

3.10. ACCURACY IN RIETVELD QUANTITATIVE PHASE ANALYSIS

result in some sample-related effects, such as preferred orientation, microabsorption and ‘rock-in-the-dust/graininess’ effects, all powders were characterized by scanning electron microscopy (SEM). Fig. 3.10.2 shows SEM micrographs for all of the phases. All inorganic samples were single phases except for gypsum and insoluble anhydrite. The impurity-phase contents for these two samples were reported in León-Reina *et al.* (2016).

Both organic and inorganic phases were also measured using Cu $K\alpha_1$ radiation in reflection mode. As expected, a transparency effect was observed in the Cu $K\alpha_1$ patterns for organic samples (Buhrke *et al.*, 1998).

3.10.6. Limits of detection and quantification

LoD and LoQ are two important quantities in the validation of any analytical method. LoD/LoQ are terms that are used to describe the smallest concentration of an analyte that can be reliably detected/assessed by an analytical procedure, as discussed in Section 3.10.1. In techniques such as Rietveld analysis, the approach of having a powder pattern with its strongest (not overlapped) diffraction peak with an S/N ratio of larger than 3.0 is not straightforward because the full powder pattern is evaluated.

Fig. 3.10.3 shows Mo $K\alpha_1$ and Cu $K\alpha_1$ raw patterns for the inorganic series with increasing amounts of insoluble anhydrite (labelled with solid squares) and Fig. 3.10.4 shows the strongest diffraction peak for i-A in the mixtures containing 0.123 wt% anhydrite (CGpQ_0.12A) and 0.25 wt% anhydrite (CGpQ_0.25A) to evaluate the limits of detection in the conditions reported in Section 3.10.5. For CGpQ_0.12A, both laboratory powder patterns yielded peaks with S/N ratios lower than 3.0 (top panels in Fig. 3.10.4). For CGpQ_0.25A, the Cu $K\alpha_1$ pattern yielded a clear peak with S/N = 4.1; therefore, it can be concluded that the LoD for insoluble anhydrite with this radiation in this mixture is slightly lower than 0.2 wt%. For Mo $K\alpha_1$ radiation, the CGpQ_0.25A and CGpQ_0.50A samples yielded patterns with peaks with S/N ratios of 2.4 and 5.1, respectively. Hence, it can be concluded that the LoD for i-A with this radiation in this mixture is quite close to 0.3 wt%.

The LoQ for i-A in this matrix was also studied. Three Mo $K\alpha_1$ and Cu $K\alpha_1$ patterns were collected for CGpQ_0.12A. For the three Mo $K\alpha_1$ patterns, the average analysis result for i-A was 0.28 (2) wt%, but the accuracy of the obtained value is poor, as the expected value was 0.12 wt%. Similarly, the average value for the analyses of three Cu $K\alpha_1$ patterns was 0.24 (2) wt%. The RQPA results are given as supporting information in León-Reina *et al.* (2016). It was concluded that i-A can be quantified in this mixture at the level of 0.12 wt%, but with a relative error close to 100%. If the ‘acceptable reliability’ criterion in the analysis is taken into consideration, the LoQ value would be close to 1.0 wt% in order to have a relative associated error lower than 20%.

CGpQ_0.12A was also studied by SXRPD. Fig. 3.10.3(c) shows the SXRPD patterns collected at three different positions of the capillary, which were almost identical, and Fig. 3.10.4 (bottom left) shows the main diffraction peak of anhydrite. The S/N ratio for the strongest diffraction peak of anhydrite was 12.8 and hence the limit of detection for i-A with synchrotron radiation in this matrix is below 0.10 wt%.

