

CORRECTION OF MISMATCHES IN 2θ SCALES DURING DIFFERENTIAL X-RAY DIFFRACTION¹

Key Words—Differential X-ray diffraction, Iron minerals, Mismatch, Sample orientation, Soil clay, Spline function.

INTRODUCTION

Differential X-ray powder diffraction (DXRD) has successfully lowered the detection limits for goethite, hematite, lepidocrocite, and ferrihydrite in soils (Torrent *et al.*, 1980; Schulze, 1981; Schwertmann *et al.*, 1982a, 1982b; Bryant *et al.*, 1983; Campbell and Schwertmann, 1984). In the DXRD procedure, step-scanned X-ray powder diffraction (XRD) patterns of a sample are obtained before and after selective dissolution of one or more of the iron oxide components. The pattern obtained after selective dissolution is then subtracted from the pattern of the untreated sample. The result is a DXRD pattern of the minerals dissolved by the selective dissolution procedure. The pattern obtained after selective dissolution usually has greater overall intensities because the minerals not dissolved have been concentrated and because the mass attenuation coefficient of the sample is usually different after removal of the iron oxide minerals. Before the two patterns can be subtracted, the pattern obtained after selective dissolution must be scaled by multiplication by a constant so that peaks common to both patterns have the same intensity. Details of how this constant is selected by trial and error subtractions were given in Schulze (1981). A procedure for selecting the scaling constant using an internal intensity standard was described by Bryant *et al.* (1983).

The assumption in DXRD is that the XRD patterns are identical before and after the selective dissolution of the iron oxide minerals, except that the peaks of the minerals that dissolved are no longer present in the pattern of the treated material. This assumption does not always hold for two reasons. First, the relative intensities of some minerals can change after the selective dissolution treatment. Second, the 2θ scales may not match exactly.

Relative intensities can change after the selective dissolution treatment because the degree of preferred orientation of the sample may change or because the treatment may change the composition of some of the mineral phases. For example, the interlayer composi-

tion of 2:1 phyllosilicates can easily be altered by chemical treatment resulting in a change in relative intensities and peak positions. Changes in the interlayer composition may be difficult to prevent but, if one is aware that such changes and the resulting peak intensity differences occur, useful information can still be obtained from DXRD patterns. Differences in preferred orientation are usually caused by sample preparation techniques and are usually difficult to alleviate. Preferred orientation, however, does not seriously hamper the use of DXRD for the identification and characterization of iron oxide minerals in soil clays if one is aware that some mismatch due to preferred orientation may occur. Changes in relative peak intensities caused by preferred orientation or by changes in the interlayer composition may themselves provide information on the sample being studied.

Slight shifts in the 2θ scale on the order of $\pm 0.02^\circ 2\theta$ can be caused by small discrepancies in sample preparation and placement in the goniometer or by the inability of the goniometer to return to exactly the same starting point at the beginning of each run. Subtracting two identical patterns from one another should result in a spectrum which contains no peaks. If, however, one pattern is shifted slightly along 2θ , the difference pattern consists of pairs of positive and negative peaks at the positions where peaks occur. These pairs of positive and negative peaks are illustrated in Figure 1 in the pattern labeled "DXRD-shift = 0." This difference spectrum appears much like the first derivative of the original curve. These spurious peaks are artifacts of the mismatch in the 2θ scale and contribute no information about the sample. They should be eliminated from DXRD patterns.

CORRECTION OF 2θ SHIFTS

A slight mismatch in the 2θ scale can be corrected easily by shifting one pattern relative to the other during the subtraction process. The digitized, step-scanned diffraction patterns for DXRD are usually collected at increments of 0.01 to 0.05° along 2θ . If the step-scan increment is on the order of 0.01 or $0.02^\circ 2\theta$, it is sometimes possible to adjust the 2θ scale by an integral

¹ Journal article number 10,649.

