisfactory measurements can be made of crystallite sizes as large as 500A provided that B_0 and b_0 can be measured with an accuracy of ±0.01° or better for the larger sizes. For the new spectrometers with narrower x-ray sources the present curve is fairly reliable for crystallite size measurements below 500A. However, although instruments of this design are theoretically capable of application in the size range 500–1000A, the novel geometrical factors involved are such as to require a special analysis in order that a correction curve may be established for work in this size range.

If it is desired to use integral contour breadths, defined by $\beta_x = (\int I_x d_x)/(I_x)_{max}$, rather than widths at half maximum intensity, the curve marked "Integral Breadths" in Fig. 1 should be employed. This curve was derived by substituting the functions $1/(1+k_1^2x^2)$ and $\exp(-k_2^2x^2)$ respectively for $F(kx)$ and $f(x)$ in Jones' Eqs. (4) and (5).[3] The integral breadth is more convenient for mathematical analysis but less readily employed in the experimental measurement of crystallite size.

140

When measurements of the highest reliability are required, it is recommended that the Fourier transform method of Stokes be employed for determining β. Once the equipment for the rapid summation of Fourier series has been constructed and the technique for performing the operations has been mastered, the time consumption per analysis is not excessive (possibly one or two hours). The Fourier method has completely
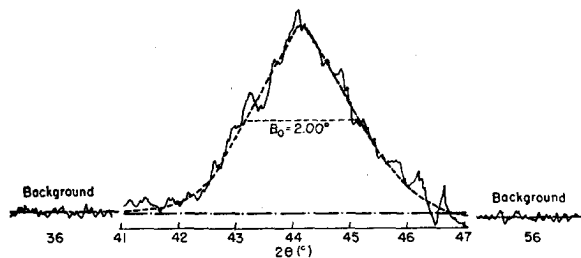

FIG. 2. Determination of the crystallite size of a nickel catalyst from an automatic strip chart record of the (111) maximum. CuKα-radiation; scanning speed 1° per minute; background measured at $2\theta=36°$ and $56°$. Neglecting b_0, $D_{111}=48$ A. Using $b_0=0.33°$ for the (220) reflection of NaCl powder, $D_{111}=49$ A.

general applicability regardless of the particular forms of the pure diffraction contour and the various instrumental broadening functions. Furthermore Kα doublet broadening is automatically allowed for.

V. PRACTICAL SUGGESTIONS FOR CRYSTALLITE SIZE DETERMINATION WITH THE X-RAY SPECTROMETER

The following discussion applies to the older spectrometer design incorporating a wide x-ray source and a working range of $2\theta=0$ to $90°$. Three crystallite size ranges will be given special consideration, each amenable to a somewhat different experimental approach.

For all except the smallest crystallite sizes it is necessary to measure the contour widths of both the material being studied (B_0) and a reference material which gives no crystallite size broadening (b_0). In order that the geometrical broadening effects may be as nearly identical as possible, the two peaks should be situated at approximately the same diffraction angle. When the linear absorption coefficients for x-rays of the "unknown" and reference powders are both high (say, $\mu=40$ or more when the interstices of the powder are included in the calculation) or when the absorption coefficients are known to be very nearly equal, good results can be obtained when the two materials are mounted and analyzed separately. However, when the coefficients are small, and in particular when they are known to differ considerably, the two materials should be intimately mixed and the measurements made on a single sample. The fact that the calculated absorption coefficients of the two solid materials are nearly equal is in itself no guarantee that the powders will absorb equally because they may not pack to the same density. When this is evidently true, or when there is any doubt

in this regard, the materials should always be mixed. Fine quartz powder manifests a fairly typical packing behavior and is found to assume a state in which solid and interstices constitute about 40 and 60 percent respectively of the total sample volume. Hence, the linear absorption coefficient of the powder is only 0.40 as large as that of the solid material [for CuKα radiation μ (quartz powder)$=0.40\times93=37$].

The above suggestions presuppose the use of a sample of sufficient thickness to give maximum absorption (see remarks in reference 6, Part VII). If sufficient intensity can be obtained with the use of a very thin sample, such as a film of powder mounted on a suitable plane substrate, the differences in absorption become much less important and it is usually unnecessary to mix the powders.

Case 1. Size Range <150A

In this range fairly good results can be had by preparing automatic strip chart records at a sufficiently slow scanning speed to yield a contour of easily measurable width. The background is also measured at selected points on either side of the maximum, after which the best straight horizontal line is drawn through the statistical fluctuations of each background record and a smooth curve is drawn to delineate the peak contour. This method is not successful unless the peaks in question are relatively strong. In favorable cases of this sort β can be determined with a probable error of 5 to 10 percent. Figure 2 illustrates the application of this method to a nickel catalyst of fine crystallite size.

