

DETERMINATION OF MEAN CRYSTALLITE DIMENSIONS FROM X-RAY DIFFRACTION PEAK PROFILES: A COMPARATIVE ANALYSIS OF SYNTHETIC HEMATITES

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Abstract—X-ray diffraction (XRD) profile analysis of eight synthetic hematite samples was performed to identify the best parameters for determining the apparent mean crystallite dimension (D) and, consequently, surface area. The samples are comparable to soil hematite with respect to crystallinity. The procedure included: a) deconvolution of the XRD peaks to Gauss and Cauchy components and subtraction of the instrumental profile, b) determination of D from full-width at half-maximum, integral breadth, and integral breadth measurements of the Cauchy component, and c) comparison of deduced surface areas with those obtained by the N_2 -BET adsorption method. As expected, D values are strongly influenced by the broadening parameters. An appropriate selection of peaks is required to obtain size values along the crystallographic axes a (hkl : 110, 300) and c (hkl : 104, 116) and to calculate reliable surface areas. Using the Cauchy component of the above peaks, the calculated surface areas compared well with those measured by the N_2 -BET adsorption method.

Key Words—BET, Hematite, Iron Oxides, Mean Crystallite Dimension, Powder X-ray Diffraction, Surface Area, XRD.

INTRODUCTION

Hematite (α -Fe₂O₃, space group $R\bar{3}c$) is a common Fe(III) oxide in soils and sediments of warm climates (Cornell and Schwertmann, 1996). Even at low (1–10 wt. %) concentrations, hematite may strongly affect chemical-physical properties such as matrix color (Torrent *et al.*, 1983), sorption of anions (*e.g.*, Torrent *et al.*, 1994), organics (Schwertmann *et al.*, 1986) and heavy metals (*e.g.*, Pb, Cu, Zn, Co, Ni, and Mn; Schwertmann and Taylor, 1989), and interactions with phyllosilicates (*e.g.*, soil structure, aggregation, and cementation; Schwertmann, 1987).

These properties are strongly affected by surface area and this, in turn, by morphology, habit, and size of the hematite crystals. The “morphology” is defined as the assemblage of the forms present in the crystal without regard to the extent of face development (Hartmann, 1973, p. 369). The “habit” of a crystal depends on the relative development of each form present in the morphology of the crystal. Therefore, crystals having the same morphology, *e.g.*, prism and bipyramid, may show different habits: prismatic habit, when the prism is the most developed form; bipyramidal habit, when the prism is negligible with respect to the well developed pyramid. Unfortunately, such crystal properties are very difficult to observe directly and to measure in the pedoenvironment because soil hematite consists of very small crystallites and is often present at low concentrations. The direct observation of hematite particles by using scanning electron microscopy, transmission electron microscopy (TEM), or

high-resolution transmission electron microscopy is not satisfactory to obtain data about behavior (*e.g.*, sorption) (Schwertmann, 1987). This is because soil is usually strongly clustered, and the habit of the constituent particles may be easily determined, but not their morphology. Furthermore, only few X-ray diffraction (XRD) peaks of soil hematite do not superpose over peaks from other minerals, thereby making analysis difficult.

The XRD method appears to be the only practical and reliable way to describe the surface area, which requires the use of crystal-size measurements. Among suitable XRD parameters, peak broadening is currently used (*e.g.*, Schwertmann and Latham, 1986) to determine the “mean crystallite dimension” (MCD) of hematite, *i.e.*, the size of the coherent scattering domain perpendicular to the diffracting (hkl) plane (Schwertmann and Cornell, 1991), or more recently, the mean coherence length (MCL, Cornell and Schwertmann, 1996), which is equivalent to MCD.

The purpose of this work is to investigate how best to evaluate the XRD profile and to determine how the choice of specific XRD reflections may influence the apparent crystal size. We then compare the specific surface area obtained by the method proposed herein and that obtained by the N_2 -adsorption method.

