

Profile Refinement of Single Crystal and Powder Data: The Accuracy of Crystallographic Parameters

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Abstract

Sakata and Cooper have recently published a comparison between profile refinement (in which each ordinate of the diffraction pattern is included separately in the least squares analysis) and, what they term, integrated intensity refinement (in which the ordinates are first summed over each Bragg peak). They find different results for the two methods and conclude that the results obtained from profile analysis are wrong. We show analytically that the two methods give identical results, and that the Sakata and Cooper analysis is in error because of the method they used to estimate integrated intensity. It is verified, using simulated data, that profile analysis gives lower values for the standard deviations of crystallographic parameters than simple ordinate summation.

1. Introduction

The Rietveld (1969) profile refinement method has made possible the use of powder data to obtain accurate positional and thermal parameters for crystals of moderate complexity. Sakata and Cooper (1979) have published a comparison of the profile refinement method and, what they term, integrated intensity. We quote in full the statements made in that publication concerning the differences in the two methods of analysing diffraction data:

'It is shown that the values obtained for the structural parameters are not exactly the same as those obtained from an integrated intensity refinement of the same data and that the standard deviations of the parameters are determined incorrectly.'

'These conclusions are confirmed by refinement of a number of data sets using both methods and in most of these cases the standard deviations are found to be underestimated by the profile refinement method by a factor of at least two.'

'These conclusions have serious implications. A large number of structural studies have been carried out during the past decade using the profile refinement method (see, for example, the references given in Table 1 of the review paper by Cheetham and Taylor 1977) and in many of these the authors have discussed the significance of positional parameters and bond lengths on the basis of the magnitude of the calculated standard deviations. Since the latter have been determined incorrectly these discussions will need to be reconsidered, as will the relative merits of powder and single-crystal techniques.'

It is the assertion that profile refinement methods lead to *incorrect* values of the standard deviations of the values found for crystallographic parameters we wish to refute.

The method Sakata and Cooper used to obtain integrated intensities, in which they discarded all information about the profile, will naturally lead to higher values for the standard deviations of crystallographic parameters.

Diamond (1969) showed that profile refinement was the best way to obtain integrated intensities from single crystal data. French (1978) extended the work of Diamond and showed that knowledge of the profile, even approximately, is an additional piece of statistical information leading to a more accurate estimate of crystallographic parameters.

We will show analytically that profile analysis, either applied directly, as is done by Rietveld (1969), or by the intermediate step of extracting integrated intensities gives identical results for the crystallographic parameters. Our conclusions are confirmed by a computer experiment.

2. Theory

A comparison of the two methods reduces to a comparison of the corresponding normal equations of the weighted least squares method for the determination of corrections Δp to an initial assumption of values for the crystallographic parameters. Parameters are labelled by the letter p .

The normal equations are

$$\mathbf{A}^T \mathbf{W} \mathbf{A} \Delta \mathbf{p} = \mathbf{A}^T \mathbf{W} \mathbf{b},$$

where \mathbf{b} is the column vector of differences, \mathbf{W} is the weight matrix and \mathbf{A} is defined by the observational equation $\mathbf{A} \mathbf{p} = \mathbf{b}$.

Profile Refinement

The measured quantities are the profile ordinates y_{ik}^{obs} , each with its variance, $\text{var}(y_{ik}^{\text{obs}})$. For later comparison with the integrated intensity refinement, i is chosen to run over the ordinates in a Bragg peak, while k labels each Bragg peak. There is no intrinsic merit in sub-dividing the ordinates in this way. It is assumed that there is no overlap between peaks.

The quantity minimized is

$$M_p = \sum_i \sum_k w_{ik} (y_{ik}^{\text{obs}} - y_{ik}^{\text{cal}})^2,$$

where the y_{ik}^{cal} are values of the ordinate obtained from a theoretical model containing trial values of the structural and thermal parameters of the crystal, and parameters which describe the profile. The question of inadequacies of the model is not relevant to the present discussion. The weight of each observation w_{ik} is $\text{var}^{-1}(y_{ik}^{\text{obs}})$. The components of the normal equations are

$$[\mathbf{A}^T \mathbf{W} \mathbf{A}]_{mn} = \sum_i \sum_k w_{ik} \frac{\partial y_{ik}^{\text{cal}}}{\partial p_m} \frac{\partial y_{ik}^{\text{cal}}}{\partial p_n}, \quad (1)$$

$$[\mathbf{A}^T \mathbf{W} \mathbf{b}]_m = \sum_i \sum_k w_{ik} (y_{ik}^{\text{obs}} - y_{ik}^{\text{cal}}) \frac{\partial y_{ik}^{\text{cal}}}{\partial p_m}. \quad (2)$$

