

## 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 H<sub>2</sub>O 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  $2\theta$  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  $\alpha$  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,  $\lambda$  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,  $V_\alpha$  is the unit-cell volume of phase  $\alpha$ , and  $\theta$  and  $\theta_m$  are the diffraction angles for the  $hkl$  reflection and the monochromator (if present), respectively.  $B$  is the mean atomic displacement parameter (ADP).  $W_\alpha$  and  $\rho_\alpha$  are the weight fraction and density of phase  $\alpha$  respectively, while  $\mu_m^*$  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  $\alpha$  (second set of square brackets), and (iii) phase-specific and whole-sample parameters including the weight fraction  $W_\alpha$  for phase  $\alpha$  (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  $\alpha$  for a specific set of

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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  $\alpha$ , (ii) measurement of peak intensity  $I_{i\alpha}$  for the standards, and (iii) estimation of the standard sample mass absorption coefficient  $\mu_m^*$ ;
- (2) measurement of  $I_{i\alpha}$  and estimation of  $\mu_m^*$  for the unknown samples; and
- (3) calculation of  $W_{\alpha}$  via equation (3.9.3).

The value of  $\mu_m^*$  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,  $\mu_m^*$  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  $\mu_m^*$  from the sum of the products of the theoretical mass absorption coefficient ( $\mu_j^*$ ) 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  $\mu_m^*$ ,

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

#### 3.9.3.2. Internal standard method

A more general, and experimentally simpler, approach is to eliminate  $\mu_m^*$  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  $\mu_m^*$  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

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

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

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

This approach, referred to as the *internal standard method*, relies on the determination of  $C_{js}^{i\alpha}$  using known mixtures of standard and analyte phases. The value of  $C_{js}^{i\alpha}$  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  $W_{\alpha}$  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  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (corundum), TiO<sub>2</sub> (rutile), ZnO (zincite), Cr<sub>2</sub>O<sub>3</sub> (eskolaite),  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (haematite), CeO<sub>2</sub> (cerianite), CaF<sub>2</sub> (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