THEORETICAL BACKGROUND

The broadening of the XRD diffraction-peak profile $h(x)$ of a microcrystalline substance is assumed to be a convolution of the pure profile $f(x)$ and the instrumental profile $g(x)$ (*e.g.*, Klug and Alexander, 1974,

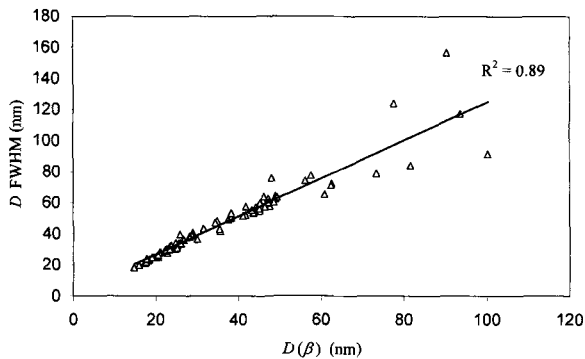


Figure 1. Relation between the mean sizes D calculated from FWHM and from β .

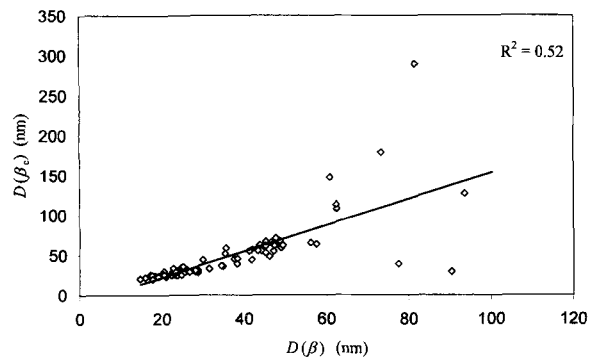


Figure 2. Relation between the mean sizes D calculated from β_c and from β .

p. 291). $f(x)$ originates from the microcrystallinity of the phase and $g(x)$ is obtained from a reference phase free of strain and 2–20 μm in size. Experimental data of $g(x)$ and $h(x)$ are usually fitted with mathematical functions such as the pseudo-Voigt or the Pearson VII functions (Howard and Preston, 1989). Methods may be adopted also to deconvolute $f(x)$ and consequently to determine the crystallite size.

In a simplified way, assuming a negligible contribution of strain in $f(x)$, the mean size, D , can be calculated by the full-width at half-maximum (FWHM) peak characteristic or by the area/height XRD-peak ratio (integral breadth, β), using the equation:

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

where K is the Scherrer constant, λ the wavelength, β the FWHM (in radians), and θ is the peak angular position. If strain and size components can be related to well-defined profile shape functions, $f(x)$ may be regarded as the convolution of a Gauss function (strain component) and a Cauchy function (size component), e.g., Langford *et al.*, 1987). Therefore, the integral breadth of the Cauchy component (β_c) can be used in Equation (1) instead of β to obtain D . Jones (1981) adopted this approach for soil hematite and, more recently, Colombo *et al.* (1994) did the same for synthetic hematite. Both β and β_c were determined here for comparison. FWHM, despite its debated physical

significance (Langford and Wilson, 1978) is used in the analysis of soil iron oxides, and the K constant is conventionally set to 0.9 (Schwertmann and Cornell, 1991).

With the use of integral breadths and the K constant set to unity, the equation allows the determination of an apparent size. In effect, because $f(x)$ is not independent of either the crystallite shape or size distribution (Wilson, 1949; Guérin and Alvarez, 1995), a proper value of constant K , which is a function of reflection and crystallite shape, must be adopted if a “true” value of D is desired. If particle shape and size uniformity are assumed, K and D can be calculated for several peaks by *least-squares* fit, as adopted by Stanjek (1991) for hematite.

In soil samples, however, diffraction peaks overlap or overlap partially from other phases, which may reduce the number of hematite peaks of satisfactory quality. Thus, the information of crystallite shape and size as derived from the diffraction peaks is not easy to obtain.