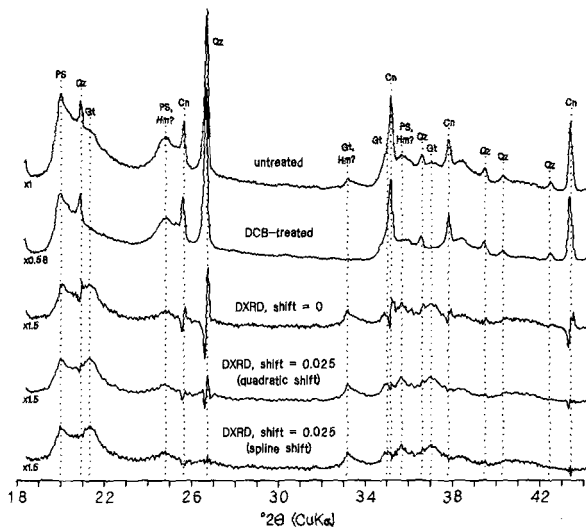


Figure 1. X-ray powder diffraction patterns of a soil clay before (untreated) and after dithionite-citrate-bicarbonate treatment (DCB-treated) to remove iron oxide minerals. Differential X-ray diffraction (DXRD) patterns obtained with no shift in 2θ of the DCB-treated pattern (shift = 0), with a shift of 0.025° using the least-squares quadratic polynomial shift procedure, and with a shift of 0.025° using the cubic spline shift procedure. $\times 1$, $\times 0.58$, $\times 1.5$ = relative scale expansion; Cn = corundum; Gt = goethite; Hm = hematite; PS = phyllosilicates; Qz = quartz. Hematite identification is uncertain because of overlap with strong phyllosilicate and goethite peaks. Samples contained 10% (w/w) of $1\text{-}\mu\text{m}$ size corundum as an internal standard. Patterns obtained from pressed powder mounts with a Siemens Type F goniometer with a graphite diffracted beam monochromator, $\text{CuK}\alpha$ radiation, counting time of 70 s, and step-scan increment of 0.05° .

number of increments to achieve adequate matching between the two patterns. It is desirable, however, to collect the data using an increment of 0.05° because such an increment is usually sufficient to define the sharpest peaks and considerably reduces the time needed to collect a diffraction pattern. It is usually not possible to correct for a mismatch by shifting an integral number of increments if such an increment ($0.05^\circ 2\theta$) is used, because the mismatch is usually smaller than the increment. One can, however, mathematically interpolate between the measured points so that the 2θ shift needed to match the 2θ scale of two different diffraction patterns can be obtained.

Linear interpolation between points

One way to correct 2θ mismatches is by using a linear interpolation between two points. First, the equation of the line passing through two neighboring points is calculated, then the X-ray diffraction intensity (Y value) for any desired intermediate 2θ (X value) is calculated. This procedure requires minimal computation, but it can introduce undesirable artifacts. For example, if two neighboring points fall about two-thirds

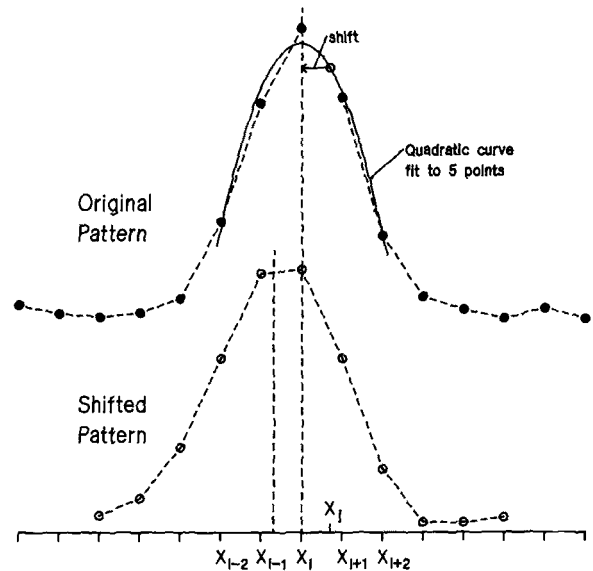


Figure 2. Illustration of the use of a quadratic polynomial curve fit to five points to shift an X-ray powder diffraction pattern.

of the way up on either side of a sharp peak, a linear interpolation gives a calculated intensity that is only two-thirds of the true peak intensity.

Least-squares quadratic polynomial interpolation between points

A better procedure is to use a polynomial curve fit to several data points. This procedure, using five points at a time, is illustrated in Figure 2. For any point, (X_i, Y_i) , it and the two preceding points, (X_{i-1}, Y_{i-1}) and (X_{i-2}, Y_{i-2}) , and the two following points, (X_{i+1}, Y_{i+1}) and (X_{i+2}, Y_{i+2}) , are taken, and a quadratic equation of the form

$$Y = A_0 + A_1X + A_2X^2 \quad (1)$$

is fit to the five points. If the increments along X are constant, computationally efficient least-squares procedures are available to determine the coefficients A_0 , A_1 , and A_2 (see, e.g., Savitzky and Golay, 1964; Steiner *et al.*, 1972). The Y value for any intermediate X value in the neighborhood of X_i can then be calculated. To shift a complete XRD pattern (Figure 2), points 1–5 must be considered and the coefficients for Eq. (1) must be calculated. Then the Y value corresponding to the desired intermediate X value is calculated and assigned to the X value corresponding to the third point. Points 2–6 are then considered to find the Y value corresponding to the fourth point. The process is repeated until all sets of five points have been considered. Note that two points must be dropped from both ends of the shifted pattern because there are no points beyond these to fit a curve to. In addition to shifting the pattern,