To quantify the accuracy of the analyses, the KLD methodology was used. The AKLD values for each analysis as well as the KLD values for i-A are reported in León-Reina *et al.* (2016). The synchrotron analyses clearly had better accuracy than those

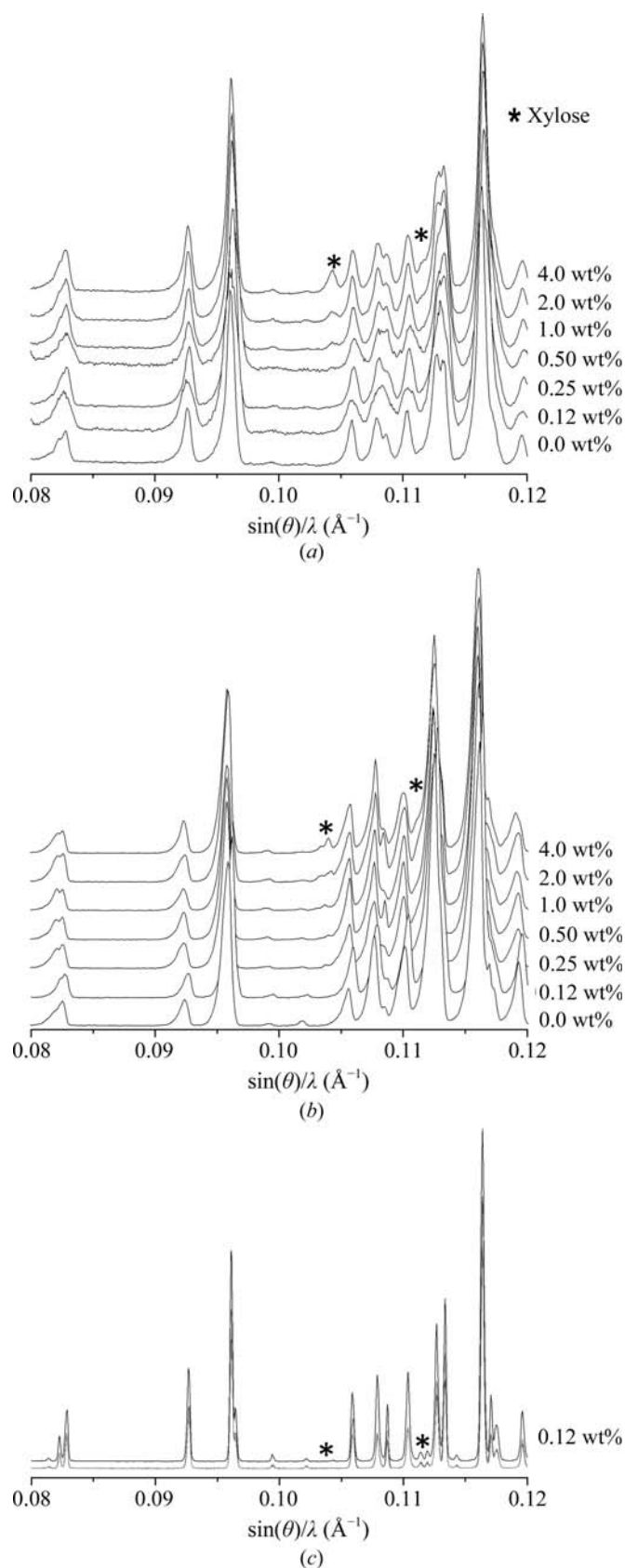


Figure 3.10.5

(a) Raw Mo $K\alpha_1$ powder patterns for the organic series composed of a constant matrix of glucose, fructose and lactose, and increasing amounts of xylose (peaks highlighted with an asterisk). (b) Raw Cu $K\alpha_1$ powder patterns for the same organic series. (c) Raw SXRPD patterns for GFL_0.12X collected at three different positions of the capillary (as collected).

using laboratory radiation. Moreover, the Mo $K\alpha_1$ radiation analyses were slightly better than those obtained using Cu $K\alpha_1$ radiation.