The most useful information about hematite crystallite size and shape may be obtained from Equation (1) and D by determining D_a and D_c values, *i.e.*, mean crystallite size parallel to crystallographic unit lengths a and c . From these values, an estimation of the surface area in hematite may be obtained assuming a quasi-cylinder shape, even though it does not always rep-

Table 1. D_a and D_c values (nm) of sample H1 obtained from different hkl and broadening parameters.

Parameter	Peaks								
	012	104	110	113	024	116	018	214	300
<i>D_a</i> values									
FWHM	9.6	12.2	29.3	21.1	9.8	12.1	3.3	21.3	32.7
β	7.6	9.9	22.5	17.3	7.7	10.0	2.7	17.4	25.2
β_c	10.2	13.8	27.7	25.6	10.1	14.8	3.8	25.4	31.2
<i>D_c</i> values									
FWHM	12.2	15.5		13.3	12.5	15.5	16.9	10.8	
β	9.7	12.5		10.9	9.8	12.7	13.7	8.8	
β_c	13.0	17.5		16.2	12.8	18.9	19.3	12.9	

Table 2. *D_a* values (nm) of the hematite samples, obtained as average of nine peaks¹. The standard deviations are reported in parentheses.

Parameter	Samples								
	H1	H2a	H2b	H3	H4	H5	H6	H8	H11
FWHM	16.8 (9.8)	46.0 (15.7)	28.8 (11.2)	34.7 (15.6)	37.7 (16.6)	21.9 (11.9)	40.2 (21.9)	47.8 (48.3)	19.8 (10.5)
β	13.4 (6.8)	40.0 (17.2)	20.3 (7.2)	28.1 (13.3)	29.7 (13.0)	16.3 (6.8)	30.3 (16.4)	31.3 (27.9)	15.1 (7.8)
β_c	18.1 (9.6)	10.9 (72.2)	16.3 (5.4)	39.9 (18.5)	39.1 (18.2)	18.5 (8.8)	35.6 (18.9)	22.8 (11.2)	18.2 (9.2)

¹ Eight peaks for samples H2a and H2b.

resent a close approximation to the actual habit (*e.g.*, Torrent *et al.*, 1987).

MATERIALS AND METHODS

Synthesis of hematite

To obtain reliable XRD and BET measurements, eight hematite samples, with comparable crystallinity to those of soil, were synthesized by various methods (Schwertmann and Cornell, 1991). Samples H1 and H2 were obtained by hydrolysis of Fe(NO₃)₃ and Fe(ClO₄)₃ solutions, respectively, and aged for 7 d at 98°C; H3 and H4 were synthesized from FeCl₃ solutions in 0.002 and 0.001 M HCl, respectively, and aged for 10 d at 98°C. Samples H5 and H8 were prepared by transformation of ferrihydrite in the presence of solutions of NaHCO₃ (2 d, 90°C) and oxalic acid (36 h, 70°C) solutions, respectively. Sample H8 was obtained by adding 40 mL 0.1 M Al(NO₃)₃ to 160 mL 0.1 M Fe(NO₃)₃, adjusting the pH to 7 ± 0.2, then washing, adjusting again to pH 7, and storing at 80°C for 70 d. Sample H11 was obtained similarly to sample H1, but aged 14 d. All products were washed with 1 N KOH, then with deionized water, dialyzed, and freeze-dried.

XRD analysis

XRD was performed with a Philips diffractometer (PW1729 generator, PW1820 goniometer) equipped with 1° diverging slit, 0.2-mm receiving slit, and 1° scatter slit. The CoK α (0.179026 nm) radiation involved a system with an Fe filter at 40 kV and 40 mA.

Self-supporting powder mounts were prepared by gently pressing 200 mg of sample into an Al holder. The powder mounts were smoothed at >0.9 mm in thickness to obtain the highest diffraction intensity (Klug and Alexander, 1974). All samples were step scanned (25–80 °2 θ , 0.02 °2 θ intervals, and 20 s counting time per increment) to include nine peaks: 012, 104, 110, 113, 024, 116, 018, 214, and 300.

