3.9. QUANTITATIVE PHASE ANALYSIS

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 over-grinding 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
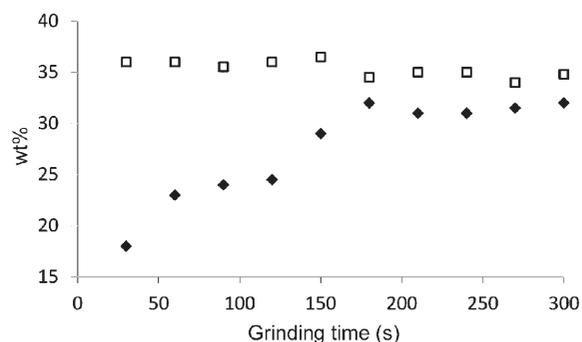

Figure 3.9.17
Variation of the magnetite (filled diamonds) and quartz (open squares) concentration of an iron-ore sample with grinding time. Stable conditions are obtained after about 180 s. Data courtesy ThyssenKrupp – Resource Technologies (Knorr & Bornefeld, 2013).

needle-like materials and the effect on the diffraction pattern is the observation of enhanced intensity along specific crystallographic directions with a subsequent decrease of intensity along other directions.

A number of sample-presentation methods can be used to minimize preferred orientation. For flat specimens, back pressing and side drifting into the sample holder can be effective. These methods tend to produce much less preferred orientation than front-mounted samples, but tend not to be very effective for chronic preferred orientation such as that exhibited by phases like clays, feldspars and chlorite. Reducing the size of the crystallites improves the probability of achieving random alignment of the crystallites in the sample holder. Gradually milling a sample and monitoring the preferred-orientation coefficients as a function of grinding time may again help to find the correct, or at least reproducible, grinding conditions (Fig. 3.9.18).

A major advantage of whole-pattern-based QPA over single-peak methods is that all classes of reflections are considered in the calculation. In this sense, the method is less prone to preferred orientation of a particular class of peaks. Furthermore, orientation effects may be corrected by applying March–Dollase (Dollase, 1986) or spherical-harmonics (Ahtee *et al.*, 1989) corrections. A properly applied correction may be of high importance for QPA in cases where a phase is present at low concentration and only a few peaks can clearly be identified in the pattern. If those peak(s) are affected by preferred orientation, the March–Dollase coefficient correlates strongly with scale factors and leads to biased QPA results. Examples of this effect occur with layered materials that have sheet-like morphology perpendicular to the c axis, including mica and clay minerals, which typically show stronger than expected intensity for the 00l reflections.

The crucial factor seems to be to what extent the orientation parameters correlate with the Rietveld scale factor. An example where the correlation is only minor is sample 2 from the IUCr CPD round robin on QPA (Scarlett *et al.*, 2002). In that example, brucite [$Mg(OH)_2$] shows strong preferred orientation along the 00l direction. This may be corrected by the March–Dollase model, which returns a refined value of 0.66. However, the introduction of this preferred-orientation correction only changes the brucite concentration from 35 to 36 wt% (weighed = 36.36 wt%); this is surprising because the orientation is strong and the weighted residual R_{wp} changes from 30 to 15%. Close examination of the correlations reveals a strong correlation between the brucite scale factor and preferred-orientation factor.
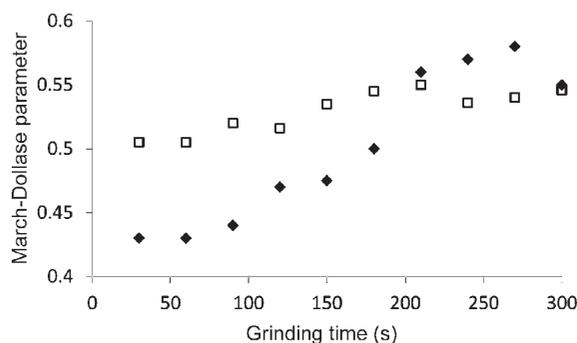

Figure 3.9.18
Increase of the March–Dollase (Dollase, 1986) parameter and related decrease of the degree of preferred orientation with grinding time for the two amphibole species actinolite (filled diamonds) and grunerite (open squares) in an iron ore. Data courtesy ThyssenKrupp – Resource Technologies (Knorr & Bornefeld, 2013).

However, the correlation of the brucite preferred-orientation parameter to the other scale factors (zincite, corundum and fluorite) is close to zero; this explains why in this example the QPA is not highly dependent on preferred orientation. In cases of strong correlation between the orientation parameter of one phase and the scale factors of other phases, preferred orientation should probably not be refined, or at least it should be verified carefully. It is worth noting that, in all Rietveld-based analyses, users should examine the correlation matrix as a matter of general practice to establish which parameters might be affecting parameters of interest.

It should be noted that sample rotation around the scattering vector (typically employed in flat-plate Bragg–Brentano geometry) during the scan does not reduce preferred orientation, since there is no change between the preferred-orientation direction and the diffraction vector. Using capillaries in transmission geometry assists in the reduction of preferred orientation, but the time-consuming nature of packing capillaries makes this technique infeasible in industrial applications where diffraction-based QPA is used for routine quality control.

3.9.10.3.3. *Microabsorption*

The strongest on-going impediment to accuracy in QPA using XRD data is microabsorption. The microabsorption effect occurs when a multiphase sample contains both low- and highly absorbing phases. For the highly absorbing phases, the X-ray beam is more likely to be absorbed in the surface layers of the grain; thus, the fraction of the grain contributing to the diffraction pattern will decrease as the size of the grain increases above the beam-penetration depth. For the low-absorbing phases, the beam penetrates further into the particle resulting in a greater likelihood of the desired 'volume diffraction' occurring (Brindley, 1945). The overall effect is the observation of a disproportionate amount of observed intensity from individual grains relative to what would be expected for the average absorption of the sample; the highly absorbing phases are under-represented relative to the low-absorbing phases. There is extensive discussion of the microabsorption issue in Zevin & Kimmel (1995).

Brindley (1945) has described the particle absorption contrast factor τ_α as

$$\tau_\alpha = (1/V) \int_0^V \exp\left(-(\mu_\alpha - \bar{\mu})\right) \mathrm{d}v, \qquad (3.9.48)$$

where V is the particle volume, and μ_α and $\bar{\mu}$ are the linear absorption coefficients of phase α and the entire sample, respectively. While it is relatively easy to calculate the absorption coefficients, equation (3.9.48) implies knowledge of the *particle* size of each component; this information is only available through independent microscope or light-scattering characterization.

This correction term is commonly incorporated into QPA through a modification to equation (3.9.26) of the form

$$W_\alpha = \frac{S_\alpha (ZMV)_\alpha / \tau_\alpha}{\sum_{k=1}^n S_k (ZMV)_k / \tau_k}. \qquad (3.9.49)$$

Brindley has also devised criteria by which to assess whether a microabsorption problem is likely to be present or not. Calculation of μD (where μ is the linear absorption coefficient and D is the particle diameter) yields the following criteria:
  (i) $\mu D < 0.01$ – fine powder. There is negligible microabsorption and hence no correction is necessary.