TECHNICAL ARTICLE

Quantitative phase analysis of challenging samples using neutron powder diffraction. Sample #4 from the CPD QPA round robin revisited

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Quantitative phase analysis (QPA) using neutron powder diffraction more often than not involves non-ambient studies where no sample preparation is possible. The larger samples and penetration of neutrons versus X-rays makes neutron diffraction less susceptible to inhomogeneity and large grain sizes, but most well-characterized QPA standard samples do not have these characteristics. Sample #4 from the International Union of Crystallography Commission on Powder Diffraction QPA round robin was one such sample. Data were collected using the POWGEN time-of-flight (TOF) neutron powder diffractometer and analysed together with historical data from the C2 diffractometer at Chalk River. The presence of magnetic reflections from Fe_3O_4 (magnetite) in the sample was an additional consideration, and given the frequency at which iron-containing and other magnetic compounds are present during *in-operando* studies their possible impact on the accuracy of QPA is of interest. Additionally, scattering from thermal diffuse scattering in the high-Q region (<0.6 Å) accessible with TOF data could impact QPA results during least-squares because of the extreme peak overlaps present in this region. Refinement of POWGEN data was largely insensitive to the modification of longer d-spacing reflections by magnetic contributions, but the constant-wavelength data were adversely impacted if the magnetic structure was not included. A robust refinement weighting was found to be effective in reducing quantification errors using the constant-wavelength neutron data both where intensities from magnetic reflections were ignored and included. Results from the TOF data were very sensitive to inadequate modelling of the high-Q (low d-spacing) background using simple polynomials. © *2016 International Centre for Diffraction Data.*
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Key words: quantitative phase analysis, neutron diffraction, microabsorption

I. INTRODUCTION

Quantitative phase analysis (QPA) is one of the major applications of powder diffraction but its use with neutron diffraction data tends to be a more limited application (Kisi and Howard, 2008) because of the limited time available on such instrumentation. There are occasions where the inherent advantages of using neutrons merit a conventional QPA analysis under ambient conditions (Small and Watters, 2015), but more often than not QPA analysis is carried out as part of a non-ambient or *in-operando* study. During such studies it is usually not possible to carry out the sample preparation that is normally an important part of QPA on a complex mixture (Whitfield and Mitchell, 2008). In order to verify that QPA of the type of coarse-grained sample expected in *in-operando* studies is accurate, a suitably coarse-grained and well-characterized sample is required. Fortunately such a sample already existed in the form of sample #4 of the International Union of Crystallography (IUCr) Commission on Powder Diffraction (CPD) QPA round robin (Madsen *et al.*, 2001). Obtaining a pristine sample was extremely difficult, as even the organizers no longer possess any of the material. However, an unopened vial of the sample was eventually procured, allowing this study to take place.

A. QPA and round-Robins

Users in industry and elsewhere are obviously interested in the accuracy that can be expected from the technique. The statement by Guinier in 1956 to the effect that 'the uncertainty of the quantitative determination of phase composition by X-ray is seldom less than several percent absolute' (Guinier, 1956) attests to some of the underlying issues that have had to be addressed. One of the major impediments to accurate QPA using X-rays is microabsorption (Zevin and Kimmel, 1995); quoting Madsen and Scarlett (2008) 'the most problematic factor affecting accuracy in QPA via X-ray diffraction (XRD) is microabsorption.' The Brindley correction (Brindley, 1945) can approximate the effect of moderate microabsorption, but it has also been demonstrated that inappropriate or unnecessary use of the Brindley correction can lead to less accurate results rather than an improvement (Madsen *et al.*, 2001). Currently, there is no satisfactory approach to obtaining accurate results from diffraction data where severe microabsorption is present.

The development of QPA methodology via the Rietveld method (Hill and Howard, 1987) has made the use of powder diffraction data for QPA more accessible, while the underlying

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problems remained. Numerous round-robins (Toraya *et al.*, 1999; Madsen *et al.*, 2001; Scarlett *et al.*, 2002; León-Reina *et al.*, 2009) have shown that the accuracy attainable is largely dependent on both the nature of the sample and the skill of the operator. Madsen and Scarlett (2008) even stated that in the absence of compositional information, QPA from X-ray data is "semi-quantitative" at best. Of course additional information over and above composition can be helpful in complex mixtures, as demonstrated by the range of techniques employed by participants in the Reynold's Cup (Omotoso *et al.*, 2006). The round robin organized by the IUCr CPD in 1996 was one of the biggest held to assess the community's skill in QPA using powder diffraction alone. A series of samples of varying difficulty was prepared and distributed to interested parties and the results submitted to the organizers. The organizers broke down the results depending on the type of instrument used to collect the data, assigning the label laboratory, synchrotron, or neutron to each.

