3.9. QUANTITATIVE PHASE ANALYSIS

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):

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

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:

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

where I^{rel} is the ratio of the intensity of the peak used for analysis to the most intense peak for the phase. $\mathrm{RIR}_{\alpha,s}$ 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):

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

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

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

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)

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

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 $W_{\alpha(\mathrm{abs})}$ 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)].

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

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

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

references