

3.9. Quantitative phase analysis

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3.9.1. Introduction

The field of quantitative phase analysis (QPA) from powder diffraction data is almost as old as powder diffraction itself. Debye and Scherrer first developed the method around 1916 (Debye & Scherrer, 1916, 1917) and between 1917 and 1925 Hull (1917, 1919) and Navias (1925) were reporting studies of QPA related to the new technique. However, further developments in QPA were relatively slow, as much of the activity in X-ray diffraction (XRD) at the time was dedicated to the solution of crystal structures rather than the extraction of other information present in a powder diffraction pattern. While a small number of QPA applications continued to be published in the intervening years, it was not until the advent of scanning diffractometers around 1947 (Langford, 2004, Parrish, 1965) and the work of Alexander and Klug in 1948 (Alexander & Klug, 1948), which provided the formal methodology and a practical approach, that the field began to expand.

Since those original developments, which utilized the intensity of individual peaks or a small group of peaks in the diffraction pattern, there have been extensions to the methodology that use whole-pattern approaches. These methods operate *via* the summation of either (i) patterns collected from pure components or (ii) component contributions calculated from their crystal structures. There are a number of benefits accruing from the whole-pattern approaches since all reflections in the pattern, which may number in the hundreds or thousands, now contribute to the final analysis.

The mathematical basis of QPA is well established and, ideally, QPA should be a relatively straightforward science. However, there are a significant number of factors, many of them experimental, that serve to decrease the accuracy that can be obtained (Chung & Smith, 2000). Some of these, such as accuracy and precision in measurement of peak position and intensity, resolution of overlapping peaks and counting statistics, relate to instrument geometry and data-collection conditions. Other sources of error derive from sample-related issues and include effects such as (i) preferred orientation (which distorts the observed relative intensities from those expected for a randomly oriented powder); (ii) crystallite size and strain broadening (leading to increased peak width and hence overlap); (iii) the grain-size effect (where there may be too few crystallites contributing to the diffraction process to ensure that a representative powder pattern can be measured);¹ and (iv) micro-absorption (where phases that strongly absorb the incident and diffracted beams are underestimated with respect to weakly absorbing phases). Of these, microabsorption remains the largest impediment to accurate QPA and is more pronounced in X-ray diffraction than in neutron-based studies.

While there is a very broad scope for the application of diffraction-based estimation of phase abundance, the perceived difficulty involved in developing and using these methods often

deters non-specialist users. Consequently, they may resort to other, non-diffraction, material characterization techniques that are more readily implemented.

Analytical techniques for most of the 92 naturally occurring elements are generally well established and, in many cases, the subject of internationally accepted standards. However, the physical properties of minerals and materials formed by these elements, and the manner in which they react, is not solely dependent on their chemical composition but also on how the constituent elements are arranged; that is, their crystal structures. This finite number of known elements combines in an almost infinite array within the 230 crystallographic space groups. Further variability is induced by factors such as solid solution, degree of crystallinity and morphology, thus making QPA by diffraction methods considerably more difficult to implement.

In industry, many manufacturing or processing lines are controlled by measurement of elemental composition alone, simply because these values can be readily obtained to a high degree of accuracy and precision. For example, a plant extracting Cu from an ore body might measure the Cu content of the feed ore and the concentrate, and the plant conditions are optimized based on efficiency of extraction. However, if the mineralogical form of the Cu changes in the feed, then it may not behave in the same manner during grinding, flotation and density separation, and this will affect the recovery. Frequently, where knowledge of the mineralogy or phase abundance is actually used in plant optimization and control, it is derived from bulk or micro-compositional analysis rather than being measured directly. This is often achieved by normative calculation, where the results of element composition analysis are assigned to specific phases based on an assumed knowledge of individual phase composition. Further details of this approach can be found in Chapter 7.7.

In materials science, new compounds are being synthesized at a rapidly increasing rate with techniques such as high-throughput synthesis capable of generating hundreds of new variants in a single experiment. Such techniques are being used in fields ranging from drug discovery, catalyst synthesis and new metal alloy design. The properties of these materials, and their suitability for their designed purpose, are not only dependent on their structural form but, for multiphase materials, on the amount of each component present. In this case, accurate, or at the very least reproducible, QPA is crucial to the screening process.

This chapter focuses on the application of QPA techniques for the extraction of phase abundance from diffraction data. While there is extensive coverage of the QPA methodology in other texts (Klug & Alexander, 1974; Smith *et al.*, 1987; Snyder & Bish, 1989; Zevin & Kimmel, 1995), some of the more commonly used approaches will be described here along with examples of their use in practical applications.

3.9.2. Phase analysis

There are a number of traditional methods for the estimation of phase abundance in multiphase materials (Zevin & Kimmel, 1995). In summary, these can be divided into two groups:

¹ It is worth noting that the grain-size effect becomes even more of an issue as the divergence of the instrument is decreased with, for example, high-resolution laboratory or synchrotron-based instruments, since fewer crystallites are likely to meet the diffraction condition.

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- (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