development of reliable structure models and enhanced computational power (Coelho *et al.*, 2016, 2015; Bette *et al.*, 2015).

3.9.6.3. *Quantitative determination of amorphous material*

Traditionally, most activity in diffraction-based QPA has been concerned with the assessment of the crystalline components. However, all materials possess a non-diffracting surface layer with some degree of disorder or contain some surface reaction products and adsorbed species. While such a layer can easily account for ∼1 wt% of the entire sample in a finely divided solid, the fraction of this surface layer will increase as the particle size decreases (Cline *et al.*, 2011). In addition, some materials can contain separate phases that may be amorphous or at least poorly crystalline. The advent of nanotechnology has served to further blur the boundaries between what is defined by powder XRD as crystalline or amorphous.

During *in situ* studies, some phases undergo transformations *via* amorphous intermediate components; the presence of these phases has the potential to influence our understanding of reaction mechanisms. Given the potential for these amorphous components to influence bulk-material properties, the need to quantify them is an increasingly important issue for analysts using diffraction-based methods. Many of the traditional phase-quantification techniques described in this chapter fail to take into account the occurrence of amorphous material in the sample and, without careful attention by the analyst, its presence may remain undetected.

Madsen *et al.* (2011) recently reviewed a range of techniques for the determination of amorphous content and assessed their applicability for various analytical situations. The study used both single-peak and whole-pattern methodology and applied it in two distinct ways.

(1) The first method used an indirect approach; the crystalline components were quantified and put onto an absolute scale using either an internal- or external-standard method. The amorphous content was then determined by subtracting the sum of the absolute weight fractions of the crystalline components from unity.

(2) The second method used a direct approach; it relied on being able to 'see' the amorphous contribution in the diffraction and being able to obtain an estimate of its intensity during analysis (Fig. 3.9.13). Intensity contributions of amorphous phases are not always evident in the diffraction pattern, especially at low concentrations. Even when their presence is apparent, it can be difficult to resolve their contribution from other components of the diffraction pattern such as pattern background. However, once an intensity estimate is obtained, and an appropriate calibration constant derived, the amorphous phase can be included in the analysis along with the crystalline components.

In general, for the determination of amorphous material the problem will dictate the method(s) used. All methods discussed in the study of Madsen *et al.* (2011) are, in principle, capable of determining the concentration of amorphous material in mixtures with similar levels of accuracy and precision as is possible for crystalline phases (down to ∼1% absolute or better). The limitations are similar to those for the QPA of crystalline phases, and are dictated by sample properties and the analytical techniques used.

A summary of the recommendations resulting from the study include:

(1) Where the intensity contribution of the amorphous content to the diffraction pattern is not evident, one of the indirect methods (internal or external standard) should be used. For indirect methods, any errors in the analysis of the crystalline phases will decrease the overall accuracy attainable since the amorphous phase abundance is determined by difference.

(2) Where intensity contributions of amorphous phases are evident in the diffraction pattern, any method based on the direct modelling of the amorphous component provides improved accuracy relative to the indirect methods.

(3) Calibration-based methods usually have the potential to achieve the highest accuracy, as residual aberrations in the data, such as microabsorption, are included in the calibration function. Caution is advised here as the magnitudes of these residual errors may change with different sample suites, and so a calibration function derived for one sample suite may not be generally applicable.

(4) A sample of pure amorphous material, or a sample where the amorphous content is high and its concentration known, is normally required to establish an accurate model for the direct methods.

Some materials contain more than one amorphous phase and there may be a desire to quantify these separately rather than as a group. This provides a significant challenge since their broad diffraction patterns will be highly overlapped, thus leading to a high degree of correlation during analysis. However, Williams *et al.* (2011) have demonstrated that, with careful experimentation and data analysis, it is possible to provide QPA for two poorly crystalline components in geopolymers.

Phase abundances reported in the literature are often provided in a manner that suggests they are absolute values. Where no specific allowance for amorphous content has been made and reported, it is better to assume that the reported phase abundances are correct relative to one another, but may be overestimated in an absolute sense. Therefore, standard practice in QPA should be to use methodology which produces *absolute* rather than *relative* phase abundances. Any positive difference between unity and the sum of the absolute weight fractions will

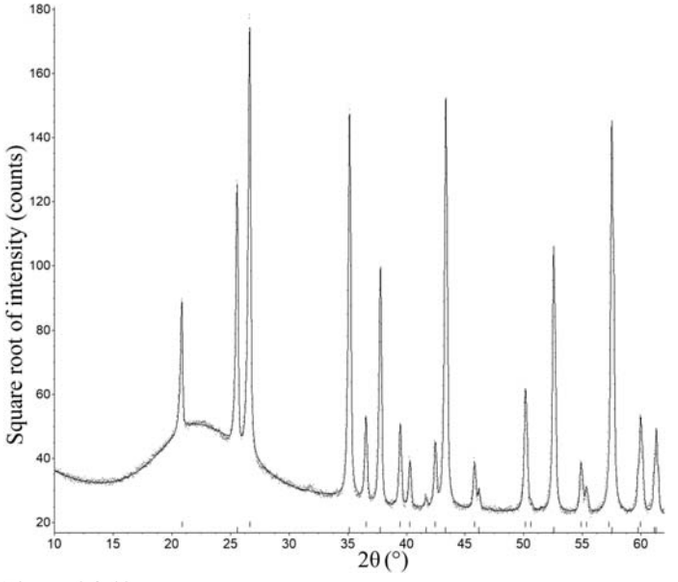

Figure 3.9.13
Output of Rietveld refinement of XRD data (Cu $K\alpha$ radiation) for a synthetic sample containing a mixture crystalline and amorphous phases. The observed data are represented as grey dots and the calculated pattern as the solid black line overlaying them. The broad peak centred at ∼22° 2θ is due to amorphous silica flour. The rows of tick marks at the bottom represent the positions of the Bragg reflections for quartz (upper) and corundum (lower).

alert the analyst to the presence of non-analysed material in the sample.

