

3.10. ACCURACY IN RIETVELD QUANTITATIVE PHASE ANALYSIS

the ALBA Light Source (Fauth *et al.*, 2013). The wavelength, $\lambda = 0.77439$ (2) Å, was selected with a double-crystal Si(111) monochromator and was determined using the NIST SRM640d Si standard ($a = 5.43123$ Å). The diffractometer is equipped with a MYTHEN-II detector system. The samples were loaded into glass capillaries 0.7 mm in diameter and were rapidly rotated during data collection to improve the diffracting-particle statistics. The data-acquisition time was 20 min per pattern to attain a very good signal-to-noise (S/N) ratio over the angular range $1\text{--}35^\circ 2\theta$. Three patterns, taken at different positions along the capillaries, were collected for each sample.

SXRPD data for the amorphous content series, CZQ_xGI, were also measured at the ALBA Light Source. The experimental setup was the same as described above but the working wavelength was $\lambda = 0.49591$ (2) Å.

3.10.4. Powder-diffraction data analysis

All powder patterns were analysed by the Rietveld method using the GSAS software package (Larson & Von Dreele, 2000) with the pseudo-Voigt peak-shape function (Thompson *et al.*, 1987) for RQPA. The refined overall parameters were phase scale factors, background coefficients (linear interpolation function), unit-cell parameters, zero-shift error, peak-shape parameters and preferred-orientation coefficient, when needed. The March–Dollase preferred-orientation adjustment algorithm was employed (Dollase, 1986). The modelling direction must be given as input for the calculations. In this case, the directions for the different phases were taken from previous studies. Alternatively, this direction can be extracted from the pattern from an analysis of the differences between observed and calculated intensities for non-overlapped diffraction peaks. The crystal structures used are reported in Table 3.10.1.

In order to provide a single numerical assessment of the performance of each analysis, a statistic based on the KLD distance was used (Kullback, 1968). This approach was previously used to evaluate the accuracy of RQPA applied to standard mixtures (Madsen *et al.*, 2001; Scarlett *et al.*, 2002; León-Reina *et al.*, 2009). Both phase-related KLD distances and absolute values of the Kullback–Leibler distance (AKLD) were calculated. Accurate analyses are mirrored by low values of AKLD.

The overall amorphous content was determined from the internal standard methodology approach (De la Torre *et al.*, 2001; Aranda *et al.*, 2012) with quartz as an internal standard [using isotropic atomic displacement parameters (ADPs) of 0.045 and 0.0087 Å² for Si and O, respectively]. If the original sample contains an amorphous phase, the amount of standard will be overestimated in RQPA. From the (slight) overestimation of the standard, the amorphous content of the investigated sample can be derived (De la Torre *et al.*, 2001). The important role of the values of the ADPs in the results of RQPA mainly in amorphous content determinations using the internal-standard method has been discussed previously (Madsen *et al.*, 2011).

3.10.5. Crystalline single phases

All of the single phases were selected according to several parameters, such as relevance to selected applications, purity, particle size of the powder and preferred orientation. In order to check the suitability of the crystal structures used, all of the phases were first studied using powder diffraction with Mo $K\alpha_1$ radiation. These preliminary studies were of special interest for organic phases, as the CIF files obtained from the Cambridge

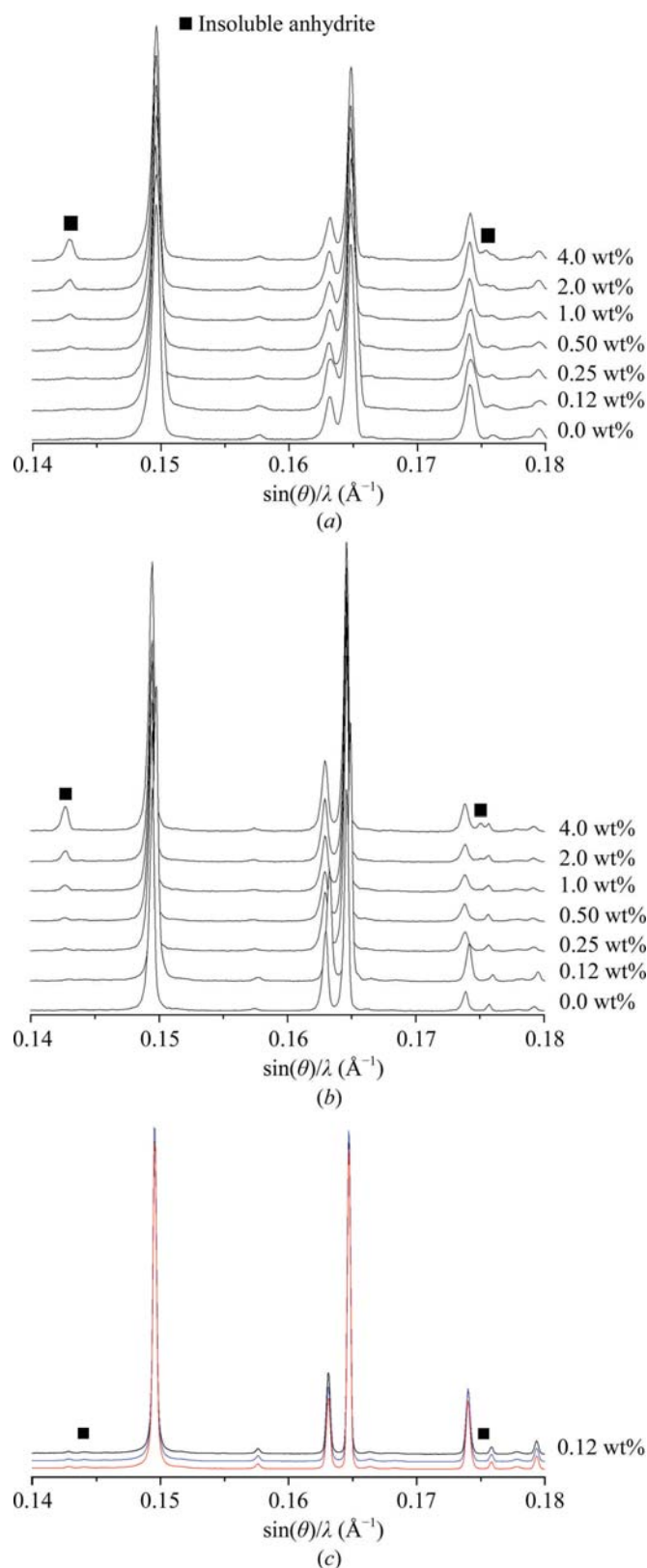


Figure 3.10.3

(a) Raw Mo $K\alpha_1$ powder patterns for the inorganic series composed of a constant matrix of calcite, gypsum and quartz, and increasing amounts of insoluble anhydrite (peaks highlighted with a solid square). (b) Raw Cu $K\alpha_1$ powder patterns for the same inorganic series. (c) Raw SXRPD patterns for CGpQ_0.12A collected at three different positions of the capillary (red, black and blue traces). The intensity values in (c) have been artificially offset to show the three different patterns.

Structural Database (CSD) did not contain the atomic displacement parameters (ADPs). For lactose and fructose, the ADPs were obtained from the original publications and were introduced manually into the GSAS control file. For glucose and