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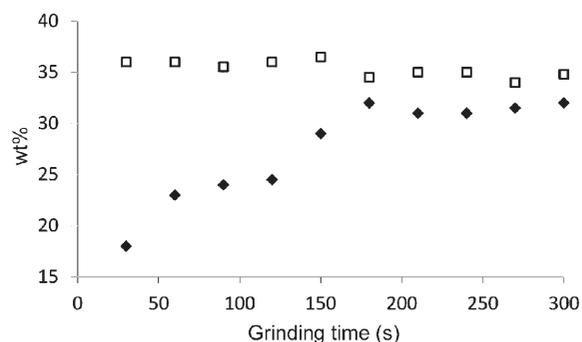
Figure 3.9.17
Variation of the magnetite (filled diamonds) and quartz (open squares) concentration of an iron-ore sample with grinding time. Stable conditions are obtained after about 180 s. Data courtesy ThyssenKrupp – Resource Technologies (Knorr & Bornefeld, 2013).

references