3. METHODOLOGY

Table 3.10.2

Rietveld quantitative phase analyses for the crystalline inorganic mixtures measured with Cu $K\alpha_1$ and Mo $K\alpha_1$ radiations

Weighed amounts (wt%) are also shown for comparison. Absolute values of the Kullback–Liebler distance (AKLD) for each mixture and the KLD value for i-anhydrite are also included. Trm, transmission; rfl, reflection.

Phases	CGpQ_0.0A			CGpQ_0.25A			CGpQ_0.50A		
	wt%	Mo trm	Cu rfl	wt%	Mo trm	Cu rfl	wt%	Mo trm	Cu rfl
C	32.9	32.6 (1)	30.4 (2)	32.8	32.0 (1)	33.6 (1)	32.7	33.2 (1)	32.8 (1)
Gp	31.7	31.7 (1)	34.5 (1)	31.7	32.5 (1)	31.6 (1)	31.6	30.1 (1)	30.7 (1)
Q	34.2	34.6 (1)	33.7 (1)	34.1	33.9 (1)	33.0 (1)	34.0	34.6 (1)	34.2 (1)
s-A	0.8	0.66 (3)	0.76 (5)	0.8	0.77 (4)	0.78 (5)	0.8	0.97 (3)	1.15 (5)
SrSO ₄	0.4	0.44 (4)	0.70 (6)	0.4	0.44 (4)	0.67 (5)	0.4	0.39 (4)	0.56 (5)
i-A	—	—	—	0.28	0.42 (3)	0.42 (4)	0.52	0.71 (3)	0.71 (4)
AKLD sum		0.0089	0.0605		0.0198	0.0235		0.0295	0.0180
(i-A) KLD					−0.001	−0.001		−0.002	−0.002

Phases	CGpQ_1.0A			CGpQ_2.0A			CGpQ_4.0A		
	wt%	Mo trm	Cu rfl	wt%	Mo trm	Cu rfl	wt%	Mo trm	Cu rfl
C	32.5	32.8 (1)	32.6 (2)	32.2	31.3 (1)	31.4 (1)	31.6	31.2 (1)	31.8 (1)
Gp	31.5	30.4 (1)	30.7 (1)	31.1	32.1 (1)	32.3 (1)	30.5	30.7 (1)	30.5 (1)
Q	33.8	34.1 (1)	33.8 (1)	33.5	33.5 (1)	32.6 (1)	32.8	32.8 (1)	32.0 (1)
s-A	0.8	1.03 (4)	1.11 (5)	0.7	0.54 (3)	0.58 (5)	0.7	0.67 (3)	0.77 (4)
SrSO ₄	0.4	0.43 (4)	0.68 (5)	0.4	0.48 (4)	0.68 (6)	0.4	0.45 (4)	0.63 (5)
i-A	1.02	1.23 (3)	1.17 (5)	2.02	2.05 (4)	2.38 (9)	4.02	4.30 (8)	4.33 (9)
AKLD sum		0.0214	0.0152		0.0218	0.0358		0.0095	0.0156
(i-A) KLD		−0.002	−0.001		0.000	−0.003		−0.004	−0.003

