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Error Analysis and Correction for Quantitative Phase Analysis Based on Rietveld-Internal Standard Method: Whether the Minor Phases Can Be Ignored?

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Abstract: The Rietveld-internal standard method for Bragg-Brentano reflection geometry ($\theta/2\theta$) X-ray diffraction (XRD) patterns is implemented to determine the amorphous phase content. The effect of some minor phases on quantitative accuracy is assessed. The numerical simulation analysis of errors and the related corrections are discussed. The results reveal that high purity of crystalline phases in the standard must be strictly ensured. The minor amorphous or non-quantified crystalline phases exert significant effect on the quantitative accuracy, even with less than 2 wt% if ignored. The error levels are evaluated by numerical simulation analysis and the corresponding error-accepted zone is suggested. To eliminate such error, a corrected equation is proposed. When the adding standard happens to be present in sample, it should be also carefully dealt with even in low amounts. Based on that ignorance, the absolute and relative error equations (Δ_{AE} , Δ_{RE}) are derived, as proposed. The conditions for high quantitative accuracy of original equation is strictly satisfied with a lower amount of standard phase present in sample, less than 2 wt%, and a higher dosage of internal standard, larger than 20 wt%. The corrected equation to eliminate such quantitative error is suggested.

Keywords: Rietveld; quantitative analysis; corrected equation; amorphous

1. Introduction

Quantitative phase analysis based on X-ray diffraction (XRD) can be traced back to as early as 1919 [1]. Hull firstly proposed that this technique had the potential to perform accurately quantitative analysis. Subsequently, Alexander developed practical XRD methods and derived the related theoretical basis [2]. With the improvements of XRD analysis, different quantitative methods have been presented in succession, such as reference intensity ratio (RIR) method [3], external standard method [4], matrix-flushing method [5], non-standard method [6], doping method [7], and Rietveld method [8]. The Rietveld method, as proposed by Hugo M. Rietveld, is widely accepted due to its whole-pattern fitting approach instead of single-peak analysis. The main advantage is that it can effectively minimize or eliminate the inaccuracies arising from preferred orientation, particle statistics, microabsorption, peaks overlapping, and detection of amorphous phase and trace phases [9–11]. Over the last two decades, it has become widely accepted by scientific community, gradually being a standard practice, as it is possible to solve those problems associated with crystalline materials. However, there are two preconditions: (1) the quantified phase is the crystalline phase, and (2) the crystal structure is known [12]. Therefore, if amorphous material is present, quantitative results could not be obtained directly. In such case, it is normal to use a reference material for the recalculation of

the phase contents [13]. This reference material is either mixed in the sample as internal standard [10] or measured separately under identical conditions as external standard [14]. The internal standard method derives the amorphous content from the comparison between the actual dosage and Rietveld result of the internal standard, Equation (1) [13]:

$$W_{Amor} = \frac{1 - W_{St}/R_{St}}{100 - W_{St}} \times 10^4 \quad (1)$$

where W_{St} stands for the actual dosage of the internal standard, and R_{St} stands for the Rietveld results of the internal standard.

Meanwhile, the external standard method focuses on determining the diffractometer constant with an appropriate standard, which is used to determine the weight fraction of each crystalline phase. From the difference between 100 wt% and the sum of the crystalline phase contents, an overall weight percentage of amorphous can be subsequently derived.

$$G = K_e = S_{St} \cdot \rho_{St} V_{St}^2 \mu_{St} / W_{St} \quad (2)$$

$$W_{Amor} = 100 - \sum S_{\alpha} \cdot \rho_{\alpha} V_{\alpha}^2 \mu_{\alpha} / G \quad (3)$$

Where S_{St} and S_{α} stands for the scale factors of the external standard and each phase in the mixture, respectively, ρ is the density, V is the unit cell volume, and μ_{St} and μ_s are the mass absorption coefficient of the external standard and the sample, respectively.

