

3.9. QUANTITATIVE PHASE ANALYSIS

- (1) *Indirect methods* – these are usually based on the measurement of total chemical composition, which is then apportioned according to an assumed composition for each phase. A very widely used form of this normative calculation approach is the Bogue method (Bogue, 1929) for the quantitative estimation of Portland cement phases. The limitations in this approach arise when the actual compositions of individual phases vary from those assumed in the calculation. This frequently occurs in the cement industry, where variance in local materials and production conditions can affect detailed phase compositions. Normative calculation has the potential to be unstable when a number of phases in the mixture have similar chemical composition and it cannot be used at all for the limiting case of polymorphs that have identical chemical composition.
- (2) *Direct methods* – these are based on a property that is specific to phases of interest in the sample. These methods are often not generally applicable to the entire sample, but are useful in estimating abundances of selected components. Examples include:
- (a) *Magnetic susceptibility* – this is applicable to samples in which component phases have different magnetic properties. The magnetic component can be separated and weighed to determine its weight fraction in the starting material. This approach assumes that the magnetic phase is well separated from non-magnetic phases and accuracy will be reduced when there is a fine inseparable intergrowth of magnetic and non-magnetic components.
- (b) *Selective dissolution* – where the rate and extent of dissolution can be phase dependent, and the weight fraction of the residue is used to determine the fractions of soluble and insoluble components.
- (c) *Density* – involves the physical separation of phases with different densities. As with magnetic separation, this approach assumes that the phase of interest is well separated from other phases.
- (d) *Image analysis* – optical microscopy using thin sections is still frequently used for the analysis of mineralogical samples. Thin sections can be time consuming to prepare and analyse, and the observations can be highly subjective depending on the analyst's experience. While automated image analysis of optical and electron-beam images brings more consistency to the estimation of phase abundance, issues in stereology may still affect the determined phase abundances.
- (e) *Thermal analysis* – where the magnitude of endo- and exothermic features during phase transitions are proportional to the amount of the phases present. This can be effective for well known and characterized phases, but is less useful for new phases or complex multiphase samples where there may be significant overlap in the features in the observed patterns. There may also be difficulty in distinguishing features related to individual minerals, for example H₂O evolution from co-existing hydrated minerals.
- (f) *Infrared (IR) techniques* – these are gaining in popularity, especially in mineral exploration environments because of their portability, speed and ability to measure directly from a cleaned drill core or section. However, because the IR beam only penetrates 1–2 μm into the sample, it is a surface-analysis technique providing a semi-quantitative analysis at best. To work effectively, the

method needs to be calibrated using other techniques such as diffraction-based phase analysis.

- (g) *Powder diffraction* may be included in the direct-methods category, as it distinguishes and quantifies phases on the basis of their unique crystal structures, giving the technique broad applicability for crystalline materials.

Quantification from powder diffraction data is reliant on determination of the contribution to the final pattern of each component phase in a mixture. Commonly used methods can be divided into two distinct groups:

- (1) The traditional 'single-peak' methods, which rely on the measurement of the intensity of a peak, or group of peaks, for each phase of interest and assumes that the intensity of these peaks is representative of the abundance of the individual phases. This is often not the case because of peak overlap and phase-dependent factors, such as preferred orientation and microabsorption, which affect the relative observed intensities.
- (2) *Whole-pattern methods*, which rely on the comparison of observed diffraction data over a wide range of 2θ with a calculated pattern formed from the summation of individual phase components which have either been (i) measured from pure phase samples, or (ii) calculated from crystal-structure information.

3.9.3. QPA methodology

The integrated intensity $I_{(hkl)\alpha}$ of reflection hkl for phase α in a multiphase mixture, measured on a flat-plate sample of infinite thickness using a diffractometer with Bragg–Brentano geometry, is given by (Snyder & Bish, 1989; Zevin & Kimmel, 1995; Madsen *et al.*, 2013)

$$I_{(hkl)\alpha} = \left[\frac{I_0 \lambda^3 e^4}{32\pi r m_e^2 c^4} \right] \times \left[\frac{M_{hkl}}{2V_\alpha^2} |F_{(hkl)\alpha}|^2 \left(\frac{1 + \cos^2 2\theta \cos^2 2\theta_m}{\sin^2 \theta \cos \theta} \right) \exp(-2B(\sin \theta / \lambda)^2) \right] \times \left[\frac{W_\alpha}{\rho_\alpha \mu_m^*} \right], \quad (3.9.1)$$

where I_0 is the incident-beam intensity, λ is the wavelength, e is the charge on an electron, m_e is the mass of an electron, r is the distance from the scattering electron to the detector and c is the speed of light. M_{hkl} and F_{hkl} are the multiplicity and structure factor of the hkl reflection, respectively, V_α is the unit-cell volume of phase α , and θ and θ_m are the diffraction angles for the hkl reflection and the monochromator (if present), respectively. B is the mean atomic displacement parameter (ADP). W_α and ρ_α are the weight fraction and density of phase α respectively, while μ_m^* is the mass absorption coefficient of the entire sample.