The digitized XRD profiles were fitted using a split pseudo-Voigt function (Howard and Preston, 1989), with a modified QBASIC program of Enzo *et al.* (1985), which included the separation of CoK α (0.17988 nm) components. Wherever possible, each peak was fitted independently and the Marquardt algorithm was used to obtain the best value of goodness-of-fit (GOF%):

$$\text{GOF\%} = 100[\sum (I_o - I_c)^2 / (I_o)^2]^{1/2} \quad (2)$$

where I_o is the observed intensity and I_c is the calculated intensity.

Data analysis

The instrumental profile, $g(x)$, was obtained based on Stanjek (1991) from a reference sample of synthetic commercial hematite (Merck, no. 3924, lot no. 548003) previously heated to 1000°C for 48 h. The 2–20- μ m size fraction was obtained by sieving and by gravity sedimentation in water. An XRD scan of this size fraction was performed at 0.01 °2 θ interval and 80 s counting time.

Table 3. *D_c* values (nm) of the hematite samples, obtained as average of seven peaks¹. The standard deviations are reported in parentheses.

Parameter	Samples								
	H1	H2a	H2b	H3	H4	H5	H6	H8	H11
FWHM	13.8 (2.2)	26.8 (18.8)	21.7 (11.2)	32.6 (7.1)	35.4 (7.3)	18.4 (3.2)	33.6 (5.2)	24.8 (1.3)	17.3 (3.2)
β	11.2 (1.8)	38.1 (16.2)	15.5 (7.2)	26.5 (5.9)	27.9 (5.8)	14.1 (2.9)	25.7 (4.4)	18.6 (1.1)	13.2 (2.3)
β_c	15.8 (2.9)	87.1 (17.0)	16.1 (5.4)	38.4 (10.0)	36.9 (8.5)	17.4 (5.4)	31.4 (7.9)	21.3 (2.8)	16.2 (2.7)

¹ Six peaks for samples H2a and H2b.

Table 4. D_a (nm) evaluated from β of selected peaks (100 and 300).

Peak	Samples								
	H1	H2a	H2b	H3	H4	H5	H6	H8	H11
110	22.5	24.4	71.0	38.7	42.6	27.4	50.0	78.6	24.4
300	25.2	21.0	62.3	47.6	48.6	28.7	56.1	77.5	26.7
Mean	23.8	22.7	66.6	43.2	45.6	28.0	53.0	78.1	25.6

For all the samples and for each peak, the Voigt function was obtained from the pseudo-Voigt parameters for $h(x)$ and $g(x)$ of both $K\alpha_1$ and $K\alpha_2$. The Cauchy and the Gaussian component of the broadening were then separately deconvoluted, and the FWHM, β , and β_c of the Voigt $f(x)$ was obtained. Details of this procedure are in deKeijser *et al.* (1982) and Crosa (1996). The value of D , perpendicular to hkl planes, was obtained from the FWHM, β , and β_c using Equation (1) with $K = 0.9$ when the value for FWHM was calculated, and $K = 1$ when the value of β or β_c was used. The thickness of the crystal (domain) along any crystallographic axis can be derived from D by multiplying by $\cos\alpha$, where α is the angle between the hkl plane and the crystallographic direction under consideration (Schwertmann, 1987). Therefore, the values of D_a and D_c were computed from D and the related cosine function.

Specific surface area

The specific surface area was measured by N_2 adsorption on samples that were outgassed (at 60°C) using a FISON Sorptomatic 9000 apparatus. Values were obtained with the BET isotherm and the software from the manufacturer.