Besides these two methods, the amorphous content could also be quantified by the 'PONKCS' (Partial Or No Known Crystal Structure) method that relies upon treating a set of peaks of amorphous phase as a single entity [15]. Amorphous phase is characterized by measured rather than a calculated structure factor.

The Rietveld-internal standard method, as the most widely used technique, is a relatively easy and direct strategy, no other measurements or calibrations are needed. If the analyses are carefully performed and the amount of amorphous content to be determined over 15 wt%, the accuracy is satisfactory, close to 1% [10,13,16–18]. On the contrary, the external and 'PONKCS' methods are more complicated and some other preconditions need to be met in the meantime. For instance, the external standard method strictly requires the identical conditions of XRD data acquisition and different mass attenuation coefficient correction between sample and standard. Though 'PONKCS' strategy may solve the problem of undistinguished ability between different amorphous phases, it depends on accurate identification and the calibration of amorphous. A problem may occur because of the complexity of this analyzing process, especially when the amorphous phases are less evident or difficult for characterization [19].

Beside the advantage of the internal method mentioned above, the determination of amorphous contents is also a very challenging operation indeed. First of all, the effects of internal standard should be well considered. A significant error may occur when the selected standard is not homogeneously mixed into the sample or when an obvious absorption contrast exists between sample and standard [20]. Furthermore, use of an appropriate amount of internal standard is also a key point to guarantee the accuracy. Discussions about that influence on accuracy of amorphous phase quantitation have been reported [21,22]. The results illustrated that the quantitative accuracy of amorphous phase follows a nonlinear function by Rietveld-internal standard method, which in turn leads to a serious error in determining the minor amount of amorphous content. Most of these issues can be mitigated based upon the above results by adequate sample preparation and correct data acquisition [23–26]. However, there are still some factors that need further attention. Here, we study the error analysis that was introduced by some minor phases that are related to the internal standard. They include the minor impurity phases of the internal standard and the sample containing the same crystalline phase as the internal standard. There is often an overlook about contribution of these minor phases. The basic goal is to understand such effect on the quantitative accuracy. In order to do so, a three-dimensional numerical

simulation database, where the information includes absolute and relative errors is conducted, and relative corrected equations have been proposed. This study is a step forward to better understand quantitative phase analysis based on Rietveld-internal standard method.

2. Materials and Methods

2.1. Raw Materials

The Powders of SiO₂ [ABCR GmbH. Co. KG (Karlsruhe, Germany)] and ZnO [Sigma-Aldrich, Co. LLC (St. Louis, MO, USA)], purity of 99.9%, are chosen as the internal standard in this work. They were sieved firstly through 74 µm prior to be used. The glass powder was adopted as amorphous component, ground with particle sizes less than 20 µm (80% in number statistics), and surface area 500 m²/kg determined by specific surface area measuring instrument. The glass has a chemical composition (wt% of oxides) determined by XRF, of SiO₂ (72.5), Al₂O₃ (1.8), CaO (5.8), Na₂O (13.3), K₂O (1.6), MgO (3.8), and ZnO (0.8).

2.2. Sample Preparation

The powders of SiO₂, ZnO and glass were weighed, with a designed mass ratio of 45%:45%:10%, as 4.507 g, 4.473 g, and 1.033 g, respectively. The above powders were subsequently mixed and homogenized by hand for 30 min in an agate mortar. Finally, they were uniformly filled into the holder and slightly leveled for XRD measurement. That mixtures were prepared and then underwent XRD tests by triplicate. XRD patterns didn't show significant differences.

2.3. Data Collection and Processing

Chemical composition of glass was determined by the X-Ray Fluorescence (SRS3400, Bruker AXS Corporation, Karlsruhe, Germany). Particle statistic of powders was measured by laser particle size analyzer (LS 230 from Beckman Coulter, Brea, CA, USA). The X-ray diffraction patterns of mixtures were measured in Bragg-Brentano reflection geometry ($\theta/2\theta$) on an X'Pert MPD PRO diffractometer (PANalytical International Corporation, Almelo, Netherland) and GSAS-EXPGUI software (Los Alamos National Laboratory, Los Alamos, NM, USA) [27]. The detailed instrument settings for XRD are summarized in Table 1.

