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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 $CaCl_2$ 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 $K\alpha$ 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.

	Phase		
$n = 3$	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 ± 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

aberrations, the collection of highly precise data will not improve the accuracy of the resulting analysis significantly.

Therefore, the most important approach to improving the accuracy of an analysis is to eliminate the systematic errors. Given that the largest sources of error in QPA are experimental (Chung & Smith, 2000) and relate to sampling and specimen preparation, then this is the area on which the most careful attention needs to be focused. A detailed discussion of sample preparation and data-collection procedures is beyond the scope of this chapter but further details can be found in Chapter 2.10, and in Hill & Madsen (2002) and Buhrke *et al.* (1998).

3.9.10.3. *Minimizing sample-related errors*

3.9.10.3.1. *Crystallite-size issues*

Crystallite size is considered here as the length of a coherent scattering domain and should not be confused with the terms grain or particle size used frequently in powder diffraction to describe the macroscopic size of the components in the sample. The macroscopic size of the particle is somewhat irrelevant (as in ceramics or other solid pieces of samples) as long as the crystallites (or domains) that comprise the particle are (i) sufficiently small to ensure that there are enough crystallites contributing to the diffraction process (Smith, 1992) and (ii) randomly oriented, thus ensuring a true powder-average representation of intensities. However, for large domains or crystallites this assumption is usually not fulfilled and therefore it is necessary to reduce the crystallite size by reducing the size of the particles or grains that constitute the macroscopic objects of a powder.

Most issues in sample preparation are related to crystallite size and preferred orientation of the particles in the sample holder. For QPA a representative sampling of all possible orientations of crystallites with respect to the diffraction geometry is required. Rotation of the sample improves the particle statistics, since more crystallites can satisfy the diffraction condition (Elton & Salt, 1996).

Large-crystallite issues are easily detected using two-dimensional (2D) detectors, where the Debye rings show a 'spotty' intensity distribution. However, most QPA measurements are performed using 0D (point) or 1D (strip) detectors. The effect of large crystallites in a 1D pattern is that a few crystallites may contribute to irregularly high intensities for selected reflections. In the diffraction pattern, this situation is usually identified by intense reflections having a sharp peak profile compared with the surrounding peaks in the pattern. Furthermore, in a Rietveld refinement this situation is manifested by large intensity differences between the observed and calculated pattern that may not be associated with a particular crystallographic direction and hence to preferred orientation. Another way of detecting inhomogeneous crystallite distributions is to measure a series of scans from the same specimen at various rotation angles and comparing the relative peak intensities. It is worth noting that the push towards ever higher resolution in both laboratory and synchrotron instruments serves to further exacerbate the crystallite-size issue. This arises from the use of beams with decreased divergence, resulting in fewer crystallites likely to satisfy the diffraction condition.

There is no simple mathematical correction for large-crystallite issues and the effect is often misinterpreted in Rietveld refinement as preferred orientation. In this case, the correction would typically involve use of several directions for March–Dollase-type functions (Dollase, 1986) or an increasing order of spherical-harmonics coefficients (Ahtee *et al.*, 1989). In any case, this is an improper use of these corrections and the necessity to do so clearly points to deficiencies in the sample preparation and data-collection regime.

The best way to minimize the large-crystallite issue is to reduce the crystallite size through grinding of the sample. However, size-reduction methods need to be carefully assessed, since overgrinding can cause peak broadening due to (i) a decrease of long-range order and hence crystallite size and (ii) the introduction of microstrain (Hill & Madsen, 2002). The practical effect of peak broadening is increasing peak overlap, which may complicate the phase identification. For whole-pattern-based QPA, overgrinding is not as serious as long as it does not yield nanometre-sized particles or amorphous materials. This is because the integral intensity of the peaks is preserved. It should be noted that some phases can undergo transformation to other polymorphs or decompose to other phases during grinding (Hill & Madsen, 2002).

In practice, there is no generally applicable comminution strategy. For each material, a suitable milling device and grinding strategy needs to be identified. Inhomogeneous materials such as ores, concentrates and other mineralogical materials may have very different comminution properties for their constituents, leading to size fractionation during grinding. Large-crystallite issues are frequently observed for hard minerals (*e.g.* quartz, feldspar) while the grain size of soft minerals (*e.g.* talc) is reduced more rapidly.

A practical way of finding a best compromise for the milling conditions of a mixture may be the analysis of a series of samples of the same material where, for example, the grinding time is successively increased and the quantification results are compared. Fig. 3.9.17 shows the variation of analysed wt% with grinding time for two minerals: a stable result is eventually obtained.

There is a more extensive discussion of the impact of large-crystallite size on observed diffraction data (Smith, 1992) and ways to minimize its effect (Elton & Salt, 1996) in the published literature.

3.9.10.3.2. *Preferred orientation*

In order to generate peak intensities that accurately represent the intensity-weighted reciprocal lattice, the crystallites in the powder must not only be sufficient in number, but they must also be randomly oriented. In other words, each crystal orientation should have the same probability of diffracting. Preferred orientation can arise when particles align in the sample holder according to their morphology. This is most common with platy or
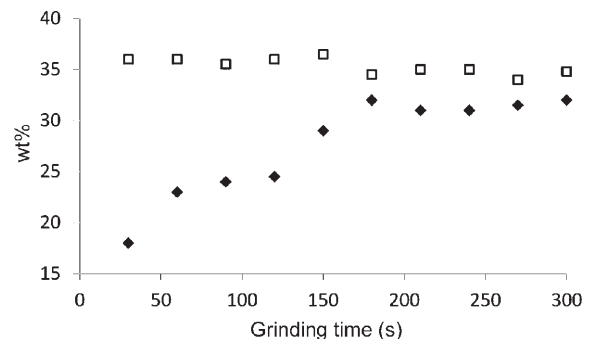

Figure 3.9.17
Variation of the magnetite (filled diamonds) and quartz (open squares) concentration of an iron-ore sample with grinding time. Stable conditions are obtained after about 180 s. Data courtesy ThyssenKrupp – Resource Technologies (Knorr & Bornefeld, 2013).