A number of the responses used neutron diffraction data for the analysis. Neutron powder diffraction data has a number of advantages over the use of X-ray data for QPA (Kisi and Howard, 2008). In addition to the lack of microabsorption, the increased penetrating power of neutrons allows for sampling of larger volumes, improving the sampling statistics for inhomogeneous and large-grained samples (Kisi and Howard, 2008). Sample #4 was deliberately prepared with coarse grains to present major difficulties with regard to microabsorption and particle statistics with all common X-ray wavelengths. It was prepared by the organizers from pure phases of corundum (Al_2O_3), zircon ($ZrSiO_4$), and magnetite (Fe_3O_4) with crystallites between 20 and 36 μm in size. Table I shows the breakdown in the results from different techniques for sample #4 as described by Scarlett *et al.* (2002). The overall X-ray results included a number of significant outliers, although the 50th % figures were still significantly higher than the neutron results. The results returned from data collected using neutron powder diffraction had higher accuracy with less scatter, but still with errors of over 1 wt%. No distinction was made in the published analysis between constant wavelength and time-of-flight (TOF) neutron instruments for sample #4. Errors of <1 wt% in QPA by XRD are of significant interest in the analytical industry (Salter and Riley, 1994; Madsen *et al.*, 1995) as such accuracies are required to support legislation with regard to respirable silica.

One complication using neutron diffraction data from sample #4 was the presence of magnetite, which as its name suggests is magnetic. Neutrons are sensitive to magnetic moments and Bragg reflections are produced from ordered magnetic structures (West, 1984). In many circumstances, the magnetic structure produces extra reflections that could be excluded from a refinement. However, magnetite is what is known as a ferrimagnet (West, 1984) which changes the intensities of the existing Bragg reflections, so the magnetic contribution can't be treated separately. An important difference between magnetic and nuclear reflections is that the former have a form-factor whereas the latter do not (Kisi and Howard, 2008), meaning that the intensities of the magnetic structure decrease more rapidly with increasing two theta angle (or decreasing *d*-spacing) than the nuclear reflections. Consequently fits using data with near-constant statistics with angle (or *d*-spacing) should suffer if the intensity from the magnetic contribution is not accounted for. A Bayesian approach to dealing with impurities was proposed by David (2001), where experimental intensities that are above calculated intensities, and hence more likely because of impurities, are down-weighted compared with other sections in the refinement. This is achieved by modifying the 'χ^2' function used in the least-squares refinement from a quadratic to a weaker logarithmic penalty (David, 2001). Theoretically at least this approach should remove some of the bias from the missing intensities even where the magnetic reflections overlap perfectly with the nuclear reflections. TOF data which commonly have statistics heavily weighted in favour of low *d*-spacing may not be affected as severely. Data from the POWGEN TOF instrument at the Spallation Neutron Source (SNS) have statistics of this type (Huq *et al.*, 2011) with a significantly larger number of detectors in the backscattering region than the forward scattering region.

TABLE I. Aggregated mean results from the CPD round robin for the different types of source.

	Number of datasets	Al_2O_3 (wt%)	Fe_3O_4 (wt%)	$ZrSiO_4$ (wt%)
Weighed		50.46	19.64	29.90
Lab X-ray	39	57 (7)	19 (6)	24 (5)
Lab X-ray (50th %)	18	53 (2)	19 (3)	28 (2)
Synchrotron	1	43.2	20.9	35.9
Neutron	6	52 (2)	22 (4)	27 (5)
Neutron (50th %)	5	51 (1)	20.1 (8)	28.6 (8)

Given the presence of duplicate measurements the errors are real standard deviations. The best 50th % results for laboratory X-ray and neutron data are also given. Data from Scarlett *et al.* (2002).