Table 1. The Instrument Settings for X-ray Diffraction (XRD).

| Scanning Type Detector | Continuous Scanning X'Celerator Detector |
|---|---|
| Geometry | Reflection/flat sample |
| X-ray radiation/tube working conditions | CuK α_1 , 45 kV/40 mA |
| Primary Monochromator | Ge (111) |
| Anti-scatter slit/° | 1/2 |
| Soller slit (rad) | 0.04 |
| Divergence slit/° | 1/2 |
| Angular range, 2 θ /° | 5–70 |
| Step width/° | 0.0167 |
| Measure time/h | 2 |
| Sample spinning speed (r.p.m) | 15 |

3. Results and Discussion

3.1. Quantitative Error Induced by Minor Impurity Phase of Internal Standard

The XRD pattern of that mixture was analyzed by Rietveld whole-pattern fitting based upon GSAS-EXPGUI software. The starting crystalline structure models of SiO₂ [28] and ZnO [29] were imported from literature. The instrument function file was chosen based on CuK α_1 as the incident

X-ray and Germanium as the monochromator (monochromatic model with wavelength of 1.54056 and polarization fraction value of 0.8). For the refinement of peak shape parameters, pseudo-Voigt function [30] with asymmetry correction [31] was chosen and the peak width and asymmetry factor, such as LY, GW, H/L, and S/L were initially set to 12 (0.01°), 5 (0.01°), 0.02, and 0.02, respectively. The refined parameters included unit-cell parameters, zero-shift correction, background parameters, phase fractions, and peak shape parameters (LY and GW). A linear interpolation function was chosen to fit the background with polynomial term gradually increasing to 36. Peak shapes were fitted by refining the Gaussian contribution and Lorentzian contribution separately when appropriated. During the process of Rietveld refinement, the refined parameters had regular convergence and least-square R factors, assessing the fitness of pattern, decreased gradually. Figure 1 shows the Rietveld refinement pattern of the artificial mixture. The stable refinements and satisfactory fits, as indicated by the smoothness of the Yobs-Ycalc curve illustrated the Rietveld refinement was reliable. Moreover, the analysis was performed by triplicate in order to assess the precision. The results are close but not identical with relative errors lower than 1%. The quantitative results are listed in Table 2, which also includes the quantitative phase analysis corrected by taking into account the microabsorption effect [32,33]. This is important in this mixture as linear absorption coefficient for SiO_2 is 92 cm^{-1} , while that for ZnO is 290 cm^{-1} . Both standards have very similar particle size ($\sim 4 \mu\text{m}$); consequently, ZnO will always be underestimated.

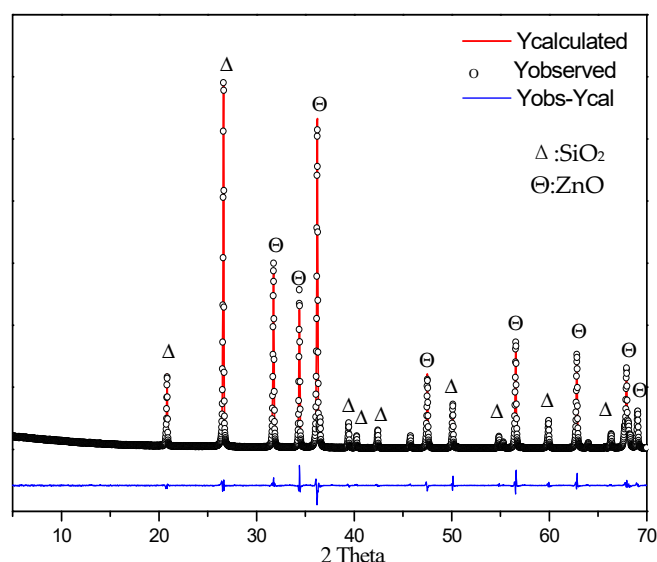


Figure 1. Rietveld XRD pattern of an artificial mixture (The circles correspond to observed data, the thin line is the calculated patterns by the Rietveld method. The Yobs-Ycal stands for the difference pattern plotted as blue line at the bottom). Main peaks due to each phase have been labeled Δ : SiO_2 ; Θ : ZnO .

