

E.S.D.'s and Estimated Probable Error Obtained in Rietveld Refinements with Local Correlations

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Abstract

Estimated standard deviations which are obtained in Rietveld refinements are known to decrease towards zero with the recording step, but serial correlations appear at the same time. A simple calculation which takes into account local correlations has been developed to furnish a reliable estimate of the values they would have if these correlations vanish.

1. Introduction

A good refinement method must provide reliable estimated standard deviations (e.s.d.'s) of the various refined parameters. These values are related to the quality of the refinement and are indications of the relevance of parameters. These values or related error values are also useful in deciding whether two samples (or two models), say *A* and *B*, have to be considered as significantly different or not. Moreover, if parameters refined from data obtained with various experimental procedures are compared (especially powder and single-crystal data), correct e.s.d.'s are necessary.

The significance of the standard deviations, as measures of 'accuracy' only, calculated by the now widely used Rietveld (1969) method, has been discussed for a long time (Sakata & Cooper, 1979; Scott, 1983). Young (1979) presented evidence that parameters derived from refinements of identical samples could differ by more than three standard deviations. He concluded that this method probably systematically underestimates the statistical dispersions. This problem was underlined by the recent adaptation of the Rietveld method, which was originally developed for neutron diffraction, to X-ray experiments. This experimental method offers much better resolution: the line widths are usually at least twice as narrow as for neutrons. This naturally leads crystallographers to increase the number of recorded observations: first, in order to obtain sufficient definition of the Bragg diffraction lines, which are much

narrower; and, secondly, in order to obtain accurate size and strain information.

Unfortunately, the problem of the value of e.s.d.'s is considerably worsened by such an increase in the resolution of the powder scan because the weaknesses of the usual profile models are then revealed.

Even in this case Rietveld e.s.d.'s remain an unbiased estimate of the parameter precision, but the model used in the refinement does not take into account all available evidence and the procedure may give precise but inaccurate (wrong) results (Schwarzenbach, Abrahams, Flack, Gonschorek, Hahn, Huml, Marsh, Prince, Robertson, Rollet & Wilson, 1989).

A few methods have already been put forward to overcome this problem. Optimal data collection strategies were developed by Hill & Madsen (1984, 1986, 1987). Such strategies are efficient, but they presuppose a previous knowledge of the sample properties (in terms of line broadening) and prevent us from taking full advantage of the resolution commonly reached in X-ray powder diffraction to obtain both structural and non-structural information. The aim of this paper is to show that one can deduce from Rietveld e.s.d.'s – without setting limits to the resolution potentialities – the value they reach when correlations between neighbouring points disappear, that is the value obtained when the model takes into account all available evidence.

First, we briefly recall the fundamental features of the conventional calculation of e.s.d.'s in the Rietveld method and describe the mechanism responsible for their systematic underestimation (§II). The most significant bias lies in the calculation of integrated intensities and in possible inadequacy between the profile model used in the least-squares refinement procedure and the actual data. Hereafter, we will first have to detect such inadequacies, and then quantify them in order to derive a correction (§III). The method is then improved to give a homogeneous correction, independent of any interval of confidence.

II. E.s.d.'s in the Rietveld method

The first refinement algorithms in crystal structure analysis with powder samples used integrated intensities as input data, which had to be extracted in a first refinement stage. The basic principle of the Rietveld method is to work directly on the whole diffraction pattern, and to consider each observation Y_{oi} of the scan as an independent measurement of intensity, FWHM *etc.* We thus try to minimize

$$S = \sum w_i (Y_{oi} - Y_{ci})^2 = \sum w_i D_i^2, \quad (1)$$

in which Y_{ci} is the value of the calculated intensity at angle i ; the weighting factor w_i is usually related to the variance of the observation Y_{oi} . The summation is performed over all angles of the recorded pattern.

The profile D_i differences appear to be the sum of two contributions, the first having a statistical character [Y_{oi} being a Poissonian random variable whose standard deviation is $s^2(Y_{oi}) = Y_{oi}$], the second having a systematic character, related to the chosen least-squares model (evolution of FWHM and of profile shape function with respect to the Bragg angle *etc.*). The problem is that all refinement indicators are calculated on a purely statistical basis.

A classical indicator which is used to estimate the quality of the refinement is the residual factor

$$R_{wp}^2 = S / (\sum w_i Y_{oi}^2) \quad (2)$$

whose limit, for purely statistical fluctuations, is for N observations and P parameters

$$R_{exp}^2 = (N - P) / (\sum w_i Y_{oi}^2). \quad (3)$$

Thus, it is possible to assess the general quality of the fit by comparing R_{wp} with its limit. But this theoretical limit is reached, for very large N , only if profile D_i differences do not contain any systematic contribution.