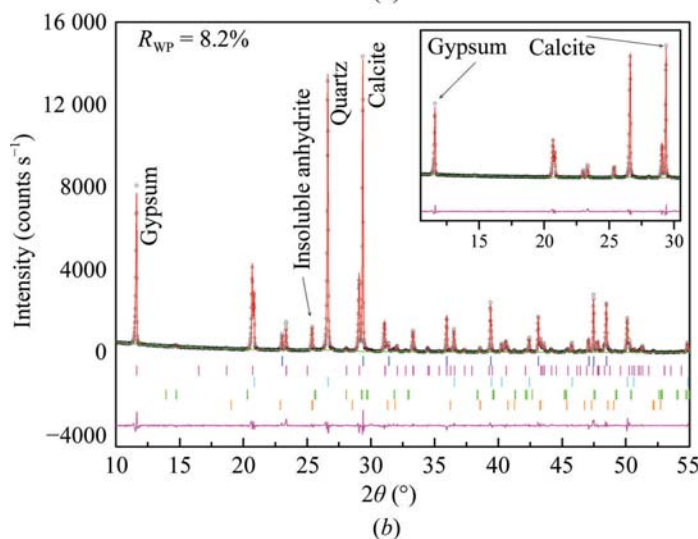
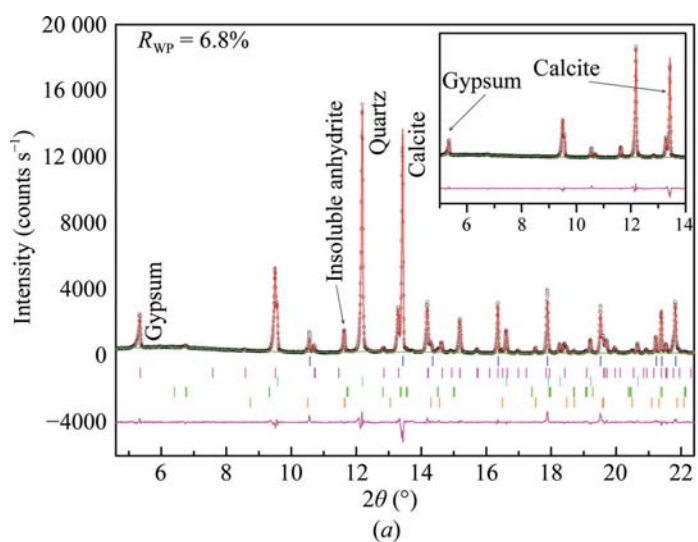


Figure 3.10.6

Selected range of the Rietveld plots for CGpQ_4.0A: (a) Mo $K\alpha_1$ and (b) Cu $K\alpha_1$ patterns. The inset highlights the effect of preferred orientation for gypsum and calcite.

Fig. 3.10.5 shows Mo $K\alpha_1$ and Cu $K\alpha_1$ raw patterns of the organic mixtures with increasing amounts of xylose. The strongest powder-diffraction peak for xylose in the GFL_0.12X patterns (with both Mo and Cu radiations) was not observed. The corresponding peak was observed in the GFL_0.25X patterns. Therefore, the LoD can be established as close to 0.25 wt%. The analysis results for xylose in GFL_0.25X were reported in León-Reina *et al.* (2016). These values showed that the results from Mo $K\alpha_1$ powder diffraction were slightly more accurate.

The LoQ for xylose was also studied. Once again, three Mo $K\alpha_1$ and Cu $K\alpha_1$ patterns were collected for GFL_0.12X. The average value for the analysis of the three Mo patterns was 0.18 (8) wt%. Similarly, the average result for the analyses of three Cu patterns was 0.34 (6) wt%. Full RQPA results are reported in the supporting information of León-Reina *et al.* (2016). The LoQ for xylose in this mixture for the two radiations can be established as close to 0.12 wt%. Indeed, if one applies an ‘acceptable reliability’ criterion, the LoQ would be much higher at above 1 wt%. The output of this study was that Cu $K\alpha_1$ radiation yielded a slightly less accurate result than that obtained from the Mo $K\alpha_1$ data.

GFL_0.12X was also studied by SXRPD in a rotating glass capillary in transmission mode. Fig. 3.10.5(c) shows SXRPD patterns for GFL_0.12X collected at three different positions of the same capillary. The powder patterns showed quite different peak ratios. It is important to bear in mind that filling a glass capillary with organic compounds is sometimes not easy due to electrostatic charge effects. For this reason, the phase ratio within the part of capillary bathed by the X-rays might not be the same as that of the sample under study. The behaviour observed in Fig. 3.10.5(c) could be explained by inhomogeneous capillary filling. Hence, in this case, the RQPA results are unreliable. Even in ‘well behaved’ samples, inhomogeneous filling of small capillaries could result in problems. Readers should be aware of this, and the authors strongly recommend that at least three patterns should be collected along the capillary and superimposed. If there is inhomogeneous filling the patterns will differ, and extreme care

has to be exercised when filling capillaries in order to minimize this problem.