Table 2. Rietveld Quantitative Phase Analysis of the Mixture.

| Phases | Weighed/wt% | SiO ₂ -ZnO-Glass | |
|------------------|-------------|-----------------------------|-------------------------------------|
| | | Riet/wt%, Uncorrected | Riet/wt%, Microabsorption Corrected |
| SiO ₂ | 45.01 | 51.1 | 48.4 |
| ZnO | 44.67 | 48.9 | 51.6 |
| Glass | 10.32 | — | — |

The middle column contains direct Rietveld results, assuming that all of the phases in the sample are crystalline phases; the right-most column contains Rietveld results corrected for microabsorption.

To obtain the quantitative results of the amorphous phase (Glass), SiO_2 and ZnO were considered as internal standards, respectively. If microabsorption effect is not considered, the errors in amorphous

determination are inevitably higher. However, even when considering that factor, the quantitative results are still not well reproducible with a significant relative deviation in the three different analysis, independently of the internal standard used (Table 3). However, when compared with different recorded XRD pattern analysis based on the same internal standard, the quantitative results show good consistency with absolute deviation of phases less than 1%.

Table 3. Rietveld quantitative results, including amorphous component derived by internal method for the artificial mixture, using the corrected values of Table 2.

| Phases | Weighed/wt% | SiO ₂ _ZnO_Glass | |
|------------------|-------------|---|---------------------------|
| | | ¹ Sta(SiO ₂)/wt% | ² Sta(ZnO)/wt% |
| SiO ₂ | 45.01 | Fixed | 41.90 |
| ZnO | 44.67 | 47.99 | Fixed |
| Glass | 10.32 | 7.00 | 13.43 |

‘1’ and ‘2’ represents quantitative results included amorphous phase (glass), taking SiO₂ and ZnO as internal standard, respectively.

To further verify this conjecture, Rietveld quantitative phase analysis of that mixture was performed by external standard method (G-factor method). For calculating the G-factor, the polished polycrystalline quartz rock was firstly considered as the standard. It has the advantage of avoiding the error induced by powder standard during the sample preparation, such as fluctuation of surface roughness, packing density, and so on. XRD data collection of the quartz rock standard was as close in time and identical in diffractometer configuration as possible to the artificial mixture sample, which could make sense of the formula of ‘G_SiO₂ = G_sample’. The mass absorption coefficient of artificial mixture sample under the condition of CuKα₁ radiation was determined as 42.34 cm²/g by Highscore Plus software (PANalytical, Almelo, Netherland). After correlative parameters obtained from Rietveld refinement and crystallinity of quartz rock obtained from former analysis, G value was calculated as 5.51×10^{-20} (Table 4). Based on this G value, quantitative results of crystalline and amorphous phases were given in Table 5. The average quantitative result of ‘Glass’ phase among three calculations is 13.08%, which is about 3% larger than the original weighed fraction. The extra part is contributed by amorphous or non-quantified crystalline phases (ACn) in SiO₂ and ZnO.

Table 4. G Value Calculation Based on Rietveld Refinement of Quartz Rock.

| Cquartz | Density [g/cm ³] | Refined Unit Cell Volume [cm ³] | Total Mass Absorption Coefficient [cm ² /g] | G Value |
|---------|------------------------------|---|--|------------------------|
| 87.9 | 2.646 | 1.13×10^{-22} | 34.84 | 5.51×10^{-20} |

Table 5. Comparison of the Weight Fractions and Rietveld Quantitative Result (G-factor Method) of Artificial Mixture.

| Phases | Weighed/% | SiO ₂ _ZnO_Glass |
|------------------|-----------|-----------------------------|
| SiO ₂ | 45.01 | 44.16 |
| ZnO | 44.67 | 42.75 |
| Glass | 10.32 | 13.08 |