II. EXPERIMENTAL

Roughly 1.56 g of sample #4 were placed in a 6 mm diameter vanadium can and data collected using the POWGEN TOF diffractometer at the SNS, Oak Ridge National Laboratory. Data were acquired at room temperature using a 1 Å bandwidth centred at 1.066 Å with the POWGEN automatic sample changer. This yielded a dataset between 0.3 and 5.25 Å. For comparison with a typical laboratory diffractometer, 140° 2θ with Cu$K\alpha$ is equivalent to approximately 0.8 Å, and 17° 2θ with Cu$K\alpha$ equivalent to approximately 5.2 Å.

In addition to the data collected on POWGEN, historical data submitted during the CPD round robin from the DUALSPEC C2 constant wavelength diffractometer at Chalk River, Ontario, Canada were obtained from the round-robin organizers. The data were analysed using a beta version of TOPAS 6 (Coelho, 2015).

Refined parameters included the lattice parameters, scale factors, atomic coordinates, isotropic displacement parameters, background, and magnetite magnetic moments, totalling approximately 50 independent variables. Literature structures for corundum (Cox *et al.*, 1980), magnetite (Fleet, 1981), and zircon (Finger, 1973) were used as starting points in the refinements. The magnetite nuclear and magnetic contributions were calculated separately to simplify the process of turning on or off the magnetic intensities. The nuclear structure for the magnetite was the cubic inverse-spinel structure in Fd-3 m. The ferrimagnetic structure of magnetite was modelled in a rhombohedral cell with the Shubnikov BNS space-group *R*-3*m*′ (166.101) (Belov *et al.*, 1955), with the scale factor

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linked to the parent spinel to account for the different cell volumes. With a phase fraction of only 19 wt% Fe_3O_4 one would not expect a refinement of the magnetic moments to be particularly accurate. Values for the moments were entered and fixed to yield the expected net moment of $4\mu_B$ per formula unit. As expected, refining the values of the individual moments did not impact the quality of fit significantly with a shallow minimum, the net moment varying between approximately 3–5μ_B.

Thermal diffuse scattering can be significant in the high-Q (low d-spacing) region of the POWGEN data. This was modelled using a Q-dependent background function, the equations of which are described as background function number 4 in the GSAS manual (Larson and Von Dreele, 1994). A 12-term Chebychev polynomial was used as an alternative simpler background function. The QPA values were calculated using the default Hill and Howard standard-less methodology (Hill and Howard, 1987), with the inherent assumptions that the sample was 100% crystalline and all phases present in the sample were accounted for. The errors quoted are those generated mathematically from the least-squares matrix and should not be taken as real estimated standard deviations. The simpler background for the C2 constant-wavelength data was modelled using a nine-term Chebychev polynomial. The effect of using the robust refinement approach on a refinement of the C2 data was examined by addition of the TOPAS macro code developed by Stone *et al.* (2009) to the refinement.

Comparisons between the refined and literature QPA values were undertaken with a couple of different measures. Taking a simplistic approach to the results, a difference between refined and weighed values relates to the accuracy in an everyday context; however, it makes no allowance for the relative abundance of the phases. For this reason the relative bias was calculated as described by Madsen *et al.* (2001) where:

$$\text{Relative bias}\,(\%) = 100 \times \frac{|\text{refined} - \text{weighed}|}{\text{weighed}}. \quad (1)$$

III. RESULTS AND DISCUSSION

A summary of the results from the different instruments is shown in Table II.

The refined phase fractions were found to be strongly affected by inadequate modelling of the high-Q background in the TOF data. The POWGEN detector arrangement at the time that these data were collected (2014) had five detector modules in the short d-spacing backscattering region vs. a single detector in the long d-spacing forward scattering region. This had a dramatic effect on the counting statistics across the pattern, strongly biasing them towards the high-Q (low d-spacing) region as hinted at by the shapes of the cumulative χ^2 curves. Such weighting makes sense when trying to extract subtle structural details such as anisotropic displacement parameters but complicates matters for QPA where easily resolved reflections are beneficial. The forest of reflections in the high-Q region becomes even more complex when multiple phases are present so the behaviour of the real background becomes even more difficult to fit in a realistic manner with a simple polynomial. Consequently, using a more simplistic background function had a more deleterious effect; when using a 12-term Chebychev polynomial the corundum and zircon errors climbed to over 2 wt% each.