When the minimum of the sum S is reached, the estimate of the standard deviation s_k associated with the k th parameter is also minimum and its value is in simple relation to this sum:

$$s_k^2 = (M^{-1})_{kk} S / (N - P), \quad (4)$$

where M is the matrix of the least-squares algorithm. The term $S / (N - P)$ is an indicator of the overall variance of the fit.

We will first establish the behaviour of e.s.d.'s for a large number of observations in a formal way and then look at some examples. Let us consider a refinement using a large number N of data. Now let the measurement step be decreased by a factor μ ; this can be done by duplicating μ times each point of the original set; the above defined characteristic quantities are then transformed as

$$\begin{aligned} N &\rightarrow \mu N & S &\rightarrow \mu S & M &\rightarrow \mu M \\ s_k^2 &\rightarrow s_k^2 / \mu & R &\rightarrow R. \end{aligned} \quad (5)$$

It is obvious that, for large N , the e.s.d.'s s_k behave like $N^{-1/2}$. In this context, any precision on parameters could be achieved at will through a sufficient densification of data, despite the fact that no additional crystallographic information has been provided, and even if the proposed model is wrong.

Let us now look at an example. Owing to our insufficient knowledge of the real line shape, the diffraction profile differs slightly from the calculated one (Fig. 1a). When we reduce the step, we obtain Fig. 1(b), in which we notice significant variations between both curves which show that correlations between neighbouring points exist. Despite the fact that there are no variations between the fits of Figs. 1(a) and (b), e.s.d.'s in case (b) are divided by $\mu^{-1/2}$.

Two explanations can be found for such a bias. First, the basic principle of this refinement method is to consider the profile data as N independent observations which is large in comparison with the actual amount of independent parameters which the powder scan really depends on (F_{hkl} 's, halfwidth parameters *etc.*). Secondly, as underlined before, the current calculation of e.s.d.'s stands on a purely statistical basis, and does not take into account any systematic contribution to the profile differences. If the least-squares model is perfectly adequate, the rapid fall-off of s_k is normal, since in this case a densification of data increases the statistical precision on the refined parameters. By contrast, if the model is imperfect, the problem of precision is complicated by that of accuracy. One can no longer use the estimated standard deviation as an estimate of probable error because a non-vanishing contribution to the estimated probable error should remain.

Some statistical indicators have already been put forward to detect aberrations in the least-squares model (Prince, 1981; Hill & Madsen, 1987; Hill &

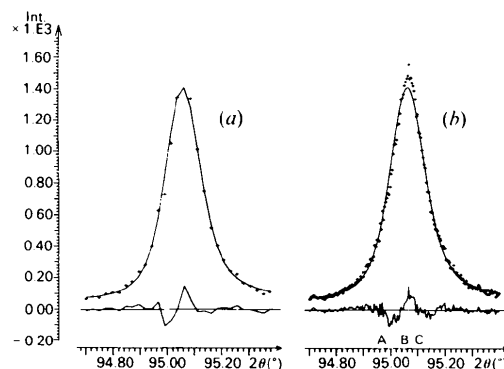


Fig. 1. Typical line profile obtained in Rietveld refinements (Pb_2CoWO_6 , $\text{Cu K}\beta$). The systematic character in errors between adjacent points which exist with a classical recording step (a) becomes obvious between A and B, or B and C, in (b) in which the step size is five times narrower.

Flack, 1987). A more pragmatic attitude has been chosen here.

III. Local correlations: a limit for the Rietveld method

Serial correlations in the profile D_i differences, or even in their normalized differences $a_i = w_i^{-1/2} D_i$, immediately show evidence of such systematic aberrations. For instance, if the integrated intensity of a diffraction line is overestimated (where the preferred orientation function or structure factors are badly adjusted, for example), Y_{ci} will tend to exceed Y_{oi} over a large angular range centred on the line; if the chosen profile shape function does not perfectly match the actual profile, zones of severe correlations will probably be detected on top of the line and in its tails (usually, these correlations have opposite signs) (Fig. 1*b*). Such line oscillations are usually seen even with very good neutron fits.

In these correlations (oscillations, misestimation), the low-frequency mode is most significant when the number of points becomes large. This allows us to find a way to obtain an estimate of error which takes into account the limit of the model. In Fig. 1*b*), we can see that points between *A* and *B*, or between *B* and *C*, contribute to the same error; their profile differences do not represent statistical fluctuations and cannot be quadratically added.

