

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 ($I_{i\alpha}$) considered by the single-peak methods. The Rietveld scale factor for phase α , $S_{i\alpha}$, can be defined as (Bish & Howard, 1988; Hill, 1991; Hill & Howard, 1987; O'Connor & Raven, 1988)

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

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} :