A combination of the fall-off of the magnetic peak intensities because of the magnetic form factor, and POWGEN statistics being heavily biased towards high-Q meant that the lack of a magnetic phase in the refinement did not adversely affect the results. The nature of POWGEN's statistics and lack of impact of the missing magnetic intensities can be seen visually in the shape of the cumulative χ^2 curves in Figures 1(a) and 1(b). Although misfits at the longer d-spacing are more noticeable to the eye, the effect on the least-squares was minimal. Displacement parameters are known to affect the quality of QPA results (Gualtieri, 2000), yet structural parameters are rarely refined during such an analysis because of the potential for correlations from massive peak overlap. The redundancy in the TOF data (total of 9476 phase reflections between 0.3 and 5.1 Å) in this case was sufficient that refinement of atomic positions and isotropic displacement parameters in such simple structures could be refined to values very close to those of the starting models. Comparisons of the starting and finishing models for each phase are shown in Supplementary Tables I-III. As one would expect the errors were larger for the minority magnetite phase but the values obtained were still very close to those of Fleet (1981). A pdCIF file detailing the nuclear/magnetic structures and Rietveld refinement is also deposited as Supplementary Material and may be read using pdCIFplot (Toby, 2003). The reported CIF value of shift/su_max (largest ratio of the final least-squares parameter shift to the final standard uncertainty) was 5.7×10^{-4}, demonstrating that the refinement was stable.

Reactor-based constant-wavelength neutron data potentially have one major advantage and one disadvantage over TOF data. The background is usually flatter and simpler to fit, but the lack of high-Q data reduces the number of

TABLE II. Refined QPA phase fractions, maximum absolute error, and maximum relative bias obtained from POWGEN and C2 data.

	Al_2O_3 (wt%)	Fe_3O_4 (wt%)	$ZrSiO_4$ (wt%)	Max absolute error (wt%)	Max relative bias (%)	R_{wp} (%)
Weighed	50.46	19.64	29.90			
POWGEN magnetic structure Q-dependent bkg	51.1 (4)	19.4 (2)	29.5 (4)	0.6	1.26	3.36
POWGEN without magnetic structure Q-dependent bkg	51.1 (4)	19.6 (3)	29.3 (5)	0.6	1.26	3.97
POWGEN magnetic structure Chebychev bkg	52.8 (3)	19.4 (2)	27.9 (3)	2.3	7.02	2.95
POWGEN without magnetic structure Chebychev bkg	52.6 (3)	19.6 (3)	27.8 (4)	2.1	7.02	3.58
C2 with magnetic structure	51.6 (7)	20.6 (4)	27.7 (8)	2.2	7.36	3.60
C2 without magnetic structure	50.9 (13)	21.9 (9)	27.3 (14)	2.6	8.70	7.85
C2 with magnetic structure (robust)	50.7 (3)	20.0 (1)	29.3 (3)	0.6	1.26	4.14
C2 without magnetic structure (robust)	51.5 (2)	20.5 (1)	28.0 (2)	1.9	6.35	4.16

Results from analyses with and without the magnetic structure are given.

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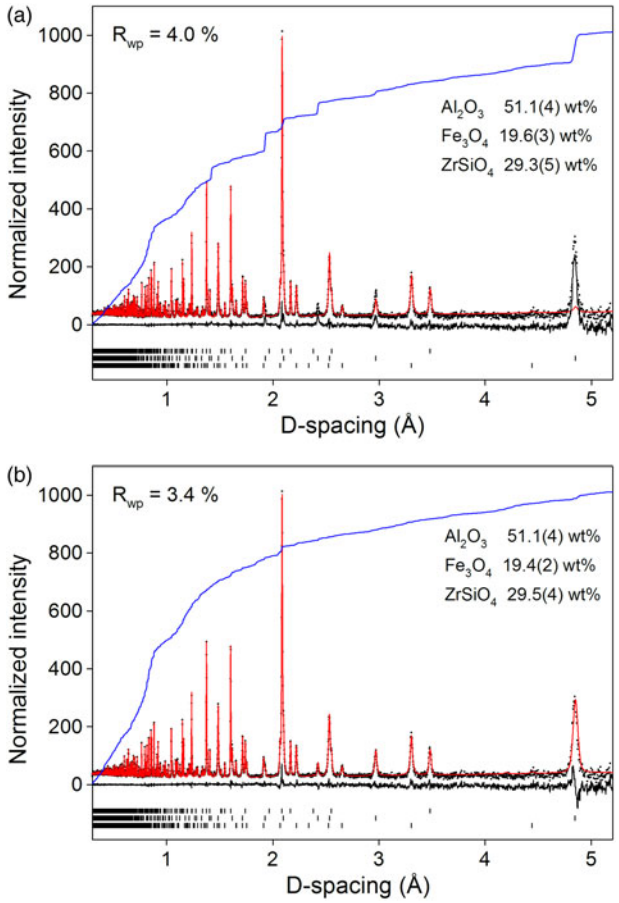