The basic factor in the calculation of the standard deviations is the sum S , which is an estimator of the general variance, or dispersion, of the refinement.

In this sum, the normalized profile a_i differences are added quadratically, as variables in a χ^2 -like distribution. This is impossible if these variable are not independent. Our idea is that, in a region of correlation, all correlated profile a_i differences contribute to the error on the refined parameter in the same way: then they should be added linearly and not quadratically. Thus we will write

$$S' = [\sum_j a_j^2] + [\sum_l (\sum_{ml} a_{ml})^2] \quad (6)$$

$$s_k'^2 = s_k^2 S'/S. \quad (7)$$

The j summation only extends to uncorrelated points. The sets of correlated regions of the scan are indexed by l , and the ml summation is performed over the correlated differences of the l set. In order to illustrate the advantage of this correction, let us again consider a fictitious scan where artificial correlations have been introduced through a duplication of each observation by a factor μ (§II). The aim of our correction is to obtain the same values of the e.s.d.'s in such a duplication of the data, which brings no additional information.

$$S' = 0 + [\sum_l (\sum_{ml} a_{ml})^2] = \sum_l (\mu a_l)^2 = \mu^2 S'_0$$

$$s_k'^2 = \mu^2 S'_0 (M_0^{-1})_{kk} / [\mu(\mu N - P)] \sim s_{0k}^2.$$

This offers us a way to obtain reliable estimated error if a valid test enables us to decide in which term of S' a given error must be included.

The first test we have used to detect local correlations is to perform the product of adjacent normalized differences. When the points are obviously correlated, their values have the same sign and are significant. If the product reaches a value higher than an arbitrarily chosen level, both points will be considered as 'correlated'.

Therefore (6) can be rewritten as

$$S' = [\sum_j (1 - t_j) a_j^2] + [\sum_l (\sum_{ml} t_{ml} a_{ml})^2] \quad (8)$$

$$a_j a_{j+1} > p \Rightarrow t_j = 1 \quad \text{or} \quad t_j = 0. \quad (9)$$

The m summation is performed while t_{ml} is non zero. Fig. 2 compares the corrected probable errors obtained with various level of p to e.s.d.'s obtained originally by the Rietveld method. All the data sets used for refinements were obtained by extracting intensity values with various steps out of the same experiment. The pattern was recorded using a high-resolution laboratory powder diffractometer (Bérar, Calvarin & Weigel, 1980) with Cu $K\alpha$ radiation on a well crystallized tetragonal lead monoxide (α -PbO) with FWHM in the range 0.06–0.08 2θ , the original step size being 0.004 2θ .

The unfavorable decrease in estimated error is avoided, and the reasonable value of the estimated error seems to correspond to a low value of the level used in the test.

Other tests using χ^2 or Poissonian properties reach the same conclusion. In all cases, the fall-off of Rietveld e.s.d.'s is avoided, and a quite reasonable value is obtained in each case for values of p in the vicinity of unity.

The obvious drawback of this method is that a level p (or an interval of confidence) must be arbitrarily chosen, on which the correction proves to be strongly dependent. The narrower this interval, the weaker the resulting correction of estimated error.

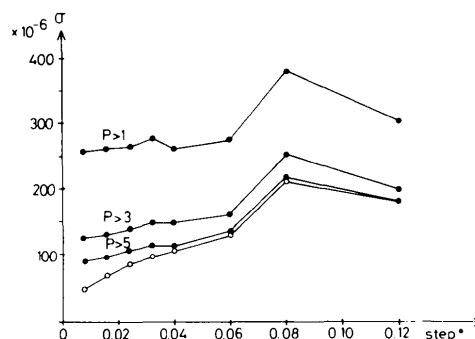


Fig. 2. E.s.d.'s (○) and estimated probable errors (●) as deduced for various confidence levels p using a product test.

IV. A homogenous correction

Our basic idea was that some profile differences had to contribute to the sum S' quadratically ('uncorrelated' differences), whereas the others had to contribute to this sum linearly ('correlated' differences). In the previous test, the differences were added to one or to the other term using a binary choice; this procedure gave us a result strongly dependent on an arbitrary confidence level. For each point, we now try to estimate its probability z_i to be correlated with its predecessor, with the intention of introducing the following correction of s_k :

$$S'' = [\sum (1 - z_i^2) a_i^2] + [\sum (\sum z_i a_i)^2] \quad (10)$$

$$s''_k^2 = s_k^2 S'' / S. \quad (11)$$

z_i can be derived from the relative values of the distribution functions of the χ^2 distributions for one and two degrees of freedom. To take into account local correlations only, we will consider that adjacent differences are automatically uncorrelated if their signs are different. If they have the same sign, we can say that z_i is proportional to the probability χ^2 being inferior to the value $(a_{i-1}^2 + a_i^2)$ in the χ^2 distribution with two degrees of freedom.