3.9.3.1. Absorption–diffraction method

The various terms in equation (3.9.1) are related to the (i) instrument configuration (first set of square brackets), (ii) crystal-structure-related parameters for reflection hkl of phase α (second set of square brackets), and (iii) phase-specific and whole-sample parameters including the weight fraction W_α for phase α (last set of square brackets).

The instrument-related and phase-dependent parameters, including phase density, can be grouped together and defined as a constant $C_{i\alpha}$ for the i th reflection of phase α for a specific set of

3. METHODOLOGY

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

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

On rearrangement, the weight fraction can be derived from

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

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 , (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

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

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^* ,

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

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 j th peak (or group of peaks) of the standard phase, I_{js} , into equation (3.9.2) yields

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

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

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

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

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

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

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

This approach, referred to as the *internal standard method*, relies on the determination of C_{js}^{α} using known mixtures of standard and analyte phases. The value of C_{js}^{α} 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 -Al₂O₃ (corundum), TiO₂ (rutile), ZnO (zincite), Cr₂O₃ (eskolaite), α -Fe₂O₃ (haematite), CeO₂ (cerianite), CaF₂ (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

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):

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

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:

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

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):

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

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

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

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:

$$\sum_{k=1}^n W_k = 1.0. \quad (3.9.14)$$

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)

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

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)].

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

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

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

3. METHODOLOGY

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 2016a,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)

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

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} :

3.9. QUANTITATIVE PHASE ANALYSIS

$$W_\alpha = \frac{S_\alpha \rho_\alpha V_\alpha^2 \mu_m^*}{K}. \quad (3.9.19)$$

O'Connor & Raven (1988) and Bish & Howard (1988) have shown that K is dependent only on the instrumental conditions and is independent of individual phase and overall sample-related parameters. Therefore a single measurement is sufficient to determine K for a given instrument configuration and set of data-collection conditions. Determination of K may be carried out by (i) a measurement of either a pure phase, or a phase of known proportion in a mixture, separately from the measurement of the actual unknown mixture, or (ii) using a phase that is present in the sample in a known amount. The value of K calculated in this way will be appropriate for the calibration of subsequent measurements as long as all instrumental and data-collection conditions remain the same as those used in its determination.

For each phase, the density ρ_α can be calculated from the published (or refined) crystal-structure information using

$$\rho_\alpha = \frac{ZM_\alpha}{V_\alpha}, \quad (3.9.20)$$

where ZM is the mass of the unit-cell contents (Z is the number of formula units in the unit cell and M is the molecular mass of the formula unit) and V is the unit-cell volume.²

Substitution of equation (3.9.20) in equation (3.9.19) shows that

$$W_\alpha = \frac{S_\alpha (ZMV)_\alpha \mu_m^*}{K}. \quad (3.9.21)$$

In this context, $(ZMV)_\alpha$ is the 'phase constant' and can be calculated from published or refined crystal-structure information alone. It is worth noting that, if the crystal structure is refined as part of the analysis, ZMV is updated and hence becomes a dynamic phase constant.

The methodology embodied in equation (3.9.21) is important in many applications in that it produces, within the limits of experimental error, *absolute phase abundances* and is referred to hereafter as the *external standard* approach. While the use of a phase that already exists within the sample to determine K may be considered as an internal standard approach, in some applications, including *in situ* studies, that phase may be removed from the system through, for example, decomposition or dissolution. However, the value of K remains valid for subsequent determination of phase abundances provided that the instrumental and data-collection conditions do not change.

Equation (3.9.21) is directly applicable to the analysis of those phases for which detailed crystal-structure information is available. For phases where only a partial structure (for example, an indexed unit cell but no atom coordinates or site-occupation factors) is available, an empirical ZMV can be derived using mixtures of the phase of interest with known amounts of a well characterized standard (Scarlett & Madsen, 2006). QPA of phases with partial structure is also possible through the use of equation (3.9.19), but an estimate of the phase density, obtained through direct measurement, is required.

The limitations of the approach embodied in equations (3.9.19) and (3.9.21) derive from the need to (i) conduct a measurement of K and (ii) estimate the value of the mass absorption coefficient μ_m^* for the sample(s) used to determine K , as well as for each

sample of interest. However, similar to the earlier discussion about the single-peak methods, μ_m^* can be determined by direct measurement or calculation using equations (3.9.4) or (3.9.5), respectively. The benefits that can be derived from the extraction of the absolute, rather than relative, phase abundances, make it worth pursuing in many analytical situations. For example, in time-resolved studies where phases transform and material is lost in the course of reaction, the calculation of relative abundances summed to 100% may give a misleading impression of increased amounts of the remaining phases.