For later comparison with the integrated intensity method it is necessary to separate the profile and crystallographic parameters. This can be done by writing

$$y_{ik} = G_{ik} I_k,$$

where I_k is the integrated intensity of each Bragg reflection and $\sum_i G_{ik} = 1$. Equations (1) and (2) then become

$$[\mathbf{A}^T \mathbf{W} \mathbf{A}]_{mn} = \sum_i \sum_k w_{ik} G_{ik}^2 \frac{\partial I_k^{\text{cal}}}{\partial p_m} \frac{\partial I_k^{\text{cal}}}{\partial p_n}, \quad (3)$$

$$[\mathbf{A}^T \mathbf{W} \mathbf{b}]_m = \sum_i \sum_k w_{ik} G_{ik}^2 (I_k^{\text{obs}} - I_k^{\text{cal}}) \frac{\partial I_k^{\text{cal}}}{\partial p_m}. \quad (4)$$

Integrated Intensity Method

In this method summation over i is carried out before entering the least squares procedure. The quantity obtained is the integrated intensity I_k^{obs} for each reflection k . This is refined against the calculated intensity I_k^{cal} by minimizing

$$M_I = \sum_k W_k (I_k^{\text{obs}} - I_k^{\text{cal}})^2,$$

where $W_k = \text{var}^{-1}(I_k^{\text{obs}})$.

The components of the normal equations become

$$[\mathbf{A}^T \mathbf{W} \mathbf{A}]_{mn} = \sum_k W_k \frac{\partial I_k^{\text{cal}}}{\partial p_m} \frac{\partial I_k^{\text{cal}}}{\partial p_n}, \quad (5)$$

$$[\mathbf{A}^T \mathbf{W} \mathbf{b}]_m = \sum_k W_k (I_k^{\text{obs}} - I_k^{\text{cal}}) \frac{\partial I_k^{\text{cal}}}{\partial p_m}. \quad (6)$$

The results of the profile and integrated intensity methods will be identical if, and only if, the relationship

$$W_k = \sum_i G_{ik}^2 w_{ik} \quad (7)$$

holds for the weights used in the two methods.

3. Choice of Weights

At each point i, k the total count y_{ik}^T is measured. A background count y_{ik}^B is found in some way and the quantity used in the refinement is given by

$$y_{ik}^{\text{obs}} = y_{ik}^T - y_{ik}^B, \quad \text{var}(y_{ik}^{\text{obs}}) = \text{var}(y_{ik}^T) + \text{var}(y_{ik}^B).$$

Rietveld (1969) made the assumption that y_{ik}^B is determined by graphical averaging over all points of the pattern not included in the Bragg peaks. Because of the large number of such points, he set $\text{var}(y_{ik}^B) = 0$. He also assumed a normal distribution of y_{ik}^T and used

$$\text{var}(y_{ik}^{\text{obs}}) = y_{ik}^T;$$

hence $w_{ik} = (y_{ik}^T)^{-1}$.

Sakata and Cooper (1979) used similar reasoning and set

$$I_k^{\text{obs}} = I_k^T - I_k^B,$$

where

$$I_k^T = \sum_i y_{ik}^T, \quad I_k^B = \sum_i y_{ik}^B, \\ \text{var}(I_k^{\text{obs}}) = I_k^T.$$

They point out that, with this definition of integrated intensity, equation (7) will only hold if y_{ik}^B and hence I_k^B are zero. We assume that it was the existence of this result that led them to question the Rietveld procedure. To show the fallacy in their reasoning we will discuss the determination of integrated intensities.

4. Determination of Integrated Intensities

There are two ways of measuring integrated intensities:

- (a) The diffractometer moves through the reflection either in steps or continuously. The number of counts received by the counter is printed out at the end of the scan. There is no record of the variation in count rate through the peak, hence all information about the peak shape is lost.
- (b) The diffractometer moves through the reflection in steps. The value of the ordinate at each point is recorded and later used to give an integrated intensity.

In (a) the only numbers we have are I_k^T and I_k^B (found by a similar scan over a region outside the peak), so that

$$I_k^{\text{obs}} = I_k^T - I_k^B, \quad W_k = (I_k^T)^{-1},$$

when we set $\text{var}(I_k^B) = 0$.

The fallacy of the Sakata-Cooper analysis is the use of a weighting scheme appropriate to (a) when analysing data collected under (b). In (b) each profile point y_{ik} gives a measure of the integrated intensity $I_k^{(i)}$ through the relation

$$I_k^{(i)} = G_{ik}^{-2} y_{ik},$$

where (i) means evaluated at i , with the variance given by

$$\text{var}(I_k^{(i)}) = G_{ik}^{-2} \text{var}(y_{ik}).$$

It is well known (Aitken 1949) that the optimal least squares estimate of I_k is the weighted mean of $I_k^{(i)}$ with weights equal to the reciprocal of the variances $\text{var}(I_k^{(i)})$. The variance of the weighted mean is given by

$$\begin{aligned} \text{var}(I_k) &= \frac{\sum \text{var}^{-2}(I_k^{(i)}) \text{var}(I_k^{(i)})}{\{\sum \text{var}^{-1}(I_k^{(i)})\}^2} \\ &= \frac{1}{\sum \text{var}^{-1}(I_k^{(i)})} \\ &= \frac{1}{\sum G_{ik}^2 \text{var}^{-1}(y_{ik})}. \end{aligned}$$

Now, in the notation of Section 2, $W_k = \text{var}^{-1}(I_k)$ and $w_{ik} = \text{var}^{-1}(y_{ik})$, hence we have the general relation (7):

$$W_k = \sum_i G_{ik}^2 w_{ik}.$$

This shows that, when the data are handled correctly, the results of a direct profile refinement and those of a refinement in which integrated intensities are evaluated as an intermediate step are identical.

