

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 over 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_{α}) 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