In some diffraction instruments, there may be decay in the incident-beam intensity during the course of measurement. This may happen on the timescale of months for a laboratory-based instrument owing to X-ray tube ageing, or on the scale of minutes at a synchrotron instrument where the storage-ring current is only refreshed once or twice per day. In this case, the change in incident intensity can be taken into account by incorporating an additional term into equation (3.9.21):

$$W_{ai} = \frac{S_{ai} (ZMV)_\alpha \mu_m^* I_0}{K I_i}, \quad (3.9.22)$$

where I_0 and I_i are the incident beam intensities present during the determination of K and the collection of data set i , respectively.

The need to measure K , and measure or calculate μ_m^* , serves to increase the overall experimental difficulty and can be eliminated in ways analogous to those used in the single-peak methodology described earlier. For a simple two-phase mixture where both phases, α and β , are 100% crystalline, the sum of their weight fractions W_α and W_β equals unity and can be expressed as (Bish & Howard, 1988)

$$W_\alpha = \frac{W_\alpha}{W_\alpha + W_\beta}. \quad (3.9.23)$$

Substitution of equation (3.9.21) for phases α and β in equation (3.9.23) results in

$$W_\alpha = \frac{S_\alpha (ZMV)_\alpha}{S_\alpha (ZMV)_\alpha + S_\beta (ZMV)_\beta}. \quad (3.9.24)$$

Alternatively, in a multiphase sample, the addition of an internal standard s in known amount W_s and taking the ratio of equation (3.9.21) for analyte and standard phases provides the relationship

$$W_\alpha = W_s \frac{S_\alpha (ZMV)_\alpha}{S_s (ZMV)_s}. \quad (3.9.25)$$

The method embodied in equation (3.9.25) is analogous to the *internal standard* approach in equation (3.9.9) and also serves to produce *absolute phase abundances* $W_{\alpha(\text{abs})}$. Once again, the benefit accruing from the use of absolute phase abundances is the ability to estimate the presence and amount of any amorphous and/or unidentified phases $W_{(\text{unk})}$ through application of equations (3.9.16) and (3.9.17).

Hill & Howard (1987) and Bish & Howard (1988) have adapted the matrix-flushing method of Chung (1974a,b) to the Rietveld analysis context. By constraining the sum of the analysed weight fractions to the assumed concentration of the crystalline components (usually unity), the weight fraction of phase α in an n -phase mixture is given by the relationship³

² When calculating phase density from crystallographic parameters, a factor of $1.6604 = 10^{24}/6.022 \times 10^{23}$ is needed to convert ρ in a.m.u. \AA^{-3} to g cm^{-3} .

³ It should be noted that the implementation of the matrix-flushing method by Bish and Howard retains the use of phase density, but their approach is essentially the same as that of Hill and Howard.

3. METHODOLOGY

$$W_{\alpha} = \frac{S_{\alpha}(ZMV)_{\alpha}}{\sum_{k=1}^n S_k(ZMV)_k} \quad (3.9.26)$$

The use of equation (3.9.26) in QPA again eliminates the need to measure the instrument calibration constant and estimate the sample mass absorption coefficient. However, the necessity of normalizing the sum of the analysed weight fractions to unity only produces the correct *relative phase abundances*. This approach is the most widely used in Rietveld-based QPA and is almost universally coded into Rietveld analysis programs. If the sample contains amorphous phases and/or minor amounts of unidentified crystalline phases, the analysed weight fractions will be overestimated. Where absolute phase abundances are required in, for example, the derivation of reaction mechanisms in *in situ* studies, then one of the methods that produces absolute phase abundances must be used.

3.9.4. Demonstration of methods

The sample 1 suite from the IUCr Commission on Powder Diffraction (CPD) round robin on QPA (Madsen *et al.*, 2001) provides a useful basis for demonstrating the applicability some of the methods described above. Sample 1 was designed to provide a relatively simple analytical system in order to determine the levels of accuracy and precision that could be expected under ideal conditions. The key design criteria required that the phases exhibit little peak overlap in the low-angle region of the diffraction pattern and the samples have at least one freestanding peak for each phase in the d -spacing range 3.7 to 1.9 Å.

The three components (corundum, α -Al₂O₃; fluorite, CaF₂; and zincite, ZnO) were prepared in a ternary design to provide a total of eight different mixtures in order to cover as wide a range of composition as possible for each phase. The result is that each phase is present in the suite with concentrations of approximately 1, 4, 15, 33, 55 and 95 wt%. The exact compositions (Madsen *et al.*, 2001) can be found in Table 3.9.1. The unique chemical composition of the component phases also allowed the weighed compositions to be confirmed by measurement of total elemental composition using X-ray fluorescence (XRF) methods.