To eliminate such quantitative errors induced by ACn in the internal standard, the original Equation (1) needs to be improved. Using Rietveld refinement, the improved equation for weight fraction of amorphous phase in original sample (W_{Amor}) can be derived as Equation (4), and the intermediate derivation process was shown in the supplementary materials.

$$W_{Amor} = \left[1 - \frac{\left(\frac{100}{R_{St}} - 1 \right) \times W_{St} \times \alpha}{100 - W_{St}} \right] \times 100 \quad (4)$$

where ' α ' is defined as the crystallinity in that internal standard. The equations of absolute error are successively derived for theoretical calculation of the error level between the original (Equation (1)) and improved equation (Equation (4)).

$$W_{Amor(impr)} - W_{Amor(origi)} = \frac{\left(\frac{1}{R_{St}} - \frac{1}{100}\right)}{\left(\frac{1}{W_{St}} - \frac{1}{100}\right)} \times (1 - \alpha) \quad (5)$$

To simplify Equation (5), R_{St} is firstly derived and expressed by crystallinity of internal standard (α) and the original sample (β) as Equation (6). The absolute error (Δ_{AE}) can be finally converted as Equation (7). Moreover, the relative error (Δ_{RE}) can be proposed as Equation (8).

$$R_{st} = \frac{W_{St}\alpha}{W_{St}\alpha + (100 - W_{St})\beta} \times 100 \quad (6)$$

$$\Delta_{AE} = W_{Amor(impr)} - W_{Amor(origi)} = \frac{1 - \alpha}{\alpha} \times \beta \quad (7)$$

$$\Delta_{RE} = \frac{W_{Amor(impr)} - W_{Amor(origi)}}{W_{Amor(impr)}} = \frac{1 - \alpha}{\alpha} \times \frac{\beta}{1 - \beta} \quad (8)$$

To evaluate the error level, the numerical simulation analysis of absolute and relative errors was performed. The results, corresponding to crystallinity of the internal standard (α) and the weight fractions of crystalline phases in original sample (β), were displayed in Figure 2. The three-dimensional (3D) pattern of error distributions was restricted to be under 100% for absolute error and 500% for relative error. The corresponding two-dimensional (2D) error areas were depicted at the bottom with color bars to distinguish the different error levels. It reveals the error becomes significant with the increase of weight fraction of crystalline phases in original sample and decrease of crystallinity of internal standard (bottom right corner), which means the original amorphous phase calculation (Equation (1)) is not applicable any more. On the contrary, the data located at the top left of 2D error areas, as shown in purple and blue colors, can be accepted and applied to original equation. When the preparatory conditions were set as ' $\Delta_{AE} \leq 10\% \cap \Delta_{AE} \leq 50\%$ ', the error-accepted zone is displayed in Figure 3. It is from the intersection operation between ' $\alpha \geq 10\beta / (1 + 10\beta)$ ' and ' $\alpha \geq 2\beta / (1 + \beta)$ '. An intersection point (8/9, 4/5) can be calculated from the above equations. Therefore, α and β should satisfy the relationship of ' $\alpha \geq 10\beta / (1 + 10\beta)$ ' when ' $\beta \in (0, 80\%)$ ' and ' $\alpha \geq 2\beta / (1 + \beta)$ ' when ' $\beta \in (80\%, 100\%)$ '.