3.10.7. Increasing inorganic crystalline phase content series

Table 3.10.2 reports the RQPA results for six inorganic mixtures with increasing amounts of i-A measured with Mo $K\alpha_1$ (transmission) and Cu $K\alpha_1$ (reflection). The Rietveld plots of the mixture with 4 wt% i-A are shown in Fig. 3.10.6. For most of the samples, the AKLD values (see Table 3.10.2) for Mo $K\alpha_1$ radiation are slightly smaller than the corresponding values obtained for Cu $K\alpha_1$ radiation. For this reason, we can conclude that the Mo $K\alpha_1$ analyses are slightly better than those derived using Cu $K\alpha_1$ radiation.

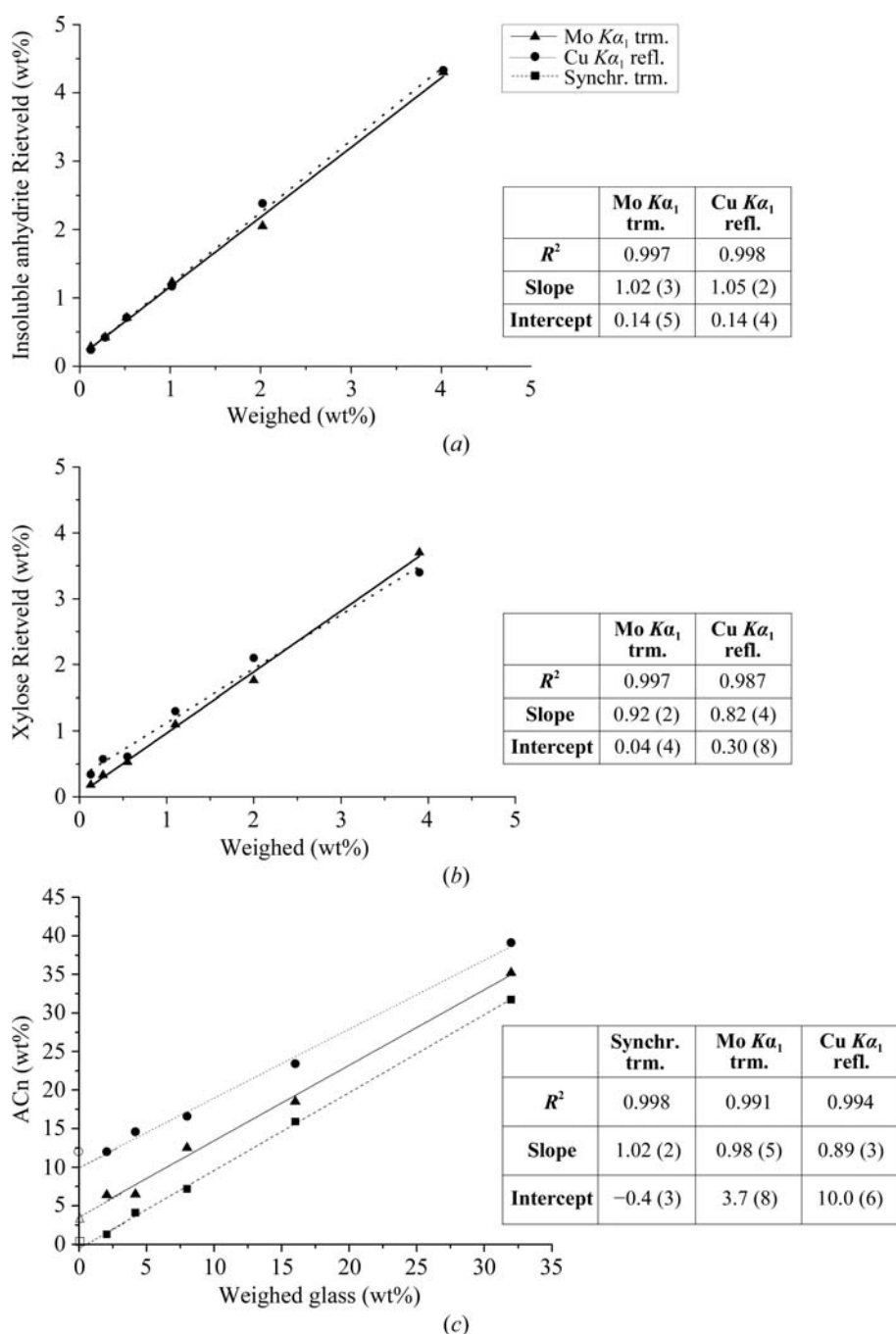


Figure 3.10.7

Rietveld quantification results for (a) the insoluble anhydrite series (within an inorganic crystalline matrix), (b) the xylose series (within an organic crystalline matrix) and (c) the ground-glass series (within an inorganic crystalline matrix) as a function of the weighed amount of each phase. Open symbols represent the derived amorphous contents in the mixtures without any added glass. The results of the least-squares fits are also shown.

On the other hand, calcite and gypsum presented preferred orientations, with the axes being [104] and [010], respectively. This effect was modelled using the March–Dollase algorithm. Preferred orientation makes the 0/0 reflections for gypsum have higher intensities in the Cu $K\alpha_1$ patterns, and smaller intensities in the Mo $K\alpha_1$ patterns, than those calculated from the crystal structure (see insets in Fig. 3.10.6). As a consequence, the refined values for flat samples in reflection and transmission geometries were smaller and larger than 1.0, respectively (Cuesta *et al.*, 2015). Although preferred orientation is present in all patterns, the Cu $K\alpha_1$ patterns were recorded in reflection geometry (flat samples), while the Mo $K\alpha_1$ measurements were collected in transmission (also flat samples). This results in opposite diffraction intensity changes and points towards another (possible) fruitful use: joint refinement of these two types of patterns to counterbalance the effects of preferred orientation in RQPA.

