

## 3.9. QUANTITATIVE PHASE ANALYSIS

hkl\_phase) is obtained *via* the use of partial structure information. Here the peak positions are constrained by a unit cell and space group but the relative intensities, in the absence of atom types and locations in the unit cell, are determined empirically from a pure sample or one where the phase is present in a mixture at a known concentration. The second method involves the use of a discrete set of peaks whose positions, intensities, width and shape are all determined empirically. Once determined using a standard sample, this group of peaks may then be scaled as a single unit and is referred to hereafter as a peaks\_phase.

The software *SIROQUANT* (Taylor & Rui, 1992) employs the simultaneous use of observed and calculated standard profiles within the framework of the Rietveld method. It draws on a library of structures that are stored as lists of reflections and intensities (hkl files). These are calculated on a cycle-by-cycle basis for well described crystalline materials but are read directly from the hkl files for poorly defined materials such as clay minerals. This method still requires some knowledge of the crystal chemistry of all phases involved and that they be included within the programme's database. By the inclusion of reflection information in this way some aberrations such as preferred orientation may be allowed for. This approach to clay mineralogy also provides for the refinement of two sets of halfwidth parameters in order to model the co-existing sharp and broad reflections generated by such minerals.

A subsequent development of the whole-pattern approach is the 'partial or no known crystal structure' (PONKCS) method (Scarlett & Madsen, 2006). This method operates within the framework of the Rietveld method but replaces the traditional crystal structure of the phases in question with an empirical set of peaks (either as an hkl\_phase or a peaks\_phase). These can then be scaled as a single unit in the course of refinement in similar fashion to the set of structure factors derived from a crystal structure. Since the full structure information is not available, it is not possible to calculate the *ZMV* phase constant normally required for quantification *via* equation (3.9.26) (Hill & Howard, 1987); hence, an empirical value must be derived through calibration.

## 3.9.6.1.1. Generation of calibrated PONKCS models

The generation of a suitable PONKCS model requires that:

- (1) The unknown phase is available as either a pure specimen or as a component of a mixture where its abundance is known (in some instances, this may be achieved by other means, such as the measurement of bulk and/or microchemical composition.)
- (2) The unknown phase does not vary considerably from the material used to derive the relative intensities of the model. Preferred orientation and other sample-related effects may be compensated for based upon an indexed diffraction pattern.

The initial step in the generation of a PONKCS model is to describe the contribution to the diffraction pattern of the phase with a series of peaks. If the phase of interest has been indexed, the Le Bail or Pawley methods (see Chapter 3.5) can be used to constrain peak positions to the space group and unit-cell parameters while the individual reflection intensities are allowed to vary to best match the observed peaks (*i.e.* an hkl\_phase). If the phase has not been indexed, a series of unrelated peaks can be refined using a standard material and scaled as a group during analysis (*i.e.* a peaks\_phase). While this approach is effective in most cases, it restricts the refinable parameters that may be used

in the treatment of systematic errors such as preferred orientation.

The next step is to calibrate the hkl\_phase or peaks\_phase and derive a 'phase constant' that is equivalent to the *ZMV* value in crystal-structure-based quantification. This is achieved by the preparation of a mixture in which there are known amounts  $W_\alpha$  and  $W_s$  of the unknown and standard, respectively. Recalling equation (3.9.25), the ratio of the weight fractions is then given by

$$\frac{W_\alpha}{W_s} = \frac{S_\alpha(ZMV)_\alpha}{S_s(ZMV)_s}, \quad (3.9.42)$$

where  $S_\alpha$  and  $S_s$  are the refined scale factors for the unknown and standard, respectively.

Rearrangement of equation (3.9.42) then provides the means for determining an empirical value of  $(ZMV)_\alpha$ , which is required for the calibration of a peaks\_phase:

$$(ZMV)_\alpha = \frac{W_\alpha S_s}{W_s S_\alpha} (ZMV)_s. \quad (3.9.43)$$

For an hkl\_phase the value of  $V$  can be determined from the refined unit-cell parameters and hence can be removed from the phase constant resulting in

$$(ZM)_\alpha = \frac{W_\alpha S_s (ZMV)_s}{W_s S_\alpha V_\alpha}. \quad (3.9.44)$$

Unlike the *ZMV* value derived from the unit-cell contents of a crystal structure, the phase constants derived using equations (3.9.43) and (3.9.44) have no physical meaning, since they have been derived by empirical measurement. For an hkl\_phase, a more physically meaningful value of *ZM* can be obtained by deriving the true unit-cell mass from the measured phase density according to

$$(ZM)_{\alpha(\text{true})} = \frac{\rho_\alpha V_\alpha}{1.6604}. \quad (3.9.45)$$

The empirical 'structure factor' values in the hkl\_phase could then be scaled according to the relation  $ZM_{\alpha(\text{true})}/ZM_\alpha$ , making them approximate 'real' structure factors for the material. Note that this final step is not necessary for quantification, but may make the method more generally applicable.

## 3.9.6.1.2. Application of the model

The PONKCS method is applicable to any mixture in which there are one or more phases that are not fully characterized crystallographically, including essentially amorphous material, provided appropriate calibration samples can be obtained. In the mineralogical context, it may not be possible to obtain pure phase specimens typical of those found in the bulk mixtures, but it may be possible to concentrate them to a point where they can be used. Methods of achieving this may include gravity or magnetic separation, or selective chemical dissolution.

The original paper describing this method (Scarlett & Madsen, 2006) gives a detailed example based upon sample 1 from the IUCr CPD round robin on QPA (Madsen *et al.*, 2001; Scarlett *et al.*, 2002). There, corundum was regarded as the unknown phase, fluorite as an impurity of known crystal structure and zincite a standard material added at known weight fraction. In the same paper, there is a more realistic example regarding the poorly ordered clay mineral nontronite, which is of commercial significance but difficult to quantify *via* traditional structure-based Rietveld methodology. Further details regarding quantification of this mineral *via* the PONKCS method is given in articles detailing