Figure 1. (Color online) Difference plot for the POWGEN refinement with a Q-dependent thermal diffuse background where the magnetic structure was (a) not modelled and (b) modelled. The cumulative χ^2 plot is the blue line.

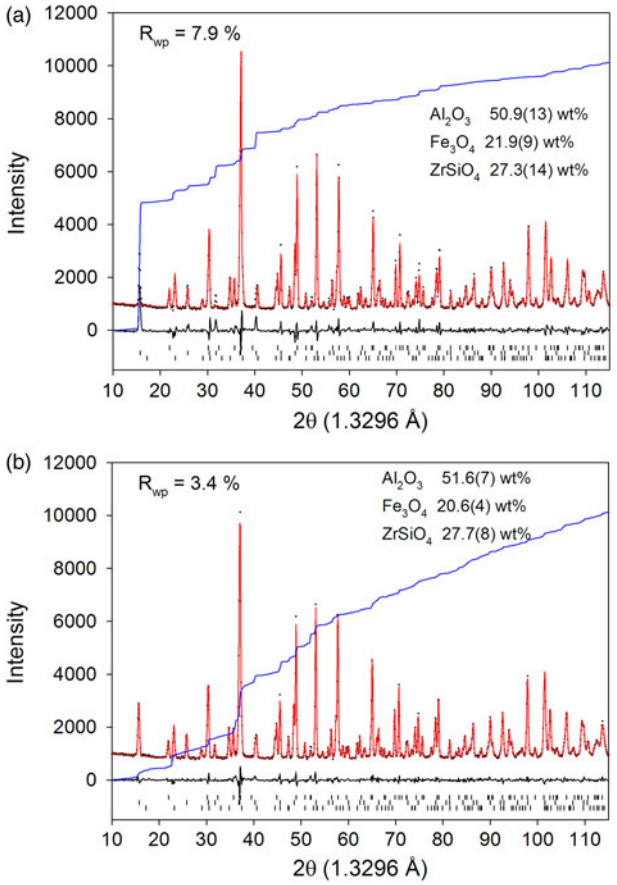

Figure 2. (Color online) Fit to the C2 data where the magnetic structure was (a) not modelled and (b) modelled. The cumulative χ^2 plot is the blue line.

reflections available for refinement. As previously mentioned it should also be more sensitive to misfits at low 2θ angles because of unfitted magnetic reflections as the counting statistics from constant wavelength data are usually Poisson in nature, relating directly to the relative peak intensities. The cumulative χ^2 plots for the fits to the C2 data in Figures 2(a) and 2(b) show how the misfits caused by the lack of intensity from the magnetic reflections impact the least-squares refinement significantly more than the POWGEN refinements in Figure 1.

The robust refinement approach (David, 2001) modifies the minimization of χ^2 during refinement by changing the weighting of the least-squares and as seen in Table II this had a beneficial effect on the overall result. The effect of the robust refinement on the least-squares minimization when ignoring the magnetic intensities can be seen in the shape of the cumulative χ^2 plot shown in Figure 3 compared with normal weighting shown in Figure 2(a). Robust refinement was beneficial whether the magnetic intensities were included or not, but had an additive effect when used together with fitting of the magnetic intensities. Use of robust refinement weighting had no effect on refinement of POWGEN data as the statistics in POWGEN TOF data already significantly under-weighted the least-squares minimization in the region of the pattern where the magnetic reflections appeared.