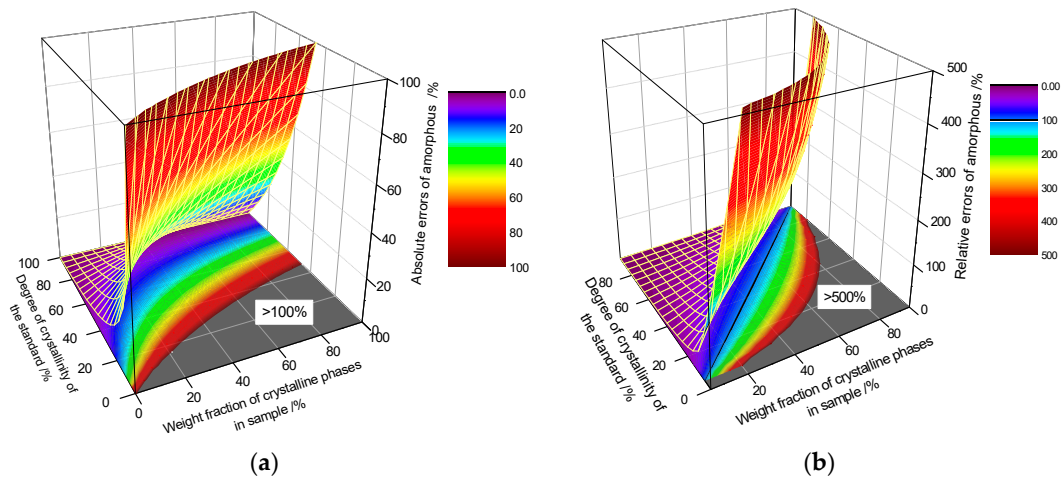


Figure 2. Error analysis between the original and improved equation (a: the absolute error (Δ_{AE}); b: the relative error (Δ_{RE})).

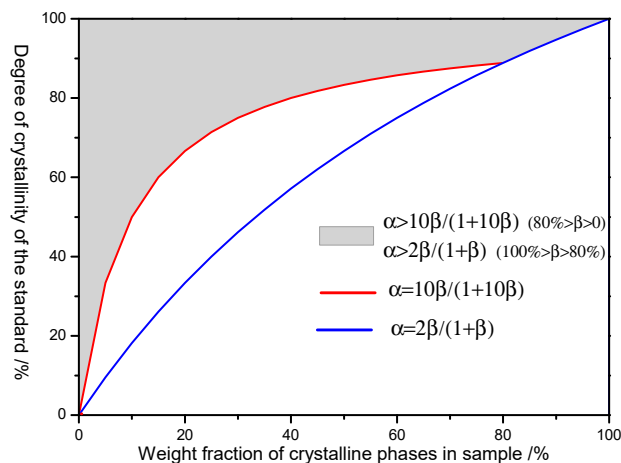


Figure 3. Accepted error-zone under the condition of ' $\Delta_{AE} \leq 10\% \cap \Delta_{AE} \leq 50\%$ '.

3.2. Quantitative Error Induced by Minor Standard Phase Present in Sample (SPS)

For the Rietveld/internal standard quantitative analysis, there is another problem that is often overlooked. It is also related to the standard besides the effect of its minor impurity phases above. The normal standards such as SiO_2 , Al_2O_3 , ZnO , and TiO_2 are preferably chosen due to their simple and known crystal structure, characteristic-sharp diffraction peaks and a variable availability of linear absorption coefficient. However, it is also important to highlight that such standards to be added for amorphous content determination may be present previously in the sample. In this work, we refer such a standard phase that is present in the sample as SPS. If SPS is minor phase and there is no better standard, they are often overlooked and assuming that contribution to quantitative accuracy is negligible. Here, we study the error analysis introduced by that extreme case and its effect on quantitative accuracy is discussed. The equations of absolute and relative errors are finally derived as Equations (9) and (10), and the intermediate derivation process was shown in the supplementary materials.

$$\Delta_{AE} = \frac{100x - y + 100}{\frac{100x}{z} + 1} \quad (9)$$

$$\Delta_{RE} = \left[\frac{100x - y + 100}{(\frac{100x}{z} + 1)y} \right] \times 100 \quad (10)$$

where x is set as ' $W_{St}/100 - W_{St}'$ while y and z stand for the weight fraction of amorphous phase (W_{Amor}^+) and the SPS phase (W_X^+) in original sample, respectively.

