

3. METHODOLOGY

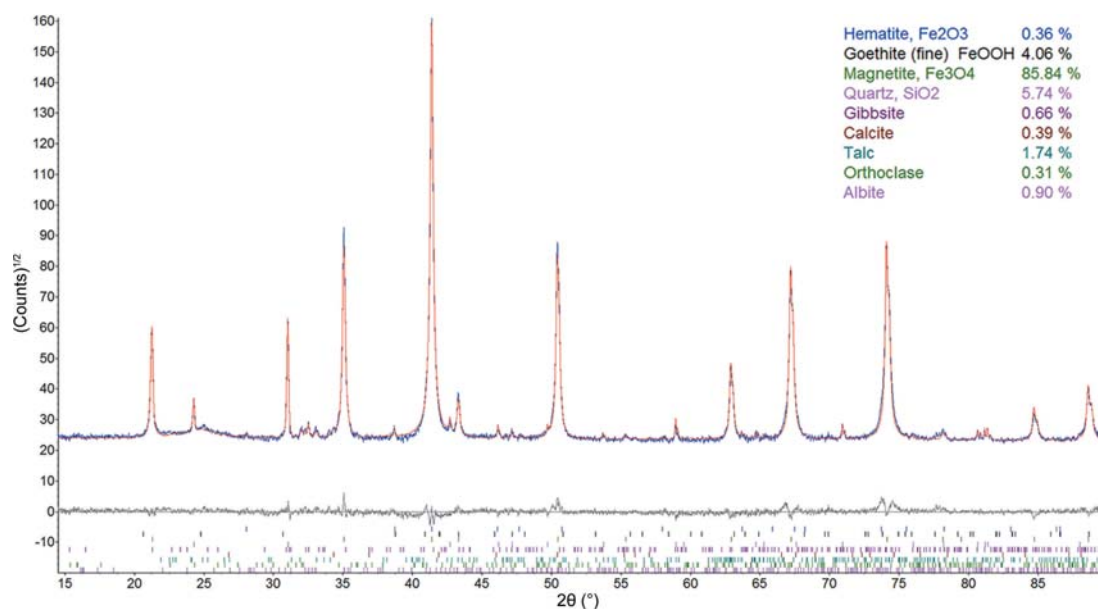


Figure 3.9.22

Output of Rietveld refinement and results of QPA for the iron-ore certified reference material SX 11-14 from Dillinger Hütte. The data were measured with Co $K\alpha$ radiation.

Finally, a number of inter-laboratory tests, or round robins, have been conducted on synthetic mixtures in order to set benchmarks for particular materials and/or the application of methods. Examples range from well ordered, high-symmetry phases discussed in earlier sections of this chapter (Madsen *et al.*, 2001; Scarlett *et al.*, 2002) to standard mixtures of geological material, granite and bauxites (Bish & Post, 1993), and technical products like artificial Portland cements (De la Torre & Aranda, 2003) where relative biases of 2–3% for the main phases and 5–10% for minor phases were found.

Very recently, the precision and accuracy of QPA for the analysis of Portland clinker and cement were determined for synthetic mixtures and commercial samples. The scatter of the results from the inter-laboratory comparison, and the fact that individual errors are much smaller than the standard deviations of all submitted results, points to the widespread presence of user-dependent systematic errors (Léon-Reina *et al.*, 2009).

One of the most challenging round robins is the Reynolds Cup (Ottner *et al.*, 2000; McCarty, 2002; Kleeberg, 2005; Omotoso *et al.*, 2006; Raven & Self, 2017), organized biannually since the year 2000 by the Clay Minerals Society. Synthetic mixtures representing typical sedimentary rock types are analysed and require a very high level of sample preparation and analytical skills because of the presence of a variety of clay minerals.

While most round robins have dealt with inorganic materials, one for pharmaceutical materials was organised by the International Centre for Diffraction Data (ICDD) together with the Pharmaceutical Powder XRD symposium series (PPXRD) (Fawcett *et al.*, 2010). A major outcome was the identification of operator errors in all steps of the analysis to be the largest source of error. This highlights the importance of reducing systematic errors for improving accuracy in QPA.

As a concluding remark, a variety of factors may influence the precision and accuracy of QPA. Nonetheless, better than 1 wt% agreement may be achieved for simple systems of well crystallized material. Moderately complex mixtures such as those routinely observed in cement plants and in the mining industry can be typically analysed at a 1 wt% level of accuracy provided that the analyst chooses the most appropriate sample-

preparation, data-collection and analysis methodologies for the samples in question.

3.9.11. Summary

The value in using diffraction-based methods for the determination of phase abundance arises from the fact that the observed data are derived directly from the crystal structure of each phase. Knowledge of phase abundance is valuable in many fields including (i) mineral exploration, where the type and amount of major minerals serve as indicators for valuable minor minerals, (ii) mineral extraction, where the performance of the process line is governed by the mineralogy, not the commonly used elemental compositions, (iii) *in situ* studies, where the mechanism and kinetics of phase evolution resulting from the application of an external variable can be examined and (iv) the optimization of production conditions for advanced materials.

The methodology of QPA is fraught with difficulties, many of which are experimental or derive from sample-related issues. Hence, it is necessary to verify diffraction-based phase abundances against independent methods. This should include calculation of the expected sample element composition (using the QPA and an assumed or measured composition of each phase) and comparing these values with the measured element composition. In those circumstances where this is not possible, the QPA values should be regarded only as semi-quantitative. While such values may be useful for deriving trends within a particular system, they cannot be regarded as an absolute measure.

References

- Ahtee, M., Nurmela, M., Suortti, P. & Järvinen, M. (1989). Correction for preferred orientation in Rietveld refinement. *J. Appl. Cryst.* **22**, 261–268.
- Alexander, L. E. & Klug, H. P. (1948). *Basic aspects of X-ray absorption in quantitative diffraction analysis of powder mixtures*. *Anal. Chem.* **20**, 886–889.
- Ballirano, P. & Caminiti, R. (2001). Rietveld refinements on laboratory energy dispersive X-ray diffraction (EDXD) data. *J. Appl. Cryst.* **34**, 757–762.
- Barnes, P., Colston, S., Craster, B., Hall, C., Jupe, A., Jacques, S., Cockcroft, J., Morgan, S., Johnson, M., O'Connor, D. & Bellotto, M.