

3. METHODOLOGY

curve (Bordas *et al.*, 1977; Buras *et al.*, 1979) or by an expansion of a power function (Glazer *et al.*, 1978). Alternatively, it may be determined experimentally by the use of standards measured under the same conditions as the experiment (Scarlett *et al.*, 2009). This latter approach allows some separation of the contributions from the instrument and the sample, and allows some degrees of freedom in the refinement of sample-related parameters that may be of benefit in dynamic experiments. Other contributions to the diffraction pattern that must also be accounted for include any fluorescence peaks arising from the sample or shielding or collimators, and any detector escape peaks from both diffracted and fluorescence peaks. Fluorescence peak positions and relative intensities should be constant throughout the measurement and may therefore be modelled using a fixed 'peak group' whose overall intensity can be refined during analysis. Escape peaks can be accounted for by the inclusion of a second phase identical to the parent phase but with an independent scale factor and a constant energy offset determined by the nature of the detector (Rowles *et al.*, 2012).

Currently, few Rietveld software packages are capable of dealing directly with the differences between EDD and ADD, specifically (i) the variance of structure factors as a function of energy, (ii) the nonlinear distribution of intensity in the incident beam as a function of energy further modified by a nonlinear detector response, and (iii) the preferential absorption of lower-energy X-rays by the sample/air. *TOPAS* (Bruker AXS, 2013) embodies algorithms that allow the pattern to be modelled directly on the energy scale and also the inclusion of equations to account for intensity variations arising from the experimental conditions. This allows quantification from such data to be achieved directly using Rietveld-based crystal-structure modelling incorporating the Hill and Howard algorithm in equation (3.9.26) (Hill & Howard, 1987). The application of *TOPAS* to a complex EDD experiment investigating the changes to the anode during molten-salt electrochemistry conducted in molten CaCl₂ at about 1223 K has been described by Rowles *et al.* (2012) and Styles *et al.* (2012).

3.9.10. Improving accuracy

There are many factors that influence the accuracy and precision of QPA results where (i) accuracy is defined as the agreement between the analytical result and the true value, and (ii) precision is the agreement between results if the analysis is repeated under the same conditions. Precision may further be split into (i) repeatability, which is the agreement between repeated measurement and analysis of the same specimen, and (ii) reproducibility, which additionally includes re-preparation, measurement and analysis of the sample.

3.9.10.1. Standard deviations and error estimates

Determination of the actual accuracy of an analysis is not a trivial task in a standardless method. In fact, it cannot be achieved without recourse to another measure of the sample that does incorporate standards. Too often, analysts will report Rietveld errors calculated in the course of refinement as the errors in the final quantification. However, these numbers relate purely to the mathematical fit of the model and have no bearing on the accuracy of the quantification itself.

Consider, for example, a three-phase mixture of corundum, magnetite and zircon. Such a sample was presented as sample 4 in

Table 3.9.4

Comparison of errors generated during the analysis of XRD data (Cu K α radiation) from three sub-samples of sample 4 from the IUCr CPD round robin on QPA (Scarlett *et al.*, 2002)

The bias values are (measured – weighed) while the values denoted XRF are the phase abundances generated from elemental concentrations measured by X-ray fluorescence methods.

<i>n</i> = 3	Phase		
	Corundum	Magnetite	Zircon
Weighed	50.46	19.46	29.90
Mean XRD measured wt%	56.52	17.06	26.42
Mean of Rietveld errors	0.15	0.11	0.11
Standard deviation of measured wt%	0.63	0.41	0.35
Mean of bias	6.06	–2.58	–3.48
XRF	50.4(2)	19.6(1)	29.5(1)

the IUCr CPD round robin on QPA (Scarlett *et al.*, 2002). Its components were chosen with the deliberate aim of creating a sample in which severe sample-related aberrations occur. Table 3.9.4 shows the weighed amounts of each component and the results of replicate analyses of three different sub-samples of this material.

It is apparent that the standard deviation of the mean abundances of the three replicates, which represents the expected precision in the analysis, is 3 to 4 times greater than the errors reported by the Rietveld software. The good level of fit achieved in conducting these analyses (evidenced by low *R* factors) could lead the analyst to conclude that the mean value \pm the standard deviation of the mean is an adequate measure of the phase abundances and their errors.

However, both the Rietveld errors and the precision are at least an order of magnitude smaller than the bias. The large bias, in this case due to the presence of severe microabsorption, represents the true accuracy that can be achieved in this example. Unfortunately, there is nothing in the XRD data and Rietveld analysis process that indicates that there may be a problem. It is only when the QPA is compared with other estimates, in this case derived from XRF chemical-analysis results, that the problem becomes apparent. The analyst must take further steps to identify sample-preparation and/or data-collection protocols that may improve accuracy and, importantly, seek ways to verify the results.

3.9.10.2. Minimizing systematic errors

The fundamental measured quantities in a diffraction pattern are the integrated intensities of the observed peaks. The precision of these measurements can be improved by: (i) increasing the primary intensity of the diffractometer using optics or higher-power X-ray sources; (ii) using scanning linear detectors (see Chapter 2.1), which have multiple detector elements to collect individual intensities many times; these are then summed to achieve higher accumulated counts; (iii) increasing the number of counts accumulated at each step, that is increasing the step counting time *T*; and (iv) increasing the number of points, *N*, measured across the peak.

Often, the temptation is to collect data with large values of *N* and *T* to maximize counting statistics. However, the resulting increased precision is only useful up to the point where counting variance becomes negligible in relation to other sources of error; thereafter data-collection time is wasted. For example, if the sample is affected by the presence of severe sample-related