

Short Communications

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Scaling of diffractometer data affected severely and variably by crystal decomposition. By JAMES A. IBERS, *Department of Chemistry, Northwestern University, Evanston, Illinois 60201, U.S.A.*

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The scale factor for a given data set is written as a power series in t_n , where t_n is the cumulative X-ray exposure of the crystal at the time the n th observation is made. The coefficients in this power series are determined, along with the structural parameters, by the usual least-squares refinement procedure. The advantage of this method of scaling the data is that it is based on all of the observations, rather than on the changes in intensity of a few, possibly atypical, check reflections. The method has been found to be effective and practical, and is especially suitable when there is appreciable and variable decomposition of the crystal in the X-ray beam.

As experience with counter methods grows it is apparent that decomposition of crystals in the X-ray beam is not uncommon. Such decomposition is usually detected by a drop-off of intensity with time of a set of standard reflections that are measured at set intervals throughout the period of data collection. (Of course, such a drop-off in intensity can also result from crystal movement, but this possibility is readily eliminated by rechecking the crystal orientation.) There are ways in which crystal decomposition may be lessened, including perhaps the use of low temperatures, a different radiation, or shorter exposure time per measurement of the crystal to the beam. Yet there are occasions when appreciable crystal decomposition cannot

be avoided and where the supply of suitable crystals is such that one must do the best he can with data affected severely and variably by crystal decomposition.

In Fig. 1 we plot the variation with exposure of the intensities of four standard reflections measured during a collection of intensity data on the compound $\text{IrCl}(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)_2 \cdot \text{C}_6\text{H}_6$ (Payne & Ibers, 1969). Note that the final intensities of the standard reflections range from about 88% to only 30% of their initial values. Although one attempts to choose standard reflections from diverse regions of reciprocal space, there is no assurance that a correction curve based on the average drop-off of these standard reflections *versus* X-ray exposure will be reliable or effective, for there is no assurance that these standard reflections are typical of the data set as a whole. Moreover, it has been our experience (McGinney, Doedens & Ibers, 1967) that even after the crystal structure has been solved it is difficult, if not impossible, to ascertain the structural changes responsible for the variations in the intensities of the standard reflections. If this were possible, then a correction for decomposition would be feasible after the structure had been solved. By necessity, then, we have devised an effective scheme for bringing diffractometer data collected in the presence of appreciable crystal decomposition to a common scale, and we describe that scheme here.

Let us denote the cumulative exposure of the crystal to the X-ray beam at the time the n th observation is made by t_n . This is a quantity easily determined during data collection, especially if the shutter closes while the motors are slewing. Let S_n be the scale factor that brings $|F_c|$ for the n th reflection to the same scale as $|F_0|$. Then let us write

$$S_n = S_0 + a_1 t_n + a_2 t_n^2.$$

Then a simple modification of existing least-squares programs, for example the Busing-Levy *ORFLS* program, enables one to determine not only the usual scale factor S_0 , but also the constants a_1 and a_2 , and hence S_n , at the same time that other parameters are being refined.

This method has been tested successfully on the example of $\text{IrCl}(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)_2 \cdot \text{C}_6\text{H}_6$ discussed above, and the broken curve of Fig. 1 is the resultant plot of S_n/S_0 *versus* n .

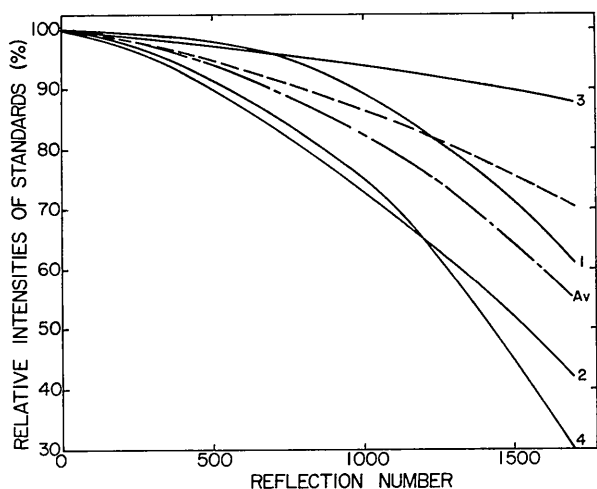


Fig. 1. The relative change with observation number (proportional to cumulative X-ray exposure) of four standard reflections (marked '1' through '4') of the compound $\text{IrCl}(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)_2 \cdot \text{C}_6\text{H}_6$. The average change in these four standards is depicted by the curve marked 'Av'. The broken curve is the one derived from all of the data by the method described in this note.