The estimation of the surface area from XRD data, by using a cylindrical shape approximation, was obtained from the formula of Torrent *et al.* (1987):

$$\text{Specific surface area (m}^2\text{g}^{-1}\text{)} = 760/D_a + 380/D_c \quad (3)$$

RESULTS AND DISCUSSION

Experimental profiles

The GOF% of all the profiles was comparable. These values were judged satisfactory for all peaks in the samples (GOF%: 0.58–1.09). The reference sample showed a GOF% slightly higher than that of each hematite, particularly for the 012 reflection, a very asymmetric peak. Also, the 018 peak often showed an overlap by a spurious peak. Sample H2 showed negative values of the Gaussian component: each peak was therefore assumed to be the sum of two Gaussian components as derived from two populations of crystals, H2a and H2b, of different mean size. From preliminary TEM photographs, there is good agreement between XRD and TEM-size determinations. From peak-integrated intensities, H2a was estimated at 32.0(1)% by volume of the total sample and H2b for the re-

maining. For a similar procedure, see Benedetti *et al.* (1988).

Influence of broadening parameters on D

From all reflections in all the samples, Figures 1 and 2 show the effect of FWHM, β , or β_c on the D values. In general, these differences are caused by the nature of $f(x)$ (Gauss/Cauchy ratio) and by the K values [Equation (1)]. In effect, in a Voigt profile (deKeijser *et al.* 1982), the FWHM/ β ratio (the so-called Voigt parameter) may range between 0.6366 (pure Cauchy) and 0.9394 (pure Gaussian). Moreover, based on the K -constant values adopted, the ratio of D values obtained from FWHM and β may range from 0.9581 to 1.4138. Furthermore, in terms of D , the β_c/β ratio may range from 0 to 1 and the FWHM/ β_c ratio may vary consequently.

In these hematite samples, a near linear regression exists between D obtained from FWHM vs. D obtained from β ($R^2 = 0.97$) and D obtained from β_c vs. D from β ($R^2 = 0.90$), if the size is <60 nm. Scattering increases strongly above the size limit (Figures 1 and 2).

D_a and D_c estimation

As an example, the values of D_a and D_c for sample H1, obtained from different peaks, are reported in Table 1. For all the samples, Tables 2 and 3 give, for comparison, the average parameters based on all reflections. Differences are evident for each peak and for the broadening parameter used. Using β as a broadening parameter, the average value of D_a ranges (excluding sample H2a) from 13.4 to 31.3 nm. Because the standard deviation of D_a in some of the samples is greater than this range and, considering also the limitations of the XRD method (to 100–200 nm) the error in the use of β as a broadening parameter may be high.

Differences among reflections may be related to the following: 1) the D value is related to an apparent size rather than an actual size; 2) the estimation of D_a from an hkl plane not perpendicular to a is dependent, at least partially, on the D_c value and *vice versa*. Consequently, the best D_a or D_c estimation may be obtained from peaks with $hk0$ - $h00$ and $00l$ Miller indices, respectively. Therefore, suitable reflections for determining D_a are 300 and 110. Table 4 shows for each sample the D_a value (from β) obtained from the above peaks. The crystallite shape (and also structural strain)

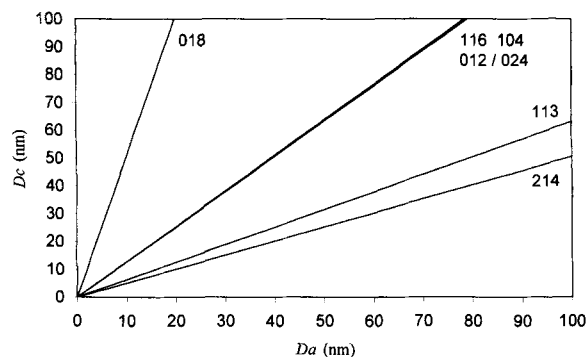


Figure 3. Maximum measurable values for D_c estimation with the $0kl$, $h0l$ and hkl peaks as a function of D_a .

may explain residual differences between values obtained from the 110 and 300 reflections. In general, the use of the mean value for D_a may be considered reliable.