If the peak contours are counted and plotted manually and if sufficient counts are taken to permit the
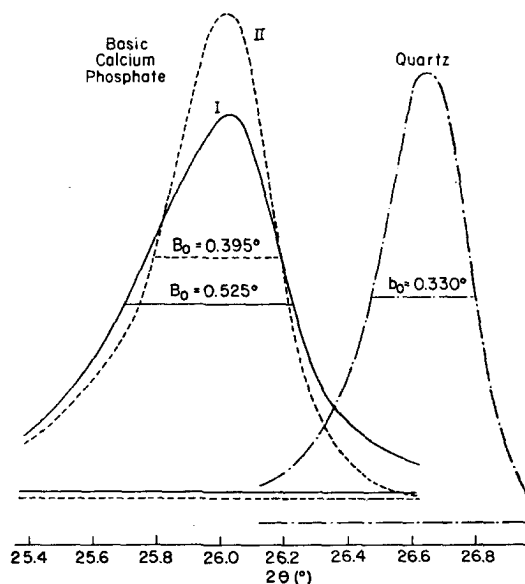

FIG. 3. Diffraction contours of basic calcium phosphate precipitate before (I) and after (II) digestion, and reference contour of quartz powder. The contours were plotted from manually recorded counting rate data. Crystallite sizes (after correcting for Kα doublet broadening): (I) 290 A, (II) approximately 800 A.
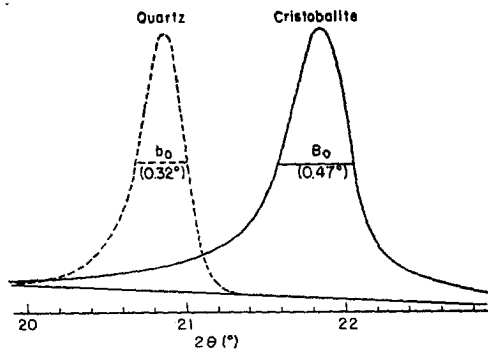
FIG. 4. Diffraction contours used in determining the crystallite size of cristobalite prepared by calcining diatomaceous earth. The contours were plotted from manually recorded counting rate data. Mean crystallite size (after correcting b_0 and B_0 for $K\alpha$ doublet broadening), 366 A.

determination of the peak height above background with a probable error from counting statistics of 1 percent or less (5000 counts per point for cases with negligibly small backgrounds), the probable error in β can be reduced to 3 percent or less. In this size range it is unnecessary to correct the observed line breadths for $K\alpha$ doublet broadening. Warren[2] has pointed out that the measured breadth of the "unknown" line, B_0, can be substituted for β directly in the crystallite size formula when $b_0 < B_0/5$, because in such instances the broadening due to the instrumental effects becomes insignificant in comparison with the pure diffraction broadening. Thus, for the nickel catalyst of Fig. 2 the calculated crystallite size was 49A when b_0 was taken into account and 48A when not.

Case 2. Size Range 150–300A

Automatic recording is not satisfactory in this range except for very rough measurements. If the heights of the peaks above background are determined with an accuracy approaching 1 percent (as limited by counting statistics), it is possible to determine β with a probable error of 5 percent. This and succeeding estimates of precision and error take into account a reasonable degree of uncertainty in the position of the spectrometer correction curve (Fig. 1). In this size range it is unnecessary to correct for $K\alpha$ doublet broadening for $2\theta < 60°$. For higher angles the error involved is sufficient to increase appreciably the 5 percent probable error quoted above.

Case 3. Size Range 300–500A

In this range it is necessary to adopt the best experimental techniques in order to secure good results. A probable error in β of considerably less than 10 percent can be attained by keeping the probable error in counting statistics at points near the tops of the peaks smaller than 1 percent and by correcting for $K\alpha$ doublet broadening *in all cases*. In addition, for the most

accurate work it is recommended that the recorded counting rates be corrected for the nonlinearity of response of the Geiger tube.[7]

Of course, care must also be exercised in defining accurately the sides of the contours at the levels at which the breadths B_0 and b_0 are to be measured. This means measuring the counting rates at two or more points in the immediate vicinities. An analysis of the counting errors involved has shown that it is satisfactory to use a constant time interval for counting all the points defining a given contour, provided only that this time interval furnishes a sufficient number of counts to determine the height of the peak above background with high precision.

The background should preferably be counted with a longer time interval because of the normally much smaller intensities involved, and it is suggested that this interval be made twice as long as that employed in counting the peak contour. When the background is abnormally high and constitutes an appreciable portion of the over-all counting rate measured at the top of the peak, it is necessary to totalize much more than 5000 counts at the top of the peak in order to reduce the probable error in the *net* peak height to less than 1 percent.[8] In any event care should also be taken that the background be measured at points sufficiently far removed from the peak to avoid contributions from the base of the peak itself. For sharp peaks an angular displacement from the peak center of 2.0° is usually satisfactory, but for the very wide maxima generated by a distribution of crystallite sizes in the range below 100A it is necessary to increase this to 5° or even more.

Figures 3 and 4 illustrate crystallite size measurements in the ranges of Cases 2 and 3. In each figure the required reference contour of a material of large crystallite size (fine quartz powder) is also shown. Actually each contour pictured was obtained using a separate sample, but the several contours have been drawn together to facilitate comparison. The growth of the basic calcium phosphate crystallites during digestion is strikingly reflected in the alteration of the diffraction contour shown in Fig. 3. The accuracy of the measurement following digestion is obviously not good (probably not better than $800\pm150A$) because the size involved is outside the satisfactory working range of the spectrometer. Figure 4 portrays the b_0 and B_0 contours which were analyzed in determining the crystallite size of cristobalite, a form of crystalline silica, prepared by calcining diatomaceous earth.

[7] Alexander, Kummer, and Klug, J. App. Phys. **20**, 735 (1949).
[8] Tracerlog No. 2, p. 5, March 1947.