(The data are plotted against n , rather than t_n , in Fig. 1 as the shutter closed in between measurements and each measurement involved the same exposure of the crystal to the X-ray beam.) The initial calculation started with $S_0 = 2.24$, and after two cycles of refinement of S_n , along with the other 97 variables in the structure, the values of S_0 , a_1 , and a_2 had converged to $2.41(4)$, $-1.8(8) \cdot 10^{-4}$, and $-1.4(4) \cdot 10^{-7}$, with n , rather than t_n , the variable. Of more significance, the conventional R factor had converged to 13.3% for observations brought to a common scale through the use of the average change in the standards. An analysis of the weighted R factor as a function of $|F_0|$, $\lambda^{-1} \sin \theta$, and n indicated that there was a marked dependence on n , presumably because the use of the average change in the standards was an ineffective method of scaling the data. When the present method of scaling was used the calculation converged to an R value of 8.8%, although only two extra variables (a_1 and a_2) had been introduced. Moreover, the weighted R factor was no longer a function of n . Note that the plot of S_n/S_0 versus n derived by the present method differs markedly from the average curve for the four standards depicted in Fig. 1. This indicates that the average decomposition of these standards is not typical of the data set as a whole.

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Layer disorders in kaolinite during dehydration. By G. B. MITRA and S. BHATTACHERJEE, *Department of Physics, Indian Institute of Technology, Kharagpur, India.*

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An attempt has been made to explain the mechanism of the phase transformation of kaolinite to metakaolin by a quantitative study of the variation of g , the mean fractional change in the interlayer spacing in the $[00l]$ direction, and γ , the proportion of planes affected by such disorder, by application of the method developed by Mitra (*Z. Kristallogr.* (1963), 119, 165). γ and g values for samples heat treated at 500 and 600°C, for which only 002 reflexions were found to be tolerably sharp, were determined by a modified single-line technique. It is seen that the formation of metakaolin and the collapse of the kaolinite structure is preceded and accompanied by a disordering of the basal planes so that the interlayer spacing is variable.

Mitra (1958) and Brindley & Nakahira (1959) have observed that basal reflexions from kaolinite become asymmetrical as a result of dehydration at the temperature at which metakaolin starts to form. The asymmetry of the intensity profiles has been attributed by Mitra (1958) to irregularities in the interlayer distances of the basal planes. Mitra (1963) observed that this disorder exists even in ordinary kaolinite not subject to any heat treatment and has developed a method for quantitative determination of g , the mean fractional change in interlayer spacing, and of γ , the proportion of planes affected by such disorders. It is felt that the study of the variation of g and γ at different stages of the dehydration leading to the formation of metakaolin will ultimately be useful in understanding the mechanism of the phase transformation from kaolinite to metakaolin.

A sample of pure kaolinite from Georgia, U.S.A. was divided into several portions, each portion being separately heat treated in a muffle furnace for 10 hours at temperatures of 200, 300, 400, 500 and 600°C. Differential thermal analysis of the sample showed a faint endothermic peak at about 150°C and a more prominent endothermic peak at 562°C. X-ray diffraction line-profiles for various reflexions from the untreated as well as the dehydrated samples

Although in some of our data sets crystal decomposition has apparently affected the chosen standards equally though appreciably (Raymond, Corfield & Ibers, 1968), the present method would seem to be preferable to a correction derived from those standards since there is no assurance that other reflections are not affected at a different rate. Moreover, the present method would seem to be especially well suited for use with the procedure (Corfield, Doedens & Ibers, 1967) of collecting intensity data within a given angular range in 2θ effectively in random order.

The rapidity of convergence and the marked improvement in the agreement between $|F_0|$ and $|F_c|$ favor retention of the rather simple expression for S_n . Probably the introduction of additional terms in the power series would do little to improve the model further.

References

- CORFIELD, P. W. R., DOEDENS, R. J. & IBERS, J. A. (1967). *Inorg. Chem.* 6, 197.
 MCGINNETY, J. A., DOEDENS, R. J. & IBERS, J. A. (1967). *Inorg. Chem.* 6, 2243.
 PAYNE, N. C. & IBERS, J. A. (1969). Unpublished results.
 RAYMOND, K. N., CORFIELD, P. W. R. & IBERS, J. A. (1968). *Inorg. Chem.* 7, 1362.

were obtained with a Norelco X-ray diffractometer fitted with G.M. tube and decade counters. The technique of fixed count point to point recording of intensity was used and the accuracy achieved was about 1%. For the samples dehydrated at temperatures up to and including 400°C all basal reflexions present were broad and asymmetrical. The 005 and 006 reflexions were present only in the untreated samples. For these samples, the γ and g values for all 00/ reflexions were determined by the method described by Mitra (1963). For samples treated at 500 and 600°C only 001 and 002 reflexions were present; the 001 reflexions in both samples were very broad and diffuse while the 002 reflexions were less so. Hence the γ and g values in these samples were determined by adopting a single-line technique similar to that developed by Misra & Mitra (1967). For this purpose, the Fourier transform of the defect line-profile for the layer structure having a variable interlayer spacing in the $[00l]$ direction as derived, by Wilson (1962), has been calculated. The expression for the variance of the defect profile was then obtained from the formula developed by Wilson (1962). The resulting expression is given by

$$W_D = \frac{1}{4\pi^2} [2Sa - a^2], \quad (1)$$