5. Computer Verification

By repeating the measurement of a single peak a large number of times we can approach the expected value of its integrated intensity with vanishing error. For each measurement we can estimate the integrated intensity either by summing the ordinates to give

$$I_k^o = I_k^T - I_k^B,$$

or by fitting a normalized profile function G_{ik} to the equation

$$y_{ik}^T = G_{ik} I_k^o + y_{ik}^B,$$

where I^o is the integrated intensity found by ordinate summation and I^e is the integrated intensity found by profile analysis.

Table 1. Comparison of integrated intensities obtained by profile analysis and ordinate summation. Here $\langle I^o \rangle$ is the average intensity by ordinate summation in 500 trials, $\langle I^e \rangle_1$ is the average value of intensity found by profile analysis with $w_{ik} = I/y_{ik}^B$, $\langle I^e \rangle_2$ is the average value of intensity found by profile analysis with $w_{ik} = I/y_{ik}^{obs}$, and $\langle \sigma(I^o) \rangle$, $\langle \sigma(I^e) \rangle$ are average values of the standard deviations

Peak height P	Background level B	True intensity I	$\langle I^o \rangle$	$\langle I^e \rangle_1$	$\langle I^e \rangle_2$	$\langle \sigma(I^o) \rangle$	$\langle \sigma(I^e) \rangle$
1000	0	8862	8843	8868	8848	93	94
500	500	4431	4415	4431	4419	122	105
100	900	886	883	885	875	141	109
100	0	886	880	883	863	30	30
50	50	443	444	445	432	39	34
10	90	89	90	88	77	44	35

It would be possible to perform an actual experiment by measuring a single peak a large number of times, however it is easier to use a random number generator on a computer to simulate such an experiment.

We have carried out a simulation using a simple gaussian for the profile function

$$G = (q\pi^{\frac{1}{2}})^{-1} \exp(-x^2/q^2).$$

The peak was sampled between $x = \pm 2q$ in steps of $\Delta x = 0.2q$ and at each step a random number generator was used to produce an ordinate y_{ik}^T with variance equal to y_{ik}^T . A least squares method was then used to determine I_k^e .

The results are given in Table 1. We have chosen six different cases for the peak height $P_k = (q\pi^{\frac{1}{2}})^{-1} I_k$ and the background level B . For each peak and background level the experiment was repeated 500 times; i.e. generation of y_{ik}^T , calculation of I_k^o and $\sigma(I_k^o)$ by summing ordinates, and least squares refinement for I_k^e and $\sigma(I_k^e)$. The values of $\langle I^o \rangle$ and $\langle I^e \rangle$ averaged over the 500 trials are shown in the table.

Different values $\langle I^c \rangle_1$ and $\langle I^c \rangle_2$ were obtained when calculated and observed ordinates respectively were used to obtain the weights. Here $\langle I^c \rangle_1$ is closer to the true value I than $\langle I^c \rangle_2$ which is always an underestimate. This result follows from the work of Price (1979) who showed that the use of the reciprocal of the observed count gave an artificially high weight to accidentally low counts. His suggestion that use of the reciprocal of the calculated count is a closer approximation is confirmed, however, the systematic error introduced through the usual practice of putting $w_{ik} = 1/y_{ik}^T$ is small compared with the statistical precision with which we can measure the integrated intensity.

These results verify our conclusion that, as the peak to background ratio decreases, profile analysis provides an increasingly better estimate of integrated intensity and hence crystal parameters.

6. Conclusions

(1) We have shown that the results of profile refinement and integrated intensity refinement using the same data are identical.

(2) We have shown that summing the ordinates of a step scan and treating the resultant as a single independent observation is a non-optimal use of the data and is the reason why Sakata and Cooper (1979) obtained larger values of the standard deviations of the crystallographic parameters. Their remark about the ordinates y_{ik} not being 'crystallographically independent' is not relevant, because this concept has no relevance to the statistical analysis. In fact, the integrated intensities of the Bragg reflections are not crystallographically independent. An extreme example is the use of data from orders of the same reflection.

(3) The results of the Rietveld (1969) method are in no sense wrong. This method gives the best least squares estimate of the parameters with minimum variance.

(4) As suggested by Diamond (1969) and French (1978), the technique of profile analysis should be used for single crystal data to permit the best possible definition of the crystallographic parameters. This is particularly important in cases where the peak to background ratio is high.

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