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):

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

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 (1974a,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, 1974a,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

reported by equation (3.9.15) and W_{unk} is the weight fraction of the unidentified and/or amorphous component in the mixture.

If an internal standard has been used, then initial calculation of its concentration *via* equation (3.9.15) may be:
  (i) the same as the weighed amount, indicating that there are unlikely to be amorphous or unidentified phases present;
 (ii) greater than the weighed amount, indicating that amorphous or unidentified phases may be present; or
(iii) less than the weighed amount, indicating operator error or the use of invalid RIR or I^{rel} values.

3.9.3.5. *Full-pattern fitting methods*

The quantitative XRD techniques described above have traditionally been applied using phase intensity estimates derived from either single peaks or a small group of peaks. This approach can be effective when there is minimal peak overlap but becomes less useful in complex phase systems where it may be difficult to identify freestanding peaks in the pattern. In addition, the presence of sample-related effects such as preferred orientation skew the measured intensities from what would be expected from an ideal powder diffraction pattern, thus reducing the expected accuracy.

Some of these effects can be partially overcome by using full-pattern fitting methods (Smith *et al.*, 1987; Batchelder & Cressey, 1998; Chipera & Bish, 2002, 2013; Eberl, 2003; Toraya & Tsusaka, 1995; Cressey & Schofield, 1996), where wide-range diffraction patterns of phases of interest are scaled, summed and compared with the observed diffraction data in a least-squares minimization process. The method relies on the generation of a library of standard patterns for each phase expected in the analysis collected under the same instrumental conditions as those used in subsequent analyses. The selection of standards that are a good match for the phases in the unknown sample is a critically important step. While the library will normally contain patterns of well ordered phases, it can also include patterns for less well ordered material such as glasses, polymers, clay minerals and gels, thus allowing their direct quantification. Where it is not possible to obtain a measured pattern, calculated patterns may also be included in the library.

Weight fractions are obtained by the solution of simultaneous equations that take into account the scale factors of the individual components and the mass absorption coefficients derived from knowledge of the elemental composition of each phase.

Alternatively, the contribution of library patterns to observed data can be normalized by scaling phases to an internal standard, typically corundum, using an RIR approach. Given the compositional and structural variability of some phases, especially in mineralogical applications, RIRs measured using the same minerals as those to be analysed are preferred to reported RIRs. Toraya (Toraya 2016*a*,*b*) has devised a QPA method which uses observed integrated peaks intensities measured of a wide 2θ range. Phase calibration constants are calculated using only their chemical formula weight and the sum of the square of the number of electrons in the formula unit. While the method is effective for wide-range data, it cannot be applied to single-peak data or data that cover only a limited 2θ range.

The full-pattern fitting method is relatively easy to use and can be applied to difficult samples containing highly disordered materials. For some disordered phases where no crystal structure is available and where peak overlap means that individual peak intensities cannot be measured, full-pattern fitting may be the most appropriate approach to QPA. The major limitations of the method include the need (i) to define and subtract the pattern background, with a subsequent impact on QPA, and (ii) to obtain or generate a library of standard patterns of the phases of interest. The use of an internal standard is recommended and the method is best applied when all standard patterns have first been normalized to an internal standard intensity (Chipera & Bish, 2002, 2013).

3.9.3.6. *Rietveld-based QPA*

The advent of the Rietveld method (Rietveld, 1969) and its extension into the field of QPA (Bish & Howard, 1988; Hill, 1983; Hill & Howard, 1987; O'Connor & Raven, 1988; Taylor, 1991) has brought some significant benefits when compared with the conventional single-peak and pattern-addition methods. Recent surveys (Madsen *et al.*, 2001; Scarlett *et al.*, 2002) show that the majority of participants, greater than 75%, use a Rietveld-based approach for QPA. The benefits derive from (Hill, 1991; Kaduk, 2000):
  (i) The use of the entire diffraction pattern. Depending on the 2θ range of the data and the crystallography of the component phases, this may involve hundreds or thousands of reflections rather than the few peaks in conventional methods. This helps to minimize the impact of some systematic sample-related effects such as preferred orientation and extinction.
 (ii) The ability to accurately deconvolute overlapping peaks to extract the component intensities, thus allowing more complex patterns to be analysed. The development of fundamental-parameters models (Bergmann *et al.*, 1998, 2000; Cheary & Coelho, 1992; Cheary *et al.*, 2004), which aim to distinguish instrument from sample contributions to the diffraction pattern, minimizes the number of profile parameters that need to be refined, further enhancing this profile-fitting step.
(iii) Refinement of the crystal structure, when supported by the data, to minimize differences between the intensities in the calculated and observed patterns. This brings additional information such as systematic changes in structure parameters from published data.
(iv) The ability to model some remaining systematic effects such as preferred orientation or anisotropic crystallite size/strain peak broadening.

The Rietveld method uses a least-squares procedure to minimize the difference between a calculated pattern and the measured data. The calculated pattern is derived from a model containing crystal-structure information for each phase included in the analysis, convoluted with expressions describing peak shape and width, along with functions to correct systematic variances such as preferred orientation. The calculated pattern is multiplied by an overall scaling factor which may be equated to the peak intensities ($I_{i\alpha}$) considered by the single-peak methods. The Rietveld scale factor for phase α, S_α, can be defined as (Bish & Howard, 1988; Hill, 1991; Hill & Howard, 1987; O'Connor & Raven, 1988)

$$S_\alpha = \left[\frac{K}{V_\alpha^2}\right]\left[\frac{W_\alpha}{\rho_\alpha}\right]\frac{1}{2\mu_m^*}, \qquad (3.9.18)$$

where K is an 'experiment constant' used to put W_α on an absolute basis, and V_α, W_α and ρ_α are the volume of the unit cell, the weight fraction and the density for phase α, respectively.

Since equation (3.9.18) inherently contains the weight-fraction information, it can be rearranged to derive W_α:

references