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.

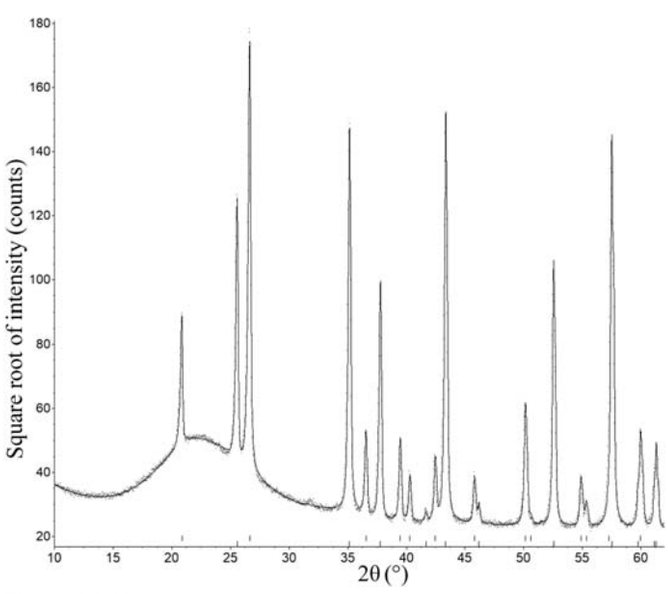


**Figure 3.9.13**
Output of Rietveld refinement of XRD data (Cu $K\alpha$ radiation) for a synthetic sample containing a mixture crystalline and amorphous phases. The observed data are represented as grey dots and the calculated pattern as the solid black line overlaying them. The broad peak centred at ~22° $2\theta$ 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).

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

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