3. METHODOLOGY

measurement conditions. This greatly simplifies the relationship between reflection intensity and weight fraction to

$$I_{i\alpha} = C_{i\alpha} \frac{W_\alpha}{\mu_m^*}. \qquad (3.9.2)$$

On rearrangement, the weight fraction can be derived from

$$W_\alpha = \frac{I_{i\alpha} \mu_m^*}{C_{i\alpha}}. \qquad (3.9.3)$$

Application of equation (3.9.3) (Klug & Alexander, 1974), referred to as the absorption–diffraction method, requires:
(1) the determination of $C_{i\alpha}$ using a rearranged equation (3.9.3) by (i) the preparation of standards with known additions W of phase α_α, (ii) measurement of peak intensity $I_{i\alpha}$ for the standards, and (iii) estimation of the standard sample mass absorption coefficient μ_m^*;
(2) measurement of $I_{i\alpha}$ and estimation of μ_m^* for the unknown samples; and
(3) calculation of W_α *via* equation (3.9.3).

The value of μ_m^* can be estimated by direct measurement of the beam intensity through a sample of known thickness t in a beam of the same wavelength as that used in the XRD data collection. Following measurement of the beam intensity with the sample in (I) and removed from (I_0) the beam, μ_m^* can be calculated using

$$\frac{I}{I_0} = \exp(-\mu_m^* \rho_m t). \qquad (3.9.4)$$

However, this usually involves (i) the preparation of an additional, thinner, sample for presentation to the X-ray beam, (ii) in some cases, the addition of a diluent with a low mass absorption coefficient to produce I/I_0 ratios in a range where reasonable accuracy can be achieved, and (iii) knowledge of the 'mass thickness' $\rho_m t$. It should also be noted that there are few commercially available instruments that would be suitable for such measurements due to safety-related issues in accessing the X-ray beam path.

An alternative approach is to calculate μ_m^* from the sum of the products of the theoretical mass absorption coefficient (μ_j^*) of each element (or phase) and the weight fractions (W_j) of all n elements (or phases) in the sample. The elemental composition may be determined, for example, by X-ray fluorescence (XRF) measurement and its use is more accurate than the use of phase composition as it takes into account any amorphous material not represented by peaks in the diffraction pattern but which still contributes to μ_m^*,

$$\mu_m^* = \sum_{j=1}^n \mu_j^* W_j. \qquad (3.9.5)$$

3.9.3.2. *Internal standard method*

A more general, and experimentally simpler, approach is to eliminate μ_m^* from the analysis altogether *via* the inclusion of an internal standard s in known weight fraction W_s. Substitution of the measured intensity of the jth peak (or group of peaks) of the standard phase, I_{js}, into equation (3.9.2) yields

$$I_{js} = C_{js} \frac{W_s}{\mu_m^*}. \qquad (3.9.6)$$

The ratio of equations (3.9.2) and (3.9.6) gives

$$\frac{I_{i\alpha}}{I_{js}} = \frac{C_{i\alpha}}{C_{js}} \frac{W_\alpha}{W_s}. \qquad (3.9.7)$$

Since μ_m^* now appears both in the numerator and denominator, its effect on the analysis, and hence the need to measure or calculate it, is removed from the calculation. Rearrangement of equation (3.9.7) yields

$$\frac{I_{i\alpha}}{I_{js}} \frac{W_s}{W_\alpha} = \frac{C_{i\alpha}}{C_{js}} = C_{js}^{i\alpha}, \qquad (3.9.8)$$

where $C_{js}^{i\alpha}$ is a calibration constant specific to the phase and internal standard used. Once $C_{js}^{i\alpha}$ has been determined, the weight fraction of the unknown, W_α, can then be determined from

$$W_\alpha = \frac{W_s}{C_{\alpha s}^{ij}} \frac{I_{i\alpha}}{I_{js}}. \qquad (3.9.9)$$

This approach, referred to as the *internal standard method*, relies on the determination of $C_{\alpha s}^{ij}$ using known mixtures of standard and analyte phases. The value of $C_{\alpha s}^{ij}$ will be specific to the diffraction peaks used in its determination; if other lines are used in subsequent analysis, then an appropriate value of C will have to be redetermined.

