

The effect of reference material crystallinity on absolute quantitative phase analysis using the internal standard method

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Equations are given which allow an analyst to obtain a correct absolute quantitative phase analysis via the internal standard method when a reference material with a known crystallinity of less than 100% is used. Comparisons are made with previous equations, and a numerical example is given.

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I. INTRODUCTION

Quantitative phase analysis from powder diffraction data is nearly as old as powder diffraction itself (Madsen et al., 2019). There are many methods by which diffraction data can be quantified, including single peaks, groups of peaks, whole-pattern modeling, and whole-pattern summation. For a detailed review, see Madsen et al. (2019) and references therein.

The most popular quantification methods (Madsen et al., 2001; Raven and Self, 2017) are the Rietveld method (Loopstra and Rietveld, 1969; Rietveld, 1969) coupled with the Hill–Howard algorithm (Hill and Howard, 1987) and the reference intensity ratio (RIR) method (Hubbard and Snyder, 1988). Other quantitative algorithms have been given by Bish and Chipera (1987), Toraya (2016), and Li et al. (2022). These methods all provide relative weight fractions. That is, the amounts of the crystalline phases reported by these methods are correct relative to each other but may not be correct in an absolute sense due to the presence of amorphous or unanalyzed phases. In order to place these values on an absolute scale, an internal standard can be used, whereby the known addition (Westphal et al., 2009) of a well-characterized reference material to the sample of interest is used to normalize the relative weight fractions.

In applying this normalization, the crystallinity of the reference material is paramount. The established methodologies assume that the reference material is 100% crystalline, although this is rarely the case. Deviations from this assumption will cause significant biases in quantitative phase analyses using such a reference material. Here, equations are given that allow for the correct normalization when using a reference material with a known crystallinity of less than 100%. Although the Hill–Howard algorithm and the RIR method are used as exemplars, the equations are generally applicable to any methodology that produces relative weight fractions.

II. CALCULATION OF ABSOLUTE WEIGHT FRACTIONS

The relative weight fraction, w^r , of a phase α , in a diffraction pattern, can be calculated, for instance, using the Hill–Howard algorithm or the RIR method as follows:

$$w_{\alpha}^r = \frac{(sMV)_{\alpha}}{\sum_j (sMV)_j} \quad (1)$$

or

$$w_{\alpha}^r = \frac{I_{\alpha}^i / \text{RIR}_{\alpha,c}}{\sum_j [I_j^i / \text{RIR}_{j,c}]} \quad (2)$$

respectively, where s is the Rietveld scale factor as defined in Hill and Howard (1987), M is the unit cell mass, and V is the unit cell volume. I_{α}^i is the intensity of some peak, or group of peaks, i , of phase α , and $\text{RIR}_{\alpha,c}$ is the reference intensity ratio of phase α taken with respect to some well-characterized calibration phase, c . The summation in each case is taken over all j phases present in the specimen. All weight fractions are in the range (0.0, 1.0] and $\sum_{j=1}^n w_j^r = 1$.

A. 100% crystalline reference material

As given previously in the literature (Madsen et al., 2019), the reference material is assumed to be 100% crystalline, and so the absolute weight fractions, w^a , of the crystalline phases and amorphous fraction in the specimen containing the internal standard are given as follows:

$$w_{\alpha}^a = w_{\alpha}^r \frac{w_s^k}{w_s^r} \quad (3)$$

$$\begin{aligned} w_{\text{amor}}^a &= 1 - \sum_j w_j^a \\ &= 1 - \frac{w_s^k}{w_s^r} \end{aligned} \quad (4)$$

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where w_s^k is the known, weighed, addition of the reference material expressed as a weight fraction, and w_s^r is the relative weight fraction of the reference material as determined by the analysis. w_s^r must always be greater than w_s^k ; otherwise, a physically meaningless, negative amorphous weight fraction will be calculated.

The absolute weight fractions of the phases present in the original specimen, w^o , prior to the addition of the reference material are the values often of most interest. These values can be calculated by normalizing the previously calculated absolute fractions by removing the reference material, as shown in the following equations:

$$w_\alpha^o = \frac{w_\alpha^a}{1 - w_s^k} \quad (5)$$

$$\begin{aligned} w_{\text{amor}}^o &= \frac{w_{\text{amor}}^a}{1 - w_s^k} \\ &= \frac{w_s^r - w_s^k}{w_s^r(1 - w_s^k)} \end{aligned} \quad (6)$$

B. Less than 100% crystalline reference material

Allowing for a reference material that is not 100% crystalline involves incorporating an additional variable for the degree of crystallinity. This value must either be taken from the material's certification, or be determined by using a certified reference material, such as NIST SRM676a (Cline et al., 2011), to calibrate the reference material used in the measurement by either the internal standard method as described here, or by the external standard method (O'Connor and Raven, 1988).