The numerical simulation analysis of absolute and relative errors was successively performed. The results, corresponding to W_{St} and W_X^+ , were displayed in Figure 4. Figure 4a,c,e shows the absolute error distribution in which the content of amorphous phase is assumed to be 10%, 20%, and 50%, respectively. The corresponding 2D error patterns, reported by Figure 4b,d,f, displayed the relative errors distributions. It is concluded that the error level of amorphous phase quantitation is positively correlated with W_X^+ and negatively correlated with W_{St} . The amorphous phase error becomes more sensitive with smaller of W_{St} or larger of W_X^+ . When compared with the results from 10 wt% to 50 wt% of the amorphous content, the conclusion can be drawn that quantitative error gradually dropped down at a higher dosage of internal standard. The relative errors displayed in Figure 4f are all less than 100% when the weight fraction of amorphous phase reaches 50 wt%. Likewise, the error is related with the weight fraction of standard phase present in sample and dosage of internal standard. The conditions for high quantitative accuracy of original equation are strictly satisfied with a lower amount of SPS phase, less than 2 wt%, and a higher dosage of internal standard, larger than 20 wt%. For example, if the weight percentage of SPS phase is set as 2 wt%, the absolute and relative

errors are as high as 8% and 39%, respectively, when the amorphous content and dosage of internal standard are less than 20%.