Data sets were collected from three replicates of the eight mixtures using a Philips X'Pert diffractometer equipped with a Cu long fine focus tube operated at 40 kV and 40 mA. The beam path was defined with 1° divergence, 0.3 mm receiving and 1° scatter slits. A curved graphite post-diffraction monochromator was fitted to eliminate $K\beta$ radiation. Data were collected from 15 to 145° 2 θ in increments of 0.02° using a counting time of 1.5 s per step. These data sets are available as supporting information from <http://it.iucr.org/> for any reader wishing to develop and test their skills in various methods.

For the single-peak methods, the net intensity for all peaks in the range 22 to 65° 2 θ was extracted using a fundamental-parameters approach to peak fitting coded in the *TOPAS* software package (Bruker AXS, 2013). The choice of peak profile type is important, since any misfit will be reflected in the estimation of peak area and hence in the QPA. Unless otherwise stated, QPA was undertaken using the strongest peak in the pattern for each phase (corundum 113, $d = 2.085$ Å; fluorite 022, $d = 1.932$ Å; zincite 011, $d = 2.476$ Å). The average values for these peaks can be found in Table 3.9.2. For those methods requiring knowledge of the mass absorption coefficient, μ_m^* for each sample was calculated from the XRF chemical analysis results.

Table 3.9.1

Weighed composition (weight fraction) of the eight mixtures comprising sample 1 in the IUCr CPD round robin on QPA (Madsen *et al.*, 2001)

Sample	Corundum	Fluorite	Zincite
1A	0.0115	0.9481	0.0404
1B	0.9431	0.0433	0.0136
1C	0.0504	0.0136	0.9359
1D	0.1353	0.5358	0.3289
1E	0.5512	0.2962	0.1525
1F	0.2706	0.1772	0.5522
1G	0.3137	0.3442	0.3421
1H	0.3512	0.3469	0.3019

Table 3.9.2

Average values ($n = 3$) of net peak intensity derived using profile fitting for the strongest peaks of corundum (113), fluorite (022) and zincite (011)

The figures in parentheses are the standard deviations of the means. The sample mass absorption coefficient μ_m^* was calculated from the XRF-L determined composition.

Sample	Corundum	Fluorite	Zincite	μ_m^* (cm ² g ⁻¹)
1A	34.8 (0.6)	8958.7 (33.0)	509.9 (6.0)	93.02
1B	6561.3 (28.6)	1095.5 (7.1)	474.3 (3.8)	34.45
1C	244.4 (0.9)	250.9 (10.1)	22898.0 (37.0)	49.03
1D	474.5 (3.5)	6559.6 (2.8)	5468.5 (9.5)	71.71
1E	2525.3 (27.9)	4835.5 (27.0)	3370.7 (16.3)	53.17
1F	1251.3 (7.8)	2935.8 (9.0)	12494.9 (22.4)	52.67
1G	1295.0 (8.7)	5041.7 (17.0)	6787.9 (26.6)	59.64
1H	1436.5 (7.3)	5132.0 (13.6)	5996.8 (59.5)	59.10

3.9.4.1. Absorption–diffraction method

In this method, the QPA of each phase is conducted independently of the others. For each phase, the determination of a specific calibration constant, C , was achieved using a rearranged equation (3.9.3). The sample where the relevant phase was present at about 55 wt% (sample 1E for corundum, 1D for fluorite and 1F for zincite) was taken to be the calibration sample.

For fluorite the determination of C proceeded using

$$C_{i,\alpha} = I_{i,\alpha} \frac{\mu_m^*}{W_{\alpha}} = 6559.6 \times \frac{71.71}{0.5358} = 877\,919. \quad (3.9.27)$$

All data sets were then analysed using equation (3.9.3), as demonstrated here using sample 1H.

$$W_{\alpha} = I_{i,\alpha} \frac{\mu_m^*}{C_{i,\alpha}} = 5132.0 \times \frac{59.1}{877919} = 0.3455, \quad (3.9.28)$$

compared with a value of 0.3469 added to the sample by weight. Fig. 3.9.1 shows the analysed concentration for all 24 fluorite measurements along with the bias from the known values. The bias (analysed – known) all fall within the range –0.3 to 0.5 wt% with no systematic bias as a function of concentration. The similar results achieved for corundum and zincite demonstrate the validity of the approach where there is minimal peak overlap.

3.9.4.2. Internal standard method

Application of the internal standard method normally requires the addition of an appropriate phase in known amount to each sample to be analysed. In order to use this data for demonstration of the internal standard method, it is necessary to designate one of the existing phases as the internal standard. Sample 1H has been used to derive the calibration constant, with fluorite considered to be the phase of interest while zincite is designated