It should be noted that the presence of systematic errors (such as preferred orientation and microabsorption) that influence the measurement of intensity and vary as a function of W_α will not be detected through application of equation (3.9.9). The use of consistent sample-preparation and presentation techniques is required to minimize the effect of these aberrations on the analysis (Zevin & Kimmel, 1995).

3.9.3.2.1. *Selection of an internal standard*

The selection of an appropriate material for use as an internal standard for QPA is not always straightforward. Ideally, the material selected should:
(1) Have a simple diffraction pattern resulting in minimal overlap with peaks of interest in the sample.
(2) Have a mass absorption coefficient similar to that of the sample to avoid introducing microabsorption effects and thus reducing accuracy.
(3) Have minimal sample-related aberrations that may affect observed intensities. For example, it should be fine-grained to ensure minimal grain-size effects on the observed intensities and not be subject to preferred orientation. Importantly, it should have 100% (or known) crystallinity.
(4) Be stable over an extended time and be unreactive, especially for *in situ* studies where it may be subjected to extreme conditions.

Some possibilities for use as internal standard include α-Al_2O_3 (corundum), TiO_2 (rutile), ZnO (zincite), Cr_2O_3 (eskolaite), α-Fe_2O_3 (haematite), CeO_2 (cerianite), CaF_2 (fluorite) and C (diamond). Cline *et al.* (2011) have described the certification of the standard reference material SRM 676a with accurately known amorphous content for use as an internal standard for QPA (see Chapter 3.1). Alternatively, it is possible to use an independent measure (*e.g.* chemical analysis) to derive the concentration of a phase already present in the sample and then to designate it as the internal standard.

Selection of the amount of internal standard to add is often based on folklore or local practices with reported additions ranging from 5 to 50 wt%. Westphal *et al.* (2009) have described the mathematical basis for selecting the optimal internal standard addition in the context of amorphous phase determination. The

amount of internal standard added has a strong influence on the precision of the determination of amorphous content and 'a poor choice can make determination impossible, while a clever choice can enhance the precision'.

With the exception of diamond, all of the phases listed above tend to have absorption coefficients that are too high for use with organic materials. The development and verification of a suitable low-absorption-coefficient standard material that meets the criteria given above remains an important area of research.

3.9.3.3. *Reference intensity ratio methods*

The reference intensity ratio (RIR) (Hubbard *et al.*, 1976; Hubbard & Snyder, 1988) is an instrument-independent phase constant developed specifically for use in quantitative phase analysis and is defined as the ratio of strongest peak of phase α to the strongest peak of standard s. The RIR can be derived directly from equation (3.9.8):

$$\text{RIR}_{\alpha s} = C_{js}^{i\alpha} = \frac{I_{i\alpha}}{I_{js}}\frac{W_s}{W_\alpha}. \tag{3.9.10}$$

In some cases, the strongest lines of either the standard or phase of interest may not be accessible for measurement if, for example, they strongly overlap with peaks from another phase or if they are out of the 2θ range considered. Equation (3.9.10) can be generalized (Hubbard & Snyder, 1988) to use less intense peaks while keeping the same value of RIR:

$$\frac{I_{i\alpha}}{I_{js}}\frac{I_{js}^{\text{rel}}}{I_{i\alpha}^{\text{rel}}}\frac{W_s}{W_\alpha} = \text{RIR}_{\alpha s}, \tag{3.9.11}$$

where I^{rel} is the ratio of the intensity of the peak used for analysis to the most intense peak for the phase. $\text{RIR}_{\alpha,s}$ is now the generalized reference intensity ratio for phase α with respect to standard s.

Quantification of the unknown phase in the presence of a known standard addition can be achieved by the rearrangement of equation (3.9.11):

$$W_\alpha = \frac{I_{i\alpha}}{I_{js}}\frac{I_{js}^{\text{rel}}}{I_{i\alpha}^{\text{rel}}}\frac{W_s}{\text{RIR}_{\alpha s}}. \tag{3.9.12}$$

The generally accepted reference material for QPA *via* the RIR method is corundum because of its relatively simple diffraction pattern, stability and availability as a highly crystalline and pure single phase. If corundum is used, the RIR equates to I/I_c (or 'I over I corundum') for the phase; these are the most commonly reported values in the literature.