$a_i a_{i-1} > 0 \Rightarrow z_i = [2(a_i^2 + a_{i-1}^2)]^{1/2} \{2 + [2(a_i^2 + a_{i-1}^2)]^{1/2}\}^{-1}$
or

$$z_i = 0. \quad (12)$$

It can be noticed that the individual test on each couple of points may have a very questionable meaning; but as this test runs over the full range of angles, a good estimate of the correlation influences is obtained. This can be seen in Fig. 3 in which we observe that the corrected e.s.d.'s reach a stable value which does not depend on the recording density.

We have plotted in Fig. 4, as an example, the values of the cell parameter a of α -PbO obtained

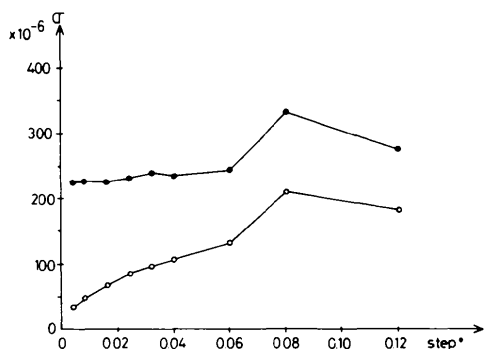


Fig. 3. E.s.d.'s (○) and estimated probable errors (●) obtained by the homogeneous formulation as a function of the recording step.

after refinements with various recording steps. The 3σ confidence interval obtained with the corrected estimated error is in good agreement with the fluctuations observed on the parameter itself when the recording step increases.

The above correction has been implemented in our local version of *DBW3.2* (Wiles & Young, 1981) and the lines added to the *CHISQ* subroutine are given in the Appendix.

V. Concluding remarks

Since this correction only involves normalized differences, it also takes into account the effect of large counting times, which tend to make inadequacies in the profile model more significant.

Moreover, if we consider the problem of multi-phase refinement in which the lines of the first phase are much broader than the lines of the other, the e.s.d.'s will increase by the same factor for both phases, and the refinement minima of one phase will be influenced by the correlation one can detect on the other. For all these reasons, one can consider modifying the Rietveld procedure in order to minimize not the sum S but the sum S'' which takes into account the local correlations.

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APPENDIX

The following modification was introduced in the *DBW3.2* subroutine *CHISQ*, this loop is added before the end.

```
SCOR = XVAL = XDEL = XD = 0
XY = 1
IX = -1
DO 100 I = 1, NPTS
```

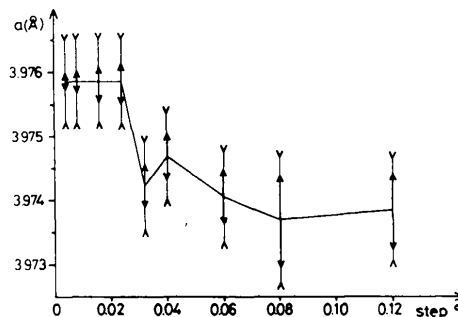


Fig. 4. Variation of the parameter a of α -PbO with 3σ error bar on e.s.d.'s and estimated probable errors.

```

IF((NBCKGD.NE.0.AND.KR(I).EQ.0).OR
.KR(I).EQ.2048) GOTO 100
DEL = Y(I)-BK(I)-YC(I)
IF((I-IX).EQ.1.AND.DEL*XD.GT.0) THEN
  XD = XD**2/XY
  COREL = (DEL**2/Y(I)) + CD
  PROB = SQRT(2*3.1416*COREL)
  PROB = PROB/(2 + PROB)
  XDEL = XDEL + PROB*SQRT(XD)
  SCOR = SCOR + (1-PROB**2)* XD
ELSE
  SCOR = SCOR + XDEL**2
  XDEL = ABS(XD)/SQRT(XY)
ENDIF
IX = I
XD = DEL
XY = Y(I)
100 CONTINUE
SCOR = SCOR + XDEL**2
SCOR = SQRT (SCOR/S2)
WRITE (6,101) SCOR
101 FORMAT ('ESD'S HAVE TO BE MULTI-
PLIED BY: ',F6.3)

```

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