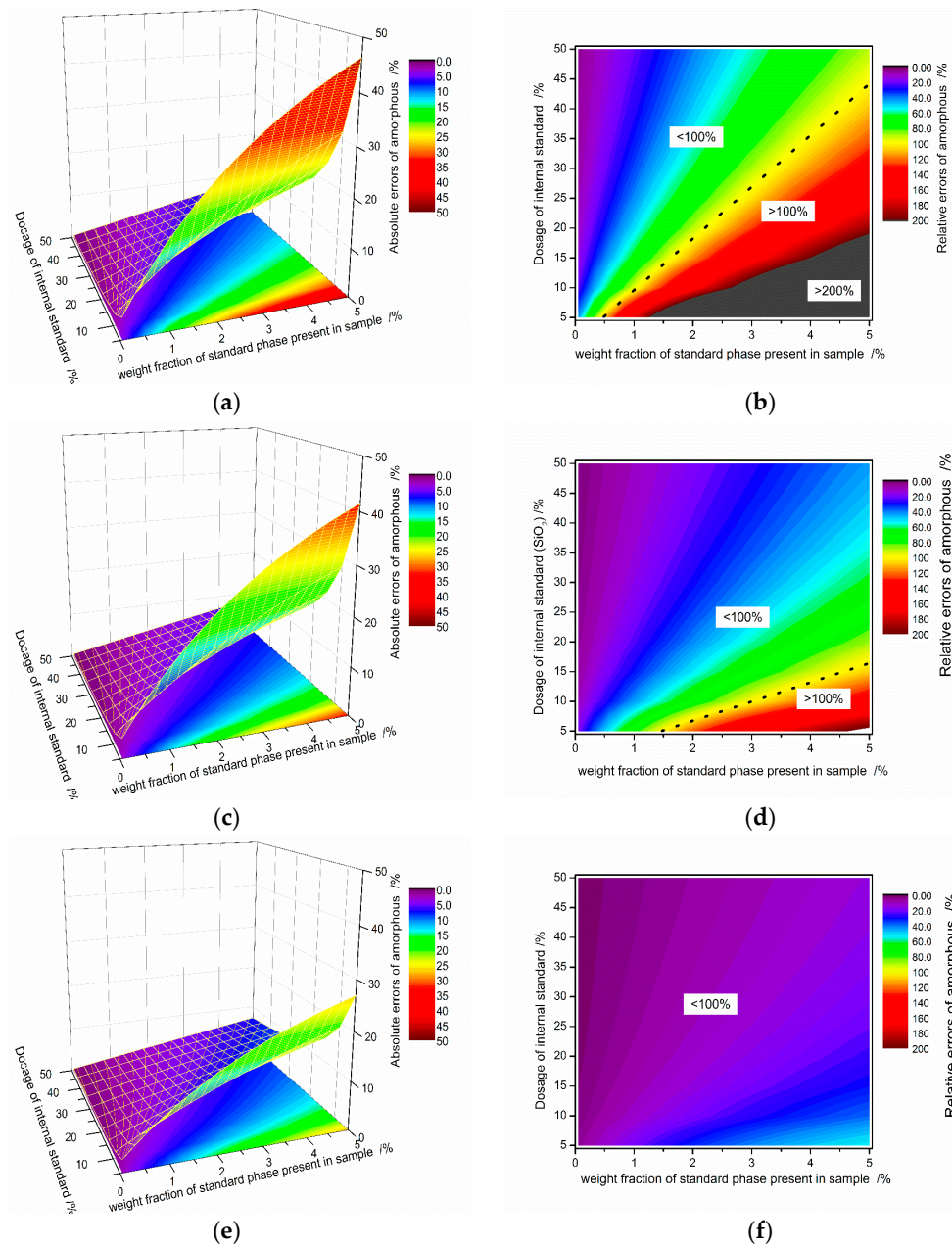


Figure 4. Absolute and relative errors analysis of amorphous phase. (a,c,e): the absolute error distribution in which the content of amorphous phase is assumed to be 10%, 20%, and 50%, respectively; (b,d,f) The corresponding 2D relative errors patterns of (a,c,e), respectively.

For the above quantitative errors reduction, the corrected equation for amorphous phase can be finally proposed as Equation (11), with the intermediate derivation process shown in the supplementary materials.

$$W_{Amor}^+ = 100 - \frac{W_{St}(R_{St} - 100)}{(R_X^+ - R_{St})(100 - W_{St})} \times 10^2 \quad (11)$$

where R_{St} and R_X^+ stand for the Rietveld quantitative result of internal standard and the standard phase present in sample.

4. Conclusions

For Bragg-Brentano diffraction, the ignorance of the amorphous or non-quantified crystalline phases (ACn) in standard exerts significant effect on the quantitative accuracy by the Rietveld-internal standard method. The error level is only related to the crystallinity of internal standard (α) and weight percentage of amorphous phase in original sample (β), and the equations of absolute/relative errors (Δ_{AE}/Δ_{RE}) are derived as proposed. The numerical simulation analysis reveals the original equation is not applicable in most of the cases and the corresponding error-accepted zone is suggested from the relationship between α and β . When the preparatory conditions are set as ' $\Delta_{AE} \leq 10\% \cap \Delta_{RE} \leq 50\%$ ', then the error-accepted zone can be expressed as ' $\alpha \geq 10\beta/(1 + 10\beta)$ ', ' $\beta \in (0.80\%)$ ' and ' $\alpha \geq 2\beta/(1 + \beta)$ ', ' $\beta \in (80\%, 100\%)$ '. For the above quantitative error elimination, the equation for ACn has been improved as proposed.

Based upon Bragg-Brentano diffraction, the ignorance of minor SPS phase in original sample also has significant effect on the quantitative accuracy by the Rietveld-internal standard method. The effect is evaluated from absolute/relative errors (Δ_{AE}/Δ_{RE}) analysis with error-equations derived as proposed. The numerical simulation analysis reveals that the quantitative error has a positive relationship with the content of the SPS phase (W_X^+) and negative relationship with internal standard (W_{St}). The error becomes more sensitive with smaller of W_{St} or larger of W_X^+ . The error-zone demonstrates that original ACn equation is inapplicable ($\Delta_{AE} > 7.8\%$, $\Delta_{RE} > 38.9\%$) under the condition of higher content of SPS phase ($W_X^+ > 2\text{wt}\%$), while the internal standard is under 20 wt%. The improved equation for such quantitative error elimination is suggested.

Supplementary Materials: The following are available online at www.mdpi.com/2073-4352/8/3/110/s1. Part S1: the intermediate derivation process of Equation (4), Part S2: the intermediate derivation process of Equations (9) and (10), Part S3: the intermediate derivation process of Equation (11).

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