Quantitative Analysis of Multicomponent Powders by Full-Profile Refinement of Guinier–Hägg X-ray Film Data

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(Received 1 August 1978; accepted 26 September 1978)

Abstract

Full-profile analysis of microdensitometer-measured Guinier–Hägg X-ray powder film data (strictly monochromatized Cu Kα1 radiation) [see Malmros & Thomas (1977). J. Appl. Cryst. 10, 7–11] is here extended to treat a multicomponent system where two of the components are refinable. The method is demonstrated for the case of: (a) α-Bi₂O₃/KCl (standard), and (b) CaF₂/SiO₂ (α-quartz) together with a Mg(OH)₂ matrix. In (a), a weight ratio Bi₂O₃/KCl of 1:1 gave an experimental result of 0.96(9):1. In (b), a number of admixtures have been studied in the range 1–60 wt% SiO₂ all with 10 wt % CaF₂. The agreement between weight ratios and profile refinement results suggests that the formal temperature factors function as effective absorption correction parameters. It is thus shown that approximate quantitative analysis is feasible from Guinier–Hägg diffraction data without any previously determined calibration curve. Moreover, the method permits the use of all available overlapping data in the refinement of a structure without needing to exclude data from known impurities [see Waltersson, Werner & Wilhelmi (1977). Cryst. Struct. Commun. 6, 231–235]. This feature is likely to prove the most common application of the method.

The analysis method

The procedure for refinement of a two-component system follows exactly that used for the single-component case: see Rietveld (1969) and Malmros & Thomas (1977), hereafter: MT. The combined data file is created in a preparation program where all pertinent input information needed for the individual components is supplied in sequence. The quantitative analysis of the admixture is achieved by the refinement of an overall scale factor together with a common 'occupation' parameter (n₁) for all atoms within one of the components (naturally, taking account of different atom-site multiplicities). The common occupation parameter for the other component (n₂) is fixed at some arbitrary value in the refinement. For components with formula weights M₁ and M₂ and with Z₁ and Z₂ formula units/cell, the weight percentages ω₁ and ω₂ are related such that:

$$ω_1 = ω_2(Z_1M_1/Z_2M_2)(n_1/n_2)^2.$$  (1)

The square of the occupation parameters is a measure of the quantity of the substance present. It is thus assumed that absorption errors are corrected for in the refinement. The use of the term occupation parameter originates in single-phase work, and is somewhat misleading in the context of two simultaneously occurring structures. Within each of the structures,
however, the internal relation between occupation numbers is unchanged.

(a) $\alpha$-Bi$_2$O$_3$ + KCl

A preliminary test took the form of a straightforward refinement of the entire intensity profile for $\alpha$-Bi$_2$O$_3$ + KCl obtained in MT. The $\alpha$-Bi$_2$O$_3$ and KCl had not earlier been weighed, so that no quantitative check could be made. No significant differences were observed in the refined $\alpha$-Bi$_2$O$_3$ parameters as a result of the inclusion of the KCl regions. In fact, the results obtained were virtually equivalent, demonstrating that structure refinement was technically feasible in the presence of calibration or impurity lines.

A weighed sample of 50–50 mol% $\alpha$-Bi$_2$O$_3$/KCl was then refined to test the possibility of performing quantitative analysis. A very small amount of sample was used to minimize the effect of absorption. All $\alpha$-Bi$_2$O$_3$ positional parameters were here fixed to the values given in MT. Only an overall scale factor and profile parameters $U$, $V$, $W$, and $P$ were refined for each of the compounds. Certain constraints had also to be applied to the temperature factors in order to achieve a quantitatively correct analysis (within the estimated standard deviations). It was found necessary to fix an overall KCl temperature factor (to 0.5 Å$^2$) to avoid correlations between temperature factors and occupation numbers. An overall (refined) isotropic temperature factor was also added to the individual $B$ values obtained earlier in MT for $\alpha$-Bi$_2$O$_3$ to serve as an empirical absorption correction.

That absorption became so serious a problem here is presumably related to extremely high X-ray absorption of $\alpha$-Bi$_2$O$_3$ ($\mu = 203$ mm$^{-1}$). An absorption correction parameter has, in fact, been included in the program, but no convergent refinement has been achieved on simultaneous refinement of $B$'s and the absorption coefficient. This is not unexpected in view of the strong correlation between absorption and temperature parameters discussed by Sas & de Wolff (1966).

It was also discovered that, because of the small number of calibration lines, the $U$, $V$, $W$, values for KCl had to be constrained to take the $\alpha$-Bi$_2$O$_3$ values.

For fixed arbitrary occupation number 1.0 for $\alpha$-Bi$_2$O$_3$, the value 0.722(33) was obtained for KCl. This corresponds to $(n_{\text{Bi}_2\text{O}_3}/n_{\text{KCl}})^2 = (1.92/0.722)^2 = 1.92(18)$, and should be 2.0 from equation (1), since the KCl atoms lie on special positions in the structure.