A comparison of the POWGEN result with those submitted from neutron instruments during the round robin is shown in Table III in terms of the maximum relative bias obtained. It is not known whether any of the participants added the magnetic structure in their refinement as this information was not recorded by the organizers. All but one used GSAS for the refinement so it was feasible. In the round robin results, data from the TOF instruments yielded better results than the CW instruments except for participant #198. The small relative bias in that constant wavelength case suggests that a magnetic model was added to the refinement. The best POWGEN

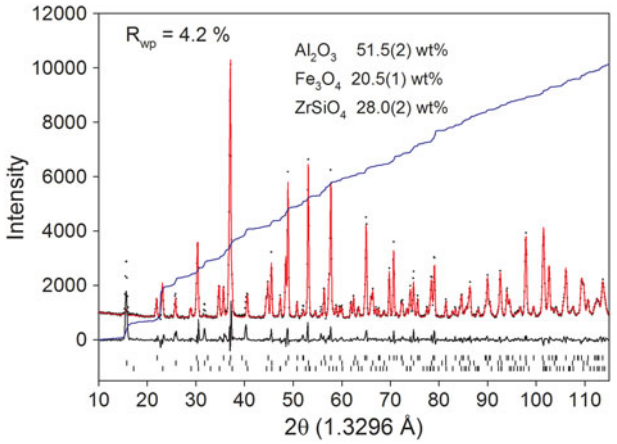

Figure 3. (Color online) Fit to the C2 data where the magnetic structure was not modelled and a robust refinement weighting applied. The cumulative χ^2 plot is the blue line.

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TABLE III. Comparison of selected POWGEN and C2 results with the participants in the CPD round robin who submitted neutron data for sample #4.

CPD round robin participant number	Maximum relative bias (%)	Technique	Software
157	48.72	CW	GSAS
198	2.55	CW	GSAS
205	6.35	TOF	GSAS
208	7.54	CW	LHPM
209	3.58	TOF	GSAS
POWGEN (high-Q bkg & magnetic structure)	1.26	TOF	TOPAS
POWGEN (Chebychev bkg & magnetic structure)	7.02	TOF	TOPAS
POWGEN (high-Q bkg)	1.26	TOF	TOPAS
POWGEN (Chebychev bkg)	7.02	TOF	TOPAS
C2	8.70	CW	TOPAS
C2 (magnetic structure)	7.36	CW	TOPAS
C2 (magnetic structure and robust refinement)	1.26	CW	TOPAS

Data courtesy of Ian Madsen (CSIRO).

results were significantly better than those obtained in the round robin, the maximum relative bias being half of that of the best round robin result. The results highlight the importance of modelling the high-Q background in TOF data to obtain accurate QPA results, and the insensitivity of a refinement using TOF data to a magnetic structure modifying the low-Q reflections. Analysis of the results from C2 suggest that use of the robust refinement methodology together with fitting the magnetic contribution can significantly improve the accuracy of the refinement, matching the accuracy of the POWGEN data, and improving upon the analysis of the same data reported to the CPD organizers.

IV. CONCLUSION

That accurate QPA results can be obtained from difficult samples using X-rays is not in doubt as demonstrated by competitors in the Reynold's Cup run by the Clay Minerals Society (Omotoso *et al.*, 2006). Additionally, using neutron powder diffraction data for QPA is no guarantee of success as shown by the round robin results of Scarlett *et al.* (2002). However, the lack of microabsorption and large sampling volumes means that accurate results are possible with coarse samples that are practically impossible using X-rays. This makes neutron diffraction particularly useful for *in-operando* studies where accurate QPA results are required from samples with no prospect of any sample preparation. The presence of a magnetic phase in sample #4 added a complication to the analysis of neutron diffraction data not present in X-ray data, but the presence of magnetic phases in many mineral samples and functional materials meant this was not a unique case. Analysis of data collected on POWGEN and C2 showed that it is possible to obtain results with less than 1 wt% accuracy from this challenging mixture without any form of sample preparation. The relative statistics in the POWGEN TOF data and d-spacing dependence of the magnetic form factor effectively cancelled each other out, leaving the high-Q background as the major contribution to errors in the phase fractions. With constant-wavelength neutron data improvements could be made by either modelling the magnetic intensities or using robust refinement, but an accuracy equalling that of the TOF data could be obtained by using both together. The results give some confidence that accurate QPA results should be possible during complex, *in-operando* experiments on powder diffractometers at both reactor and spallation sources by taking reasonable care during analysis. In common with observations from the IUCr CPD round robin, the residuals indicating quality of fit of a Rietveld refinement did not necessarily indicate accuracy of the QPA results.

SUPPLEMENTARY MATERIAL

The supplementary material for this article can be found at http://dx.doi.org/10.1017/S088571561600021X.

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