this procedure also smooths the data. A DXRD pattern obtained by using this procedure to shift the "DCB-treated" pattern by $0.025^\circ 2\theta$ is illustrated in Figure 1. Note the considerable improvement in the DXRD pattern with the shift compared to the DXRD pattern without the shift. The match is not always optimal, however; note the remaining spurious peak in the vicinity of the strong quartz peak at about $26.4^\circ 2\theta$. Other slight mismatches are also visible at the positions of some of the corundum peaks. These mismatches are not eliminated by choosing other values for the 2θ shift. The reason for this remaining mismatch is illustrated by Figure 2. The shifted peak in Figure 2 is slightly wider than the original peak. The position of the shifted peak is also not where it should be. The short vertical dashed line is the calculated center of the shifted peak; it should split the peak into 2 halves of equal area, but it does not. The quadratic curve is not a good approximation of the curve shape because of the small number of points used to define the peak. The resulting distortion in the sharp peaks prevents optimal matching of the 2θ scales and results in some residual mismatch in the DXRD patterns.

Cubic spline interpolation between points

Another procedure involving a spline function provides a more accurate interpolation between data points (Erh, 1972). A spline function is the mathematical equivalent of the draftsman's spline, the flexible ruler used to draw smooth curves through adjacent points. A cubic spline function was used to calculate the solid line connecting the adjacent data points in the "original pattern" in Figure 3. The data points are the same as those used in Figure 2. The spline function does a much better job of interpolation than the quadratic curve of Figure 2. The peak shifted using the cubic spline interpolation has the same width at half-height as the original peak. The calculated centerline of the shifted peak, the short vertical dashed line in Figure 3, also splits the shifted peak into two halves of equal area.

By using the spline function, an XRD pattern can be shifted any desired amount with a minimum of distortion to the peaks. The DXRD pattern obtained using the spline shift completely eliminates the spurious peaks in the position of the strong, sharp quartz and corundum peaks (Figure 1). It is clearly better than the DXRD pattern obtained using the quadratic shift.

Calculation of the cubic spline function

A discussion of the properties of spline functions is given in Ahlberg *et al.* (1967). The following procedure to calculate the cubic spline function follows Erh (1972).

Consider an interval $A \leq x \leq B$ that is subdivided into n divisions:

$$A = X_0 < X_1 < \dots < X_n = B$$

having n corresponding real numbers y_0, y_1, \dots, y_n .

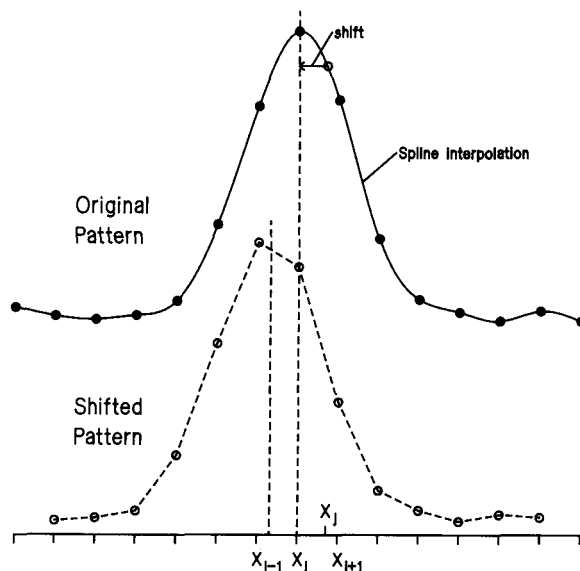


Figure 3. Illustration of the use of a cubic spline function to shift an X-ray powder diffraction pattern.

The spline function, $\phi_i(X)$, over the interval $[X_i, X_{i+1}]$ is given by the relationship:

$$\begin{aligned} \phi_i(X) = & \{(X_{i+1} - X)^3 \mu_i \\ & + (6y_i - h_i^2 \mu_i)(X_{i+1} - X) \\ & + (X - X_i)^3 \mu_{i+1} \\ & + (6y_{i+1} - h_i^2 \mu_{i+1})(X - X_i)\} / 6h_i, \quad (2) \\ & i = 0, 1, 2, \dots, n-1, \end{aligned}$$

where $h_i = (X_{i+1} - X_i)$. The solution to Eq. 2 requires knowing the value of μ_i corresponding to each datum point $[X_i, Y_i]$. The coefficients μ_i are calculated as follows. First, the variables q_i and u_i are calculated using the formulae:

