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DETERMINATION OF  
PARTICLE SIZE BY THE X-RAY  
POWDER METHOD

BY

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## INTRODUCTION

It is a well-known fact that the lines of an X-ray powder diagram are broad and diffuse when the elementary particles of the powder are very small<sup>1)</sup>. Several physicists, especially SCHERRER<sup>2)3)</sup>, LAUE<sup>4)5)</sup>, and BRILL<sup>6)7)8)9)</sup>, have devised methods for the determination of particle dimensions in a powder from the "line breadth" of its X-ray diagram. The new method to be described in the following is more accurate than SCHERRER's and, compared with the methods described by LAUE and BRILL, it has the advantage that diagrams taken with the ordinary technique (relatively short exposures) may be employed. Unlike BRILL's methods, it does not require powder specimens of no, or of infinitely large absorption; neither very narrow slits in the primary beam, nor a very divergent primary beam are needed. The method is applicable in cases where the absorption in the specimen is incalculable as, for instance, when the Seemann-Bohlin focussing camera is applied, or when specimens in glass capillaries are used in the ordinary Debye camera.

The method is based upon a comparison of the line breadths in two diagrams; the first, a diagram of the powder whose particle size is to be determined, the second, a diagram of the same chemical compound in a suitably large-grained state. Otherwise, the two specimens should be identical with respect to dimensions, density, etc., and both diagrams should be taken with the same arrangement of apparatus.

### The ideal case.

The following formula has been proposed for the breadth of a Debye line in a strongly idealized case,

$$b_{hkl} = \frac{k \cdot \lambda}{t \cdot \cos \theta}, \quad \text{I}$$

where  $\theta$  is the glancing angle,  $b$  is the breadth of the line defined as the angular range between two points where the intensity has fallen to half of its maximum value,  $\lambda$  is the wave length,  $t$  is the linear extension of the reflecting crystal, and  $k$  a constant. If  $\lambda$  and  $t$  are measured in the same units and  $b$  in radians, the numerical value of  $k$  is about  $0.90^1$ .

The formula I is valid

a) if the primary beam is parallel, infinitely narrow, and reflected by a single crystal whose linear extension is  $t$ , perpendicular to the reflecting plane ( $hkl$ );

b) for a line in a powder diagram under ideal experimental conditions, i. e. parallel primary beam, infinitely thin specimen, monodispersed powder, if

1) the crystals belong to the cubic system and are developed as cubes with a side  $t$  (LAUE<sup>4</sup>, SELJAKOW<sup>10</sup>),

2) the crystals are non-cubic, but are limited by the face ( $hkl$ ) and are of a thickness  $t$  perpendicular to ( $hkl$ ) (LAUE<sup>4</sup>). A large crystal under condition a) and a powder of fairly large particles under conditions b) will give infinitely narrow reflections.

### The actual case.

For practical reasons, formula I is not applicable directly. It is impracticable to use specimens so thin and a primary beam so faintly divergent that the breadth of a line from a powder of large particles becomes infinitely thin compared with  $b_{hkl}$  in formula I. In order to secure a suitably short time of exposure, specimen dimensions and slit width should not be smaller than sufficient to ensure the resolution of the two lines that lie closest to each other in the diagram. In this case, the lines obtained are not very narrow. The intensity distribution in the lines depends in an intricate way on the dimensions of the slit and of the specimen and on the absorption in the specimen. Such an intensity distribution  $I = f(\theta)$  (vide fig. 1) results from a sum of a large number of very narrow rectangles. A rectangle between  $\theta = \theta_1$  and  $\theta = \theta_1 + \Delta\theta_1$  is the non-absorbed part of the reflected intensity from a large number of small crystals which are oriented in such a way that the plane  $hkl$  is in reflecting

<sup>1</sup> SCHERRER<sup>2)3)</sup> gives 0.94, SELJAKOW<sup>10)</sup> 0.92, LAUE<sup>4)</sup> 0.90, and W. L. BRAGG<sup>1)</sup> 0.89.

position, and so situated that the reflections fall between  $\theta = \theta_1$  and  $\theta = \theta_1 + \Delta\theta_1$  on the film. The height of the rectangle depends upon the degree of absorption of the primary and the reflected beam in the powder specimen. Let us imagine the large particles divided until every new elementary particle gives a reflection of finite breadth. The intensity which fell between  $\theta_1$

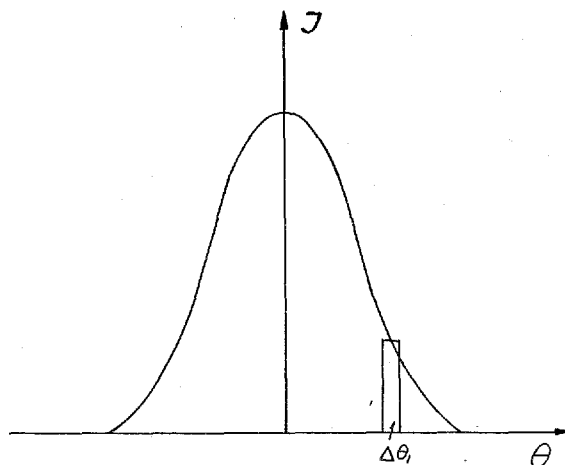


Fig. 1. Intensity distribution in a powder diagram line and one of the rectangles of which the curve is made up.