Fig. 3.10.7(a) shows the quantified i-A contents (wt%), as determined by the Rietveld methodology, as a function of the weighed i-A amount. The two R^2 values for the fits are very close to 1.00, and the intercept values are very close to zero, showing the appropriateness of the Rietveld methodology for quantifying crystalline materials. Furthermore, the slopes of the calibration curves are also 1.00 in both cases. Consequently, this study allows it to be concluded that RQPA for crystalline inorganic phases using powder-diffraction patterns collected using Mo $K\alpha_1$ radiation yields results that are as accurate as those obtained from the well established method using Cu $K\alpha_1$.

3.10.8. Increasing crystalline organic phase content series

Table 3.10.3 shows RQPA results for six mixtures prepared with G, F, L and an increasing amount of X measured with Mo $K\alpha_1$ (transmission) and Cu $K\alpha_1$ (reflection). In general, the values obtained using both radiations are quite similar to the weighed values. The AKLD values and the KLD values for the xylose phase are also reported in Table 3.10.3. The AKLD values from Mo $K\alpha_1$ and Cu $K\alpha_1$ radiations are relatively similar. The main problem for RQPA of organic mixtures measured in reflection geometry is related to the low X-ray absorption of the samples and the transparency effects that lead to poor peak shapes and even some split peaks in the powder patterns, as discussed previously (León-Reina *et al.*, 2016).

Fig. 3.10.7(b) shows the quantified xylose contents (wt%) as determined by the Rietveld methodology as a function of the weighed amount of xylose added to the mixtures. The results were plotted to obtain the calibration lines with increasing content of the analyte. Both plots gave R^2 values close to 1.0. However, the slope values were 0.92 and 0.82 for Mo $K\alpha_1$ and Cu $K\alpha_1$ radiations, respec-