$$q_i = -c_i/p_i, \quad (3)$$

$$u_i = (d_i - a_i u_{i-1})/p_i \quad (u_0 = 0), \quad (4)$$

where

$$p_i = a_i q_{i-1} + b_i \quad (q_0 = 0), \quad (5)$$

$$a_i = h_{i-1}, \quad (6)$$

$$b_i = 2(h_{i-1} + h_i), \quad (7)$$

$$c_i = h_i, \quad (8)$$

$$d_i = 6(y_{i+1} - y_i)/h_i - 6(y_i - y_{i-1})/h_{i-1}, \quad (9)$$

and

$$i = 1, 2, \dots, n-1.$$

Then the μ values are calculated using:

$$\mu_0 = \mu_n = 0, \quad (10)$$

$$\mu_i = q_i \mu_{i+1} + u_i, \quad (11)$$

$$i = n - 1, n - 2, \dots, 1.$$

Eqs. (2–9) are applicable if the interval $[X_i, X_{i+1}]$ is not constant. If the interval $[X_i, X_{i+1}]$ is constant, which is true for most step-scanned XRD data, $h_i = (X_{i+1} - X_i) = k$ and Eqs. (6–8) simplify to:

$$a_i = k, \quad (6a)$$

$$b_i = 4k, \quad (7a)$$

$$c_i = k. \quad (8a)$$

By substituting these values into Eqs. (3–5) and (9) the following equations are obtained:

$$q_i = -k/p_i, \quad (3a)$$

$$u_i = (d_i - k u_{i-1})/p_i \quad (u_0 = 0), \quad (4a)$$

where

$$p_i = k q_{i-1} + 4k \quad (q_0 = 0), \quad (5a)$$

$$d_i = \{6(y_{i+1} - 2y_i + y_{i-1})\}/k, \quad (9a)$$

$$i = 1, 2, \dots, n - 1.$$

Eq. (2) simplifies to:

$$\begin{aligned} \phi_i(X) = & \{(X_{i+1} - X)^3 \mu_i \\ & + (6y_i - k^2 \mu_i)(X_{i+1} - X) \\ & + (X - X_i)^3 \mu_{i+1} \\ & + (6y_{i+1} - k^2 \mu_{i+1})(X - X_i)\}/6k, \quad (2a) \\ & i = 0, 1, 2, \dots, n - 1. \end{aligned}$$

To calculate the values of μ for XRD data collected with a constant increment along 2θ , q_i and u_i corresponding to each point are calculated using Eqs. (3a–5a), and (9a): then the μ_i for each point is calculated using Eqs. (10) and (11). Eq. (2a) is then used to calculate the Y value for any value of X.

DISCUSSION

The DXRD patterns shown in Figure 1 were obtained using a computer program in which both the intensity and 2θ shift of the DCB-treated pattern could be varied interactively. The intensity scale factor and the 2θ shift were obtained by trial and error in only a few minutes. The addition of corundum to both of the samples before the DCB treatment (Bryant *et al.*, 1983) provided a convenient internal standard for determining the proper 2θ shift parameter. For samples containing quartz, the quartz peaks could be used for this purpose. If samples are prepared carefully, the 2θ shift is usually on the order of $\pm 0.02^\circ$. Even small shifts on the order of $0.002^\circ 2\theta$ were often found to produce a

noticeable improvement in the DXRD pattern if the spline interpolation was used. The corundum also provides a convenient standard for judging the intensity scale factor and can help in determining if preferred orientation is present. If there is considerable preferred orientation, different scale factors may have to be used for different regions of the spectrum to obtain the best profiles of the iron oxide lines. The incomplete cancellation of the phyllosilicate peaks (PS) in the DXRD pattern in Figure 1 is the result of preferred orientation. The diffraction peaks used to determine the 2θ shift and the scaling constant must be chosen carefully. The peaks must not be coincident with diffraction lines from other minerals which might be subject to preferred orientation. For example, the strong 101 peak of quartz at 3.343 Å is coincident with the 003 peak of mica. The mica is prone to preferred orientation, and may possibly cause problems if this line is used to select the scaling and shift constants.

The DXRD procedure using the quadratic shift has been used for obtaining DXRD patterns of iron oxide minerals in kaolinitic and smectitic soil clays (Santana, 1984; Schulze *et al.*, 1984; Tremocoldi, 1984). The cubic spline shift produces an even better DXRD pattern for these samples (Figure 1). The cubic spline shift is much faster and simpler to use than the profile refinement procedure proposed by Brown and Wood (1985).

ACKNOWLEDGMENTS

I thank M. H. Ebinger, J. L. White, and J. H. Cushman for critically reviewing the manuscript. J. H. Cushman suggested the use of the spline function.

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(Received 24 February 1986; accepted 29 August 1986; Ms. 1567)