(b) CaF$_2$ + SiO$_2$ ($\alpha$-quartz) + Mg(OH)$_2$ matrix

Various admixtures of CaF$_2$ and SiO$_2$ powder were prepared. For 10 wt% CaF$_2$, eight different mixtures were tested with wt% SiO$_2$ ranging from 60% down to 1%. The discrepancy in percentages was made up by appropriate amounts of Mg(OH)$_2$. The results of the analysis are summarized in Table 1 and Fig. 1. In all, eight parameters were refined: an overall scale factor together with (for both SiO$_2$ and CaF$_2$) an asymmetry parameter ($P$), a half-width parameter $W$, and an overall temperature factor $B$. The eighth parameter was the occupation number for SiO$_2$ (for full notation see MT). The relatively few lines observed in the low-angle region made it impossible to refine the half-width parameters $U$ and $V$. $W$ values for SiO$_2$ had to be fixed for the 2% and 1% cases because of their weak intensity contribution. Regions containing

![Fig. 1. Analysis by X-ray powder profile refinements of 10 wt% CaF$_2$ and various amount of \(\alpha\)-SiO$_2$ with, as matrix material, Mg(OH)$_2$. The theoretical line is drawn according to equation (2) and has a gradient 5.7717.](image)

**Table 1. Analysis by X-ray powder profile refinement of 10 wt% CaF$_2$ and various amounts of \(\alpha\)-SiO$_2$ with as matrix material, Mg(OH)$_2$.**

<table>
<thead>
<tr>
<th>Wt% SiO$_2$</th>
<th>Overall temperature factors</th>
<th>Half-width parameters*</th>
<th>Asymmetry parameters</th>
<th>Occupation Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$B_{\text{SiO}_2}(A^2)$</td>
<td>$B_{\text{CaF}_2}(A^2)$</td>
<td>$W_{\text{SiO}_2}(\text{deg}^2)$</td>
<td>$W_{\text{CaF}_2}(\text{deg}^2)$</td>
</tr>
<tr>
<td>60</td>
<td>1.6 (3)</td>
<td>0.4 (4)</td>
<td>0.027 (2)</td>
<td>0.10 (2)</td>
</tr>
<tr>
<td>40</td>
<td>-0.4 (5)</td>
<td>0.1 (4)</td>
<td>0.035 (4)</td>
<td>0.10 (2)</td>
</tr>
<tr>
<td>30</td>
<td>2.7 (4)</td>
<td>1.5 (5)</td>
<td>0.037 (5)</td>
<td>0.17 (4)</td>
</tr>
<tr>
<td>20</td>
<td>2.7 (4)</td>
<td>0.4 (3)</td>
<td>0.036 (4)</td>
<td>0.12 (1)</td>
</tr>
<tr>
<td>10</td>
<td>-1.9 (4)</td>
<td>2.6 (3)</td>
<td>0.013 (2)</td>
<td>0.069 (6)</td>
</tr>
<tr>
<td>5</td>
<td>-2.6 (6)</td>
<td>0.6 (4)</td>
<td>0.047 (7)</td>
<td>0.081 (6)</td>
</tr>
<tr>
<td>2</td>
<td>-4.3 (8)</td>
<td>0.6 (3)</td>
<td>0.048 (7)</td>
<td>0.081 (6)</td>
</tr>
<tr>
<td>1</td>
<td>-9.1 (1)</td>
<td>0.9 (2)</td>
<td>0.048</td>
<td>0.081 (6)</td>
</tr>
</tbody>
</table>

* $W$ is defined by Rietveld (1969) as the square of the half-width in $2\theta$ at half height.

† Fixed parameter.
Mg(OH)$_2$ lines were removed from the refinement. From equation 1, it follows that:

$$\omega_{\text{SiO}_2} = \omega_{\text{CaF}_2}(3M_{\text{SiO}_2}/4M_{\text{CaF}_2})(\eta_{\text{SiO}_2}/\eta_{\text{CaF}_2})^2. \quad (2)$$

The theoretical linear relation between $\omega_{\text{SiO}_2}$ and $(\eta_{\text{SiO}_2}/\eta_{\text{CaF}_2})^2$ for $\omega_{\text{CaF}_2} = 10$ is drawn in Fig. 1. This relation facilitates a quantitative analysis from a single-sample measurement. The results of the analysis using this procedure for each of the samples are also given in Table 1.

From Fig. 1 it is seen that there is good agreement between observed and calculated $\omega_{\text{SiO}_2}$ values, bearing in mind the large standard deviations obtained for the higher $\omega_{\text{SiO}_2}$ values. It should be noted here, however, that the highest relative accuracy is obtained for identical amounts (10 wt%) of $\alpha$-SiO$_2$ and CaF$_2$ (cf. Table 1). The agreement obtained suggests that absorption errors are here again compensated by refinement of the formal temperature factors. It also explains the common occurrence of negative temperature factors in this type of refinement.

**Conclusion**

Although a standard calibration approach (see, for example, Alexander & Klug, 1948) is clearly preferable for quantitative analysis purposes since it is independent of absorption in the sample, it does require a time-consuming and often tedious precalibration. We see that such a precalibration is not essential using the present method.

The present program, itself a modification of the Rietveld full-profile refinement program for neutron data (Rietveld, 1969), is currently also being applied to the refinement of multicomponent neutron profiles (Thomas, 1978).

We wish to express our sincere thanks to Professors Peder Kierkegaard and Ivar Olovsson for the research facilities placed at our disposal and their kind interest in this work. This work has received financial support from the Swedish Natural Science Research Council and from The Swedish Work Environment Fund.

**References**