and  $\theta_1 + \Delta\theta_1$  is now smeared out and no longer forms a narrow rectangle but a rounded peak with the intensity distribution  $i(\theta_1, \theta)$ .  $\theta_1$  is the middle of the peak, and  $\theta$  the point where the intensity is  $i(\theta_1, \theta)$ . The breadth  $b$  of this peak obeys equation I.

We assume that the area below the curve  $i(\theta_1, \theta)$  is equal to the area of the rectangle. The intensity in the entire line is also smeared out, and a new intensity distribution function  $I^1(\theta)$  is obtained.  $I^1(\theta)$  is somewhat broader and lower than  $I(\theta)$ .

Provided that  $I(\theta)$  and  $i(\theta_1, \theta)$  are Gaussian error functions

$$I(\theta) = I_0 \cdot e^{-H^2 \theta^2}$$

and

$$i(\theta_1, \theta) = i(\theta_1, \theta) \cdot e^{-h^2 (\theta - \theta_1)^2},$$

it is not difficult to prove<sup>1</sup> that  $I^1(\theta)$  is also a Gaussian function.

<sup>1</sup> The proof is not given here since its result is incorporated in a number of textbooks on mathematics.

Then, the breadths ( $B_1$ ,  $B$  and  $b$ ) of the three curves are connected by the equation

$$B_1^2 = B^2 + b^2. \quad \text{II}$$

Hence  $b = b_{hkl}$ , which could not be obtained in direct experiments, may be found from equation II.

Formula II is different from a formula put forward without proof by SCHERRER<sup>2)3)</sup> which in our notation reads  $B_1 = B + b$ .<sup>1</sup>

### The assumptions involved.

The intensity distribution in an X-ray reflection from a crystal consisting of  $N$  successive atomic planes obeys the equation

$$I/I_0 = \frac{\sin^2 \varphi}{\varphi^2}$$

where

$$\varphi = \frac{2 \pi N d \varepsilon \cos \theta}{\lambda} \quad (\text{BRAGG}^1);$$

in our previous notation

$$I/I_0 = \frac{\sin^2 \varphi}{\varphi^2}, \quad \text{III}$$

where  $\varphi = c \cdot \theta$  and  $c$  is a constant.

Certainly, these equations do not constitute a Gaussian function, but the deviation from a Gaussian function is negligible in this connection, as may be seen from fig. 2 which shows the intensity function III and a Gaussian function of the same height and breadth.

MURDOCK<sup>1)</sup> examined the intensity distribution function also considering the influence of the crystal shape in a few simple cases. He obtained curves which all lay extraordinarily close to a Gaussian curve.

The small differences between intensity functions for differently developed crystallites (cubes, octahedra) were of the same magnitude as the differences between the intensity functions obtained

<sup>1</sup> (Note added after completion of the paper.)

A similar method for the determination of particle size could not be found in the literature available. However, in a private communication Professor GUNNAR HÄGG called my attention to the fact that the method here described and the argument applied in a number of papers on the breadth of spectral lines have several points of resemblance. Vide e. g. A. H. COMPTON and S. K. ALLISON, X-rays in theory and experiment, (London 1935) p. 740 etc.; BURGER and VAN CITTERT, Zs. f. Physik 44 (1927) 50.

and a Gaussian function of the same height and breadth. Since the shape of crystallites in a powder to be examined by X-rays is always unknown, and since their monodispersity is often questionable, the assumption of a Gaussian function for the distribution  $i(\theta_1, \theta)$  is well warranted.

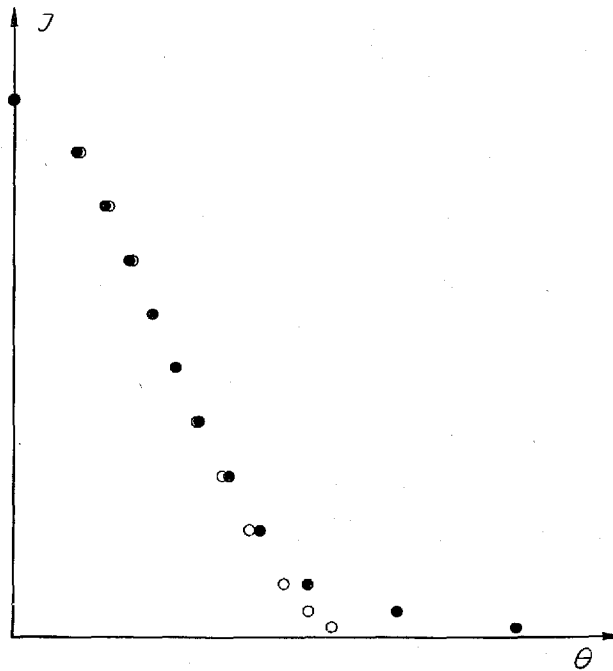


Fig. 2. Theoretical intensity distribution in a spectral line • and the corresponding Gaussian error curve ○.