In this instance, the absolute weight fractions, W^a , of the phases and amorphous fraction in the specimen containing the less than 100% crystalline internal standard are given as follows:

$$W_\alpha^a = w_\alpha^r \frac{w_s^k X_s}{w_s^r} \quad (7)$$

$$\begin{aligned} W_{\text{amor}}^a &= 1 - \sum_j W_j^a \\ &= 1 - \frac{w_s^k X_s}{w_s^r} \end{aligned} \quad (8)$$

where X_s is the crystalline fraction of the reference material and is in the range (0.0, 1.0]. The product $w_s^k X_s$ represents the crystalline weight fraction of the reference material added to the specimen.

The absolute original weight fractions, W^o , of the phases and amorphous fraction, are given as follows:

$$W_\alpha^o = \frac{W_\alpha^a}{1 - w_s^k} \quad (9)$$

$$\begin{aligned} W_{\text{amor}}^o &= \frac{W_{\text{amor}}^a - w_s^k(1 - X_s)}{1 - w_s^k} \\ &= 1 - \frac{w_s^k X_s(1 - w_s^r)}{w_s^r(1 - w_s^k)} \end{aligned} \quad (10)$$

The term $w_s^k(1 - X_s)$ represents the amorphous fraction of the reference material. The equation for the amorphous fraction in the original specimen can be described as the difference between the amorphous fraction of the original specimen + reference material and the reference material, all normalized to the phase content of the original specimen. This equation is equivalent to one mentioned briefly by Cline et al. (2011).

III. EXAMPLE CALCULATION

Imagine a three-phase sample and a 90% crystalline reference material – see Table I. The sample consists of 50 wt% phase A, 30 wt% phase B, and a 20 wt% amorphous fraction, denoted as phase C. About 33.3 wt% of the reference material is added to this sample as an internal standard, that is, 1 g of reference material is mixed with 2 g of sample. This information forms the ground truth columns as shown in Table I. The relative weight fractions [Eqs (1) and (2)], which would be determined during data analysis, are calculated from the crystalline fractions of the original sample containing the reference material. These relative weight fractions, combined with the known addition of reference material, are used to determine the weight fractions in the original specimen.

If the analyst assumes that the added reference material is 100% crystalline, then the calculations would use Eqs (3)–(6). The final values from these calculations are given in Table I and should be equivalent to the original ground truth. The biases in these values should be evident, especially in the

TABLE I. The various weight fractions, known and calculated, when adding a reference material as an internal standard to quantify the phases present in an unknown specimen.

Phase	Ground truth		Relative	Assume 100% crystalline Original [Eqs (5) and (6)]	Known crystallinity Original [Eqs (9) and (10)]
	Original	Original + RM			
A	0.5	0.333	0.400	0.556	0.500
B	0.3	0.200	0.240	0.333	0.300
C (Amorphous)	0.2	0.133	–	0.111	0.200
RM cryst.	–	0.300	0.360	–	–
RM amor.	–	0.033	–	–	–
Total cryst.	0.8	0.833	1.000	0.889	0.800
Total amor.	0.2	0.167	0.000	0.111	0.200

Here, 33.3 wt% of a 90% crystalline reference material is added to a three-phase sample. The known original and calculated relative weight fractions are compared with the calculations of using both the 100% crystalline and the known reference material crystallinity equations.

RM, reference material; Cryst., crystalline fraction; Amor., amorphous fraction.

amorphous value, which is affected cumulatively by all crystalline phases present.

If the analyst knows the crystallinity of the added reference material, then the calculations would use Eqs (7)–(10); the resultant values of which are given in the final columns of Table I. These values are clear of bias, leaving the analyst free to minimize other potential issues that may bias quantification, such as preferred orientation and microabsorption (Madsen et al., 2001; Scarlett et al., 2002).

IV. CONCLUSION

Equations for the calculation of absolute quantitative phase analysis by the internal standard method where the reference material used is not 100% crystalline have been introduced. Inspection of Table I shows the biases introduced when the incorrect equations are used in calculating absolute phase quantification if using a reference material of less than 100% crystallinity as an internal standard. The application of the correct equations [Eqs (7)–(10)] removes this bias in the calculated values, allowing for a more accurate quantification.

Conflicts of Interests

Matthew Rowles is employed by Microanalysis Australia to, in part, undertake quantitative phases analysis of diffraction data.

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