RIRs can be determined either by (i) calculation using published crystal-structure information with Rietveld analysis software set to pattern-calculation mode, or (ii) direct measurement by taking the ratio of the strongest peak of the pattern to the intensity of the strongest peak of corundum in a 50/50 weight mixture [or through use of equation (3.9.11) for non-equal proportions]. However, for some phases, there can be ambiguity about which peak is the most intense. For example, the 104 (2.551 Å) and 113 (2.085 Å) peaks of corundum have very similar observed intensities, as do the 111 (3.154 Å) and 022 (1.932 Å) peaks of fluorite. This may lead the analyst to select a peak different from that chosen for reported RIR values.

Collated lists of RIR values for frequently encountered phases can be found in the ICDD database (Fawcett *et al.*, 2017) and Smith *et al.* (1987). It is important to note, however, that the user must be very careful when selecting an appropriate RIR value for

their particular experiment. The values of RIR will depend upon the data-collection and measurement strategy employed (for example, peak height, integrated peak area, whole pattern, X-ray wavelength employed and so on) in their derivation. This must match the conditions used in the experiment to which the value is to be applied. In general, RIR values should be determined for the material currently being studied using the methodologies employed rather than relying on published values. Greater accuracy will be achieved if the relative intensities are determined as part of the calibration process using pure samples of the phase and standard or, preferably, samples in which the phases of interest have high and known concentration. If published values of RIR are used, then the determined phase abundances must be referred to as being only semi-quantitative.

3.9.3.4. *Matrix-flushing method*

An important feature of RIR-based techniques is that, once the RIRs are determined for the analyte phases of interest, the standard phase does not need to be present in the sample. The effect of the sample mass absorption coefficient is also removed by taking the ratio of the intensity of phase α to another unknown phase β. Hence the ratio of the weight fractions of the two phases can be derived from

$$\frac{W_\alpha}{W_\beta} = \frac{I_{i\alpha}}{I_{j\beta}}\frac{I_{j\beta}^{\text{rel}}}{I_{i\alpha}^{\text{rel}}}\frac{\text{RIR}_{\beta s}}{\text{RIR}_{\alpha s}}. \tag{3.9.13}$$

For a system comprising n phases, equation (3.9.13) allows the derivation of $n - 1$ weight fraction ratios. Chung (1974*a*,*b*) has demonstrated that, if all components are crystalline and included in the analysis, an additional constraint of the following form can be included:

$$\sum_{k=1}^{n} W_k = 1.0. \tag{3.9.14}$$

This forms a system of n linear equations which can be solved to give the weight fractions of all components in the analysis according to (Chung, 1974*a*,*b*; Snyder & Bish, 1989)

$$W_\alpha = \frac{I_\alpha}{\text{RIR}_{\alpha s}I_\alpha^{\text{rel}}}\left(\sum_{k=1}^{n}\frac{I_k}{\text{RIR}_{ks}I_k^{\text{rel}}}\right)^{-1}. \tag{3.9.15}$$

The weight fractions analysed *via* this method are correct relative to each other but may not be correct in an absolute sense if unidentified or amorphous materials are present in the sample. In this case, the reported phase abundances will be overestimated. The addition of an internal standard to the system, or knowledge of the amount of a component phase determined by another technique, allows calculation of the absolute amount $W_{\alpha(\text{abs})}$ of each phase [equation (3.9.16)] and thus the derivation of the amount W_{unk} of unknown (amorphous and/or unidentified) components [equation (3.9.17)].

$$W_{\alpha(\text{abs})} = W_\alpha \times \frac{W_{\text{std(known)}}}{W_{\text{std(meas)}}}, \tag{3.9.16}$$

$$W_{\text{unk}} = 1.0 - \sum_{k=1}^{n} W_{k(\text{abs})}, \tag{3.9.17}$$

where $W_{\alpha(\text{abs})}$ is the absolute weight fraction of phase α, $W_{\text{std(known)}}$ is the known weight fraction of the standard added to the sample, $W_{\text{std(meas)}}$ is the weight fraction of the standard