Fig. 3 shows how closely the intensity distribution in a line of a powder diagram approximates a Gaussian function. Fig. 3 represents a photometer tracing of three lines in a diagram of  $\text{CaCl}_2$  of medium particle size. The small circles lie on a Gaussian error curve of the same height and breadth as the second of these lines.

To the discussion following fig. 1 may be added: We presume that all particles of the powder are alike. The rectangle of breadth  $\Delta\theta$  is a sum of terms  $\tau \cdot f(\varphi, \omega, \kappa)$ , where  $\tau$  is the energy which would have been reflected from one particle if all other particles were absent and if no absorption of the primary or the reflected

beam had occurred.  $f$  is a coefficient of absorption including the absorption in the primary as well as in the reflected beam.  $(\varphi, \omega, z)$  are the cylindrical coordinates in the powder rod. The area  $A_1$  of the rectangle is

$$A_1 = \Delta\theta_1 \cdot I(\theta_1) = \Sigma \tau \cdot f(\varphi, \omega, z) = \tau \cdot \Sigma f(\varphi, \omega, z).$$

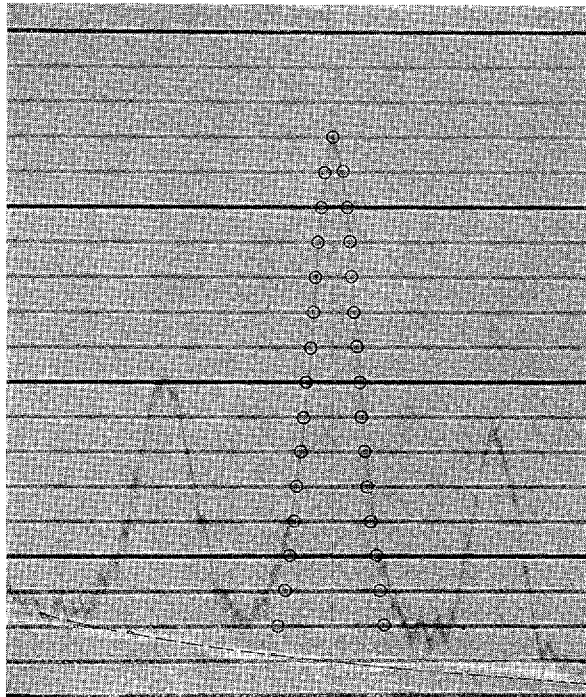


Fig. 3. Intensity distribution in powder diagram lines. The circles lie on a Gaussian error curve of the same height and breadth as the line.

$\Sigma$  designates that the summation is to be extended over all particles which have the plane  $(hkl)$  in reflecting position, and the reflections of which fall within  $\Delta\theta$  on the film.

If any particle is divided  $n$  times in every direction, the reflected energy becomes

$$A_2 = \tau' \Sigma f(\varphi, \omega, z).$$

The number of terms has been multiplied by  $n^3$ , but the function  $f$  remains unchanged, since, apart from the intensity



distribution in the primary beam, it depends only on the size and the chemical composition of the specimen, and not on the particle size.

In other words, the same function should be summed up in  $n^3$  as many points as previously. If  $\tau = n^3 \tau'$ ,  $A_1$  and  $A_2$  are equal, as assumed above. Even if  $\tau$  is different from  $n^3 \tau'$ , formula II  $B^{1^2} = B^2 + b^2$  holds. In this case,  $n^3 \tau' / \tau = \text{constant}$ , hence  $A_1 / A_2 = \text{constant}$ .  $I^1(\theta)$  will have another height than in the case  $A_1 = A_2$ , but it will show the same breadth.

### Summary.

A method for X-ray determination of particle size is described. The breadth  $B^1$  of a line  $hkl$  in a powder diagram of the substance whose particle size is to be determined, and the breadth  $B$  of the same line  $hkl$  in a "normal" diagram of the same chemical compound are measured. For the "normal" diagram, the substance is suitably large-grained, and both diagrams are taken with the same set of apparatus.  $b = \sqrt{B^{1^2} - B^2}$  is the breadth with which the line  $hkl$  would appear in a diagram of the microcrystalline substance under ideal conditions (parallel primary beam, infinitely thin specimen, etc.). From  $b$ , the particle thickness  $t$  is computed by the formula

$$b = \frac{k \cdot \lambda}{t \cdot \cos \theta}.$$

The physical conditions for the validity of the formula  $b = \sqrt{B^{1^2} - B^2}$  are discussed briefly.

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