Addenda to the Optimization of Quantitative X-ray Diffraction Analysis

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Abstract

The optimization of the quantitative X-ray diffraction analysis given by Szabó [J. Appl. Cryst. (1980), 13, 479-485] is improved in two respects. An easier use of the method for the analyst, a further saving of measuring time and a reduction of the computer running time are achieved.

Introduction

In quantitative diffraction analysis, the concentrations of the components of a powder mixture are sought, starting from the integrated intensities of the various diffraction peaks of the mixture. The optimization of this analysis has been given by Szabó (1980), referred to in the following as FP (first part). Accordingly, the precision of measurement of each peak is determined in such a manner as to minimize the total measuring time, while obtaining the concentrations with the required accuracy. This method will now be improved in two respects.

One improvement concerns the way in which the requirement of the accuracy of the concentrations is established in the optimization. In FP an equation was used with a number of free parameters. These were to be guessed by the analyst, by a tedious trial-and-error process. The method, i.e. the computer program, is changed so as to include the calculation of these parameters. Now the requirement of the accuracy of the concentrations will be established simply by giving upper bounds to their errors. This means an easier use of the method for the analyst, and we will see that the computer running time remains practically unchanged.

In FP the time involved in the tentative measurement was neglected. We will show how to take this time into account in the optimization. This second improvement results in a further reduction of the measuring time, and even the computer running time is reduced.

The notation of FP will be used. The most important symbols are: $I_k$ is the integrated intensity of, and $W_k$ is the weight assigned to, peak $k$; $C_i$ is the concentration of component $i$; $N$ is the number of components; and $\sigma(Z)$ is the standard deviation of $Z$.

First improvement

Let us first consider the constraints that are imposed on the $\sigma(C_i)$ for the optimization. Those given by the user place upper bounds on the error of the concentrations, i.e. are of the form

$$\sigma(C_i) \leq R_i, \quad (1)$$

where the $R_i$ represent these bounds. Instead, in FP the following constraint (FP 5.3) was introduced:

$$\sum_i F_i \sigma^2(C_i) = 1, \quad (2)$$

and we were directed to choose the $F_i$ by a hit-or-miss approach, each one as small as possible, so that (1) are satisfied.

There is an intimate connection between these two constraints: the $F_i$ are essentially the Lagrange multipliers associated with the constraints (1). That is, to fulfil constraints (1), we must ascertain the values of the Lagrange multipliers $F_i$ and use (2) in the optimization, just as indicated in FP.

The method will be improved if we let the computer, and not the analyst, calculate the $F_i$. This is a very sensible improvement: the hit-or-miss approach, at the disposal of the analyst, is of unpredictable length. It is performed with several trials, and consequently several runs of the computer program. But if the calculation of the $F_i$ is left to the computer then there will be only one run of the computer program and no human work involved. The task of the analyst is limited to entering the bounds $R_i$ to the computer.

The $F_i$ can be calculated easily within the iterative procedure of FP. For this, having chosen an initial set $F_i$, e.g. by putting $F_i=(NR_i^2)^{-1}$, we add a third iterative step (III) to the two already given in FP:

(III) The expected $\sigma(C_i)$ are calculated [for the present values of the $W_k$ and $\sigma(I_k)$], and each $F_i$ is multiplied by $\sigma(C_i)/R_i$.

It is easily seen that this iterative step fulfils its task:
if a \( \sigma(C_i) \) is greater than the corresponding \( R_i \), the \( F_i \) will become greater, thus by (2) forcing the \( \sigma(C_i) \) to become smaller, and vice versa; after convergence is reached, we must have (1) satisfied. More precisely, we will have either \( \sigma(C_i) = R_i \) and \( F_i > 0 \), or \( \sigma(C_i) < R_i \) and \( F_i = 0 \). These cases are in accordance with the interpretation of the Lagrange multipliers as the reaction of the system on the constraints. If in the optimum \( \sigma(C_i) = R_i \), then the optimum will depend on the constraint, i.e. on the value of \( R_i \), and so the reaction \( F_i \) will be non-zero. But if \( \sigma(C_i) < R_i \), then the optimum will not depend on the constraint, at least if \( R_i \) changes only slightly, and so the reaction \( F_i \) must be zero.

In practice, the \( F_i \) converge more rapidly than the \( W_i \) or the \( \sigma(I_k) \). In addition, the calculations required in this step (III) are quite simple: the formula (FP 3.4) for \( \sigma(C_i) \) becomes simplified to

\[
\sigma^2(C_i) = \sum_j G_{ij} G_{i\alpha} A_{\alpha j}^{-1}
\]

(3)

because of the relation (FP 4.9), which is satisfied at each step (II). These facts mean that the computer running time increases very little by the introduction of this last step (III).

Second improvement

The other respect in which we have improved the method of FP concerns an approximation made there. The optimization of FP usually shows that some peaks should not be measured at all. But these peaks have already been measured tentatively. This fact is not taken into account in FP. Thus a time waste arises: either we are throwing away information by regarding these peaks as not measured, or by using these measurements, we obtain the concentrations more accurately than needed. Of course, an analogous time waste arises whenever the optimization shows a peak to be measured less precisely than it was measured tentatively.