3.9.7. QPA from *in situ* experimentation

In situ analysis is a growth area in the field of powder diffraction (Ehrenberg *et al.*, 2013) and is dealt with in depth elsewhere in this volume (see Chapter 2.9). The technique is unparalleled in providing information about reaction mechanisms and kinetics under simulated operational conditions and without the artefacts potentially associated with post-mortem sampling or *ex situ* methods.

An *in situ* experiment collects dynamic, time-resolved data, which present unique challenges for QPA. The phase assemblages formed in such experiments may be quite complex and change dramatically over the course of the experiment. In addition, the data are generally of lower quality than those collected for *ex situ* samples at ambient conditions. This may be due to poor counting statistics resulting from the rapid counting times needed to follow various phase transitions. Data for *in situ* studies are often collected using area detectors, some of which are not photon-counting devices. Care should be taken in the error propagation and hence the weighting used during data analysis.

The data quality may also be affected by components in the sample chamber that are required in order to achieve the environmental conditions (temperature, pressure, solution or gaseous atmosphere, and so on) necessary for the experiment: these components may either attenuate the incident and diffracted beams or contribute features to the pattern resulting from scattering of the beam.

One very important issue that arises from *in situ* studies is the large number of data sets generated. The rapid counting times available at modern synchrotron and neutron facilities mean that hundreds or thousands of diffraction patterns can be collected over the duration of the *in situ* experiment.

3.9.7.1. *Data analysis*

There are usually a series of steps involved in the analysis of *in situ* diffraction data. Given the large number of data sets collected, it is generally not practicable to undertake detailed analysis of every pattern individually. Since any changes to the component phases are transitions generally observed in a sequence of patterns, data analysis focused on extracting QPA could be undertaken using the following steps:

(1) Cluster the data into a number of groups necessary to describe the major phase regions present during the reaction. This can be achieved (i) visually, using software that allows the plotting of three-dimensional data sets of the type shown in Fig. 3.9.14, or (ii) through the use of automatic clustering algorithms using, for example, principal-component analysis.

(2) Select the 'most typical' pattern of each cluster as well as the two 'least typical' patterns at the extreme ends of the cluster. These patterns are often identified by clustering software based on the statistical similarity between patterns in the cluster.

(3) Identify the phases present in each cluster using the most typical pattern. This is not always a trivial task since (i) new phases that are not currently present in databases may have been generated; (ii) effects such as thermal expansion or variation of chemical composition may have changed the peak positions so that search/match procedures are no longer successful; or (iii) impurity elements may have stabilized phases that are not expected from related phase-diagram studies.

(4) For the discussion here, it will be assumed that the quantification process will be *via* a whole-pattern method.
   (*a*) Develop appropriate (crystal structure or PONKCS) models for every phase observed within the data suite.
   (*b*) Optimize the pattern and phase-analysis parameters using the most typical pattern selected from each cluster.
   (*c*) Set the relevant parameter refinement limits using the least typical patterns. It is necessary to limit the range over which refined parameters can vary to avoid the return of physically unrealistic values.

(5) Owing to the large number of data sets, analysis for QPA will generally be approached as a batch process with limited refinement of structural parameters. This limitation on the total number of refinable parameters is necessary during batch processing in order to avoid instability in the refined values as the phases progress from major to minor concentration.

(6) Batch processing of data suites may be conducted in a variety of ways including:
   (*a*) Sequential refinement, beginning with either the first or final pattern of the suite and including all phases present in the entire suite. This methodology must be tempered by a means to either remove or severely restrict refinement of any phases that are not present in all patterns of the suite in order to avoid the reporting of 'false positives' where absent phases have been included. Some software packages allow phases to be removed from the analysis if their abundance is below a selected level or has an error that exceeds some predefined criteria (Bruker AXS, 2013).
   (*b*) Parametric Rietveld refinement (Stinton & Evans, 2007), where the entire suite of diffraction data is analysed simultaneously. Selected parameters are constrained to the applied external variable (*e.g.* temperature) with a function describing their evolution throughout the data sequence. For example, the unit-cell parameters for a phase can be constrained to vary according to their thermal coefficients of expansion. This method can bring stability to refined parameters and allows the refinement of noncrystallographic parameters such as temperature and reaction rate constants directly from the diffraction data. This methodology is particularly suited to relatively simple phase systems, but is difficult to develop for complex multiphase mineralogical systems.

(7) In selecting a model for use in QPA, it is highly recommended that one of the approaches that generate absolute phase abundances is used. Many reactions generate intermediate amorphous phases that convert to crystalline components later in the reaction. If relative phase abundances [such as those produced by the *ZMV* approach embodied in equation (3.9.26)] are used, the amounts of the crystalline phases will be overestimated and this will give misleading indications about the reaction mechanism and kinetics.

Whichever method is employed, it is always necessary to examine a sample of individual results as a test of veracity rather than just accepting the suite of numbers for parameter values and QPA resulting from batch processing.

The study of Webster *et al.* (2013) demonstrates many of these points by following the formation mechanisms of the iron-ore