The D_c estimation is more complex. Because peaks with $00l$ indices are unavailable, the estimates using $0kl$ and D_a values, and their effect on the D_c estimation, may be calculated. Figure 3 shows the maximum value for D_c , as a function of D_a . The 018 peak, which is the most favorable theoretically, does not appear as a well resolved reflection. Therefore, in the present work, the 116 and 104 peaks are used to estimate D_c (Table 5). In addition, uncertainties about $g(x)$ suggest the exclusion of the 012 reflection and the higher order 024 peak, both of which can be affected by strain.

The D_c values obtained from the 116 and 104 peaks are, for all hematite samples, always lower than the maximum values obtained from Figure 3 and, hence, underestimation of D_c may be avoided. In each sample, the differences in these D_c figures are probably due to shape and irregularities of the crystals.

Specific surface area estimation

Table 6 reports the specific surface areas calculated using XRD data and those by the N_2 -BET method. As expected, differences are evident with respect to various broadening expressions. The best agreement between the specific surface area values obtained by N_2 -BET and XRD is observed when the β_c parameter is used. Obviously, when the specific surface area estimation is based on all XRD peaks, the differences are

so high that any comparison is not significant (data not shown).

CONCLUSIONS

We conclude that: 1) the evaluation of apparent crystallite size D is clearly affected by the choice of the parameter used in the XRD analysis. 2) As expected, the reliability of D_a and D_c values depends on the use of an appropriate peak; in general only well-resolved peaks from planes perpendicular to crystallographic axes allow the determination of a reliable D_a and D_c value. Nevertheless, D_c , lacking any $00l$ peak, may be estimated from an appropriate $0kl$, $h0l$, or hkl peak, but only if D_c figures so obtained are lower than their corresponding maximum value, which can be obtained from D_a . The D_a and D_c values so obtained are only apparent sizes. However, especially for soil hematite, it is difficult to convert these values to actual size, but this is possible when both habit, and morphology of the (uniform) crystallites are known. Unfortunately, habit and morphology of hematite in a soil are not always obtainable. However, the use of apparent size does not appear to prevent a reliable surface area estimation. 3) The combination of proper peak selection with a "single-peak method" (e.g., Cauchy-broadening parameter) to obtain the size effect from a peak profile, appears to be the best procedure to determine surface area values which closely fit those of the N_2 -BET method. 4) The use of FWHM and β can be applied rigorously, but only in the absence of strain, although these two broadening parameters are the appropriate parameters to use as demonstrated by others (e.g., Torrent *et al.*, 1994). In fact, the FWHM parameter is commonly used probably because it is measurable even for low-quality XRD profiles, whereas β requires a higher quality peak profile and a fitting procedure. As noted by Borggaard (1990), the strain effect on soil iron oxides is unknown. Consequently, the application of FWHM or β may produce an incorrect evaluation of crystal size.

Despite these potential problems, the adoption of a single-peak method is to be recommended, although it requires accurate data collection and sophisticated computation procedures.

Table 5. D_c (nm) evaluated from β of selected peaks (104 and 116).

Peak	Samples								
	H1	H2a	H2b	H3	H4	H5	H6	H8	H11
116	12.7	14.3	45.0	32.4	33.4	18.2	32.0	19.3	15.2
104	12.5	18.3	49.0	32.3	34.7	16.4	29.5	20.0	15.0
Mean	12.6	22.7	47.0	32.4	34.1	17.3	30.8	19.7	15.1

Table 6. Surface area ($\text{m}^2 \text{g}^{-1}$) of hematites obtained from selected XRD peaks and the N_2 -BET method.

Parameter	Samples							
	H1	H2 ¹	H3	H4	H5	H6	H8	H11
FWHM	49.1	32.5	23.5	21.5	37.1	20.5	20.1	41.5
β	62.3	43.0	29.4	27.6	50.3	27.2	28.8	55.1
β_c	47.6	36.6	21.2	21.5	45.6	23.2	40.0	47.4
BET- N_2	43.3	36.6	23.5	21.5	47.3	27.4	41.3	48.0

¹ Weighted mean of H2a and H2b.

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