Let us include in the optimization procedure the intensity data obtained and the time involved in the tentative measurement. Denoting by \( t_k \) the measuring time of peak \( k \), and distinguishing quantities referring to the tentative measurement by a superscript 0, this is expressed mathematically in the form of the constraints

\[
t_k \geq t_k^0,
\]

(4)

which are the same as

\[
\sigma(I_k) \leq \sigma(I_k^0),
\]

(5)

in view of the relation \( t_k = U_k/\sigma^2(I_k) \) (FP 5.1). These are to be considered alongside the constraint (FP 5.4). Fortunately, this modified optimization problem can be solved by a quite similar iterative procedure. We must only add a further iterative step to those already given, to be placed between the first two:

(1a) The \( \sigma(I_k) \) are inspected. Those which are greater than \( \sigma(I_k^0) \) are made equal to the latter. Those which are less than \( \sigma(I_k^0) \) are multiplied by a common suitable number so that the constraint (FP 5.4) is satisfied. By this multiplication some of the \( \sigma(I_k) \) may become greater than \( \sigma(I_k^0) \). Thus step (1a) should be repeated until no change is made in the \( \sigma(I_k) \).

Although it is not usual, exceptionally it may happen that there is no \( \sigma(I_k) \) less than \( \sigma(I_k^0) \), and so the constraint (FP 5.4) cannot be satisfied. This means that, in this case, the tentative measurement has already given the concentrations more accurately than needed. Thus nothing is left to be done in this particular case.

We see that step (1a) fulfils its task by the following. It makes the constraints (5) and (FP 5.4) satisfied. Also, those \( \sigma(I_k) \) which are, and remain, less than \( \sigma(I_k^0) \) become multiplied by a constant; they will have just the value which would be obtained by the method of step (I) if we allow only these \( \sigma(I_k) \) to vary, the others being held at their fixed values \( \sigma(I_k^0) \).

This iterative procedure, with the addition of step (1a), is convergent by the same reasons as given in FP. In fact, it converges more quickly. The convergence in FP was particularly slow for small \( t_k \), especially for those which converged to zero. Now we have a lower bound for the \( t_k \) given by (4), preventing them from getting too small.

The addition of step (1a) becomes of utmost importance in the case, described in FP, when the optimized measurement turns out to be inadequate and has to be repeated, because then the time involved in the measurements already performed cannot be neglected. However, the usefulness of step (1a) is limited to the case when only one sample has to be analysed. In the case of routine analysis, where several samples of similar composition are analysed, it is sufficient to perform the tentative measurement only for the first sample. This gives a suitable indication of the measuring times to be applied for the other samples although its data evidently cannot be used for the calculation of the concentrations of the other samples.

Illustrative example

To illustrate these ideas, let us consider the following practical example. Suppose that after the measurements described in FP, there arises the necessity to determine the composition of sample 1 with less than 0.4% error in the concentrations. Thus we must consider the former optimized measurement of this sample, given in FP, as tentative, and perform the optimization once more. Then the values of the \( U_k \) will also be changed since this 'tentative' measurement is more exact than was the original one in FP; and thus it yields more precise values for these parameters. We
Table 1. Results of the optimization, without using step (Ia)

<table>
<thead>
<tr>
<th>$k$</th>
<th>$U_k$</th>
<th>$\sigma(t_k^0)$ (s)</th>
<th>$t_k^0$ (s)</th>
<th>$\sigma(t_k)$ to be attained</th>
<th>$t_k$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.94</td>
<td>0.079</td>
<td>1920</td>
<td>0.051</td>
<td>4520</td>
</tr>
<tr>
<td>2</td>
<td>10.71</td>
<td>0.058</td>
<td>3210</td>
<td>0.042</td>
<td>6050</td>
</tr>
<tr>
<td>3</td>
<td>170.43</td>
<td>0.362</td>
<td>1300</td>
<td>0.159</td>
<td>6700</td>
</tr>
<tr>
<td>4</td>
<td>75.78</td>
<td>0.236</td>
<td>1360</td>
<td>0.181</td>
<td>2330</td>
</tr>
<tr>
<td>5</td>
<td>22.98</td>
<td>0.30</td>
<td>260</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>11.22</td>
<td>0.063</td>
<td>2850</td>
<td>0.050</td>
<td>4420</td>
</tr>
<tr>
<td>7</td>
<td>14.60</td>
<td>0.052</td>
<td>5300</td>
<td>0.108</td>
<td>1250</td>
</tr>
<tr>
<td>8</td>
<td>61.26</td>
<td>0.39</td>
<td>400</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

We need not worry any more about the $F_i$ as our improved program will calculate them. We just set the $R_i$ equal to 0.4.

We first perform the optimization without taking into account the tentative measurement, i.e. without using step (Ia). Thus we obtain the results contained in Table 1 where the new values of $U_k$ and some parameters of the tentative measurement have also been included. Accordingly, we are directed to perform new measurements, with a total duration (taking now into account the tentative measurement) of 13 380 s. Evidently, peaks 5, 7 and 8 had been already measured more precisely than needed.

Table 2. Results of the optimization, using step (Ia)

<table>
<thead>
<tr>
<th>$k$</th>
<th>$\sigma(t_k)$ to be attained</th>
<th>$t_k$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.057</td>
<td>3620</td>
</tr>
<tr>
<td>2</td>
<td>0.046</td>
<td>5170</td>
</tr>
<tr>
<td>3</td>
<td>0.206</td>
<td>4030</td>
</tr>
<tr>
<td>4</td>
<td>0.183</td>
<td>2270</td>
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<tr>
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<tr>
<td>6</td>
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<tr>
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<td>5300</td>
</tr>
<tr>
<td>8</td>
<td>0.39</td>
<td>400</td>
</tr>
</tbody>
</table>

Then we perform the optimization using step (Ia). The results obtained are summarized in Table 2. These represent new measurements with a total duration of 8650 s.

Thus, had we not used step (Ia), a time waste of 4730 s would have arisen; this represents 55% of the necessary measuring time. Further, it has to be remarked that with the addition of step (Ia) the computer running time has also been reduced, by 12%.

Reference