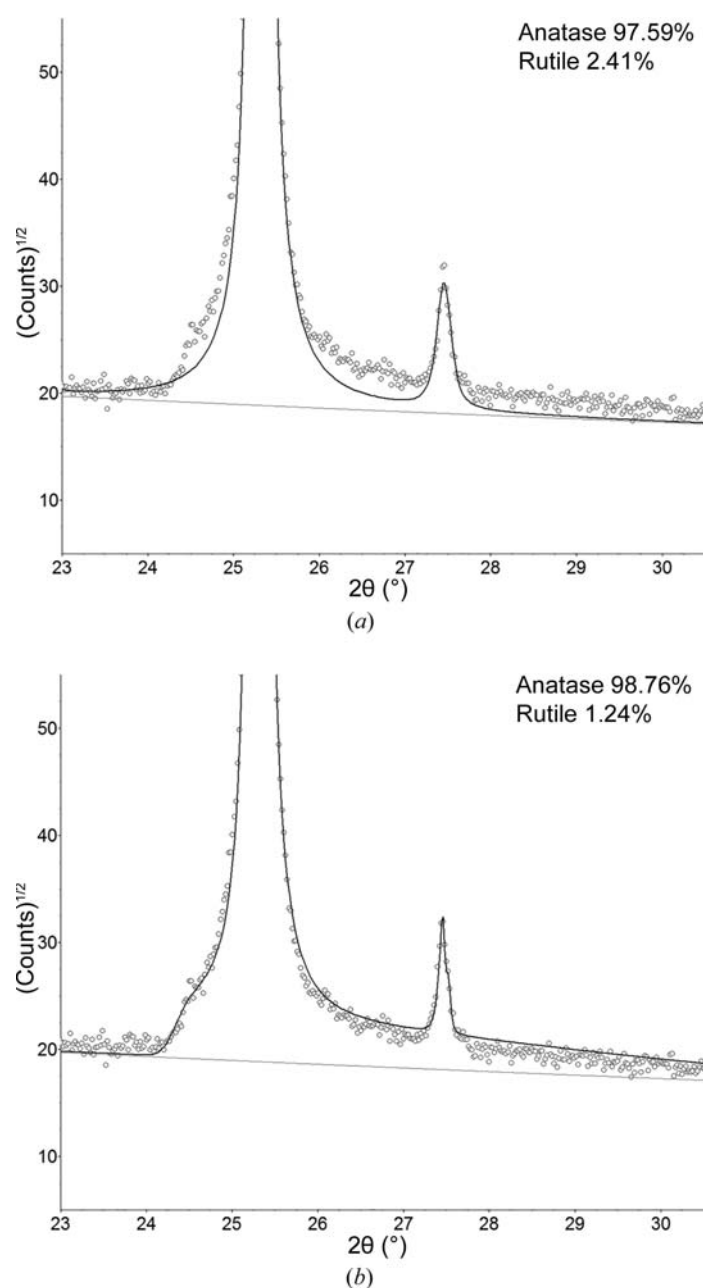


3.9. QUANTITATIVE PHASE ANALYSIS

Table 3.9.6

Compositional analysis of the Dillinger Hütte iron-ore certified reference material SX 11-14, (i) derived from QPA results, taking into account the nominal stoichiometry of the phases (XRD) and (ii) the certified analyses (Cert) (Knorr & Bornefeld, 2013)

Phase	wt%		Fe	FeO	SiO ₂	Al ₂ O ₃	MgO	CaO	K ₂ O	Na ₂ O	C
Haematite	0.37		0.26	—	—	—	—	—	—	—	—
Goethite	3.86		2.43	—	—	—	—	—	—	—	—
Magnetite	85.97		62.21	26.68	—	—	—	—	—	—	—
Quartz	5.73		—	—	5.73	—	—	—	—	—	—
Gibbsite	0.71		—	—	—	0.46	—	—	—	—	—
Talc	1.79		—	—	1.13	—	0.57	—	—	—	—
Orthoclase	0.30		—	—	0.19	0.05	—	—	0.05	—	—
Albite	0.89		—	—	0.60	0.18	—	—	—	0.10	—
Calcite	0.40		—	—	—	—	—	0.22	—	—	0.19
			Fe	FeO	SiO ₂	Al ₂ O ₃	MgO	CaO	K ₂ O	Na ₂ O	C
		XRD	64.89	26.68	7.66	0.70	0.57	0.22	0.05	0.10	0.19
		Cert	65.55	27.20	7.47	0.27	0.56	0.42	0.06	0.08	0.12
		Bias	−0.66	−0.52	0.19	0.43	0.01	−0.20	−0.01	0.02	0.07

**Figure 3.9.21**

Profile fit of anatase and rutile (a) without and (b) with a $K\beta$ filter absorption-edge correction.

result may then be evaluated by comparing the calculated elemental abundances with those determined by traditional chemical-analysis techniques. However, for the best level of agreement, this method requires that the composition of the crystalline phases be well defined. A complication, in particular for minerals, is that idealized compositions may be reported but do not necessarily match the actual composition of the species present in the sample. Where possible, detailed phase analysis using microbeam techniques should be undertaken to establish the true composition for each phase. A complication that serves to decrease the agreement is that chemically based compositional analysis does not distinguish between crystalline and amorphous phase content, while the diffraction-based QPA usually measures only the crystalline phases. Generally, the composition of amorphous phases may not be known accurately and even highly crystalline material can contain amorphous components because of non-diffracting surface layers of the grains (Cline *et al.*, 2011).

An example demonstrating the level of agreement that can be achieved is that of the iron-ore certified reference material SX 11-14 from Dillinger Hütte (Fig. 3.9.22). The material is moderately complex and consists of nine distinct mineral species. The data were measured with Co $K\alpha$ radiation and analysed using Rietveld-based QPA in *TOPAS* (Bruker AXS, 2013). The phase abundances are converted to elemental and oxide compositions for comparison with the certified elemental analyses (Table 3.9.6). There is excellent agreement between the XRD results and the chemical analysis with bias values better than ± 1 wt%.

3.9.10.3.6. Phase-specific methods: diffraction SRMs, round-robin samples and synthetic mixtures

In contrast to elemental compositional analysis, where standard reference materials (SRMs) are widespread, there are only a very limited number of SRMs available for diffraction-based QPA. Prominent examples are SRMs for the cement industry [NIST reference material clinker 8486 (Stutzman & Leigh, 2000) and ordinary Portland cement NIST SRM 2686] or ceramics materials (silicon nitride CRM BAM-S001) (Peplinski *et al.*, 2004). Similar to elemental standards, the certified values do not necessarily represent the true composition. Rather, they are published values that are typically averaged over the results from different independent methods, instruments and laboratories. Therefore, confidence limits of concentrations are provided that may be much larger than estimated standard deviations of concentrations within a single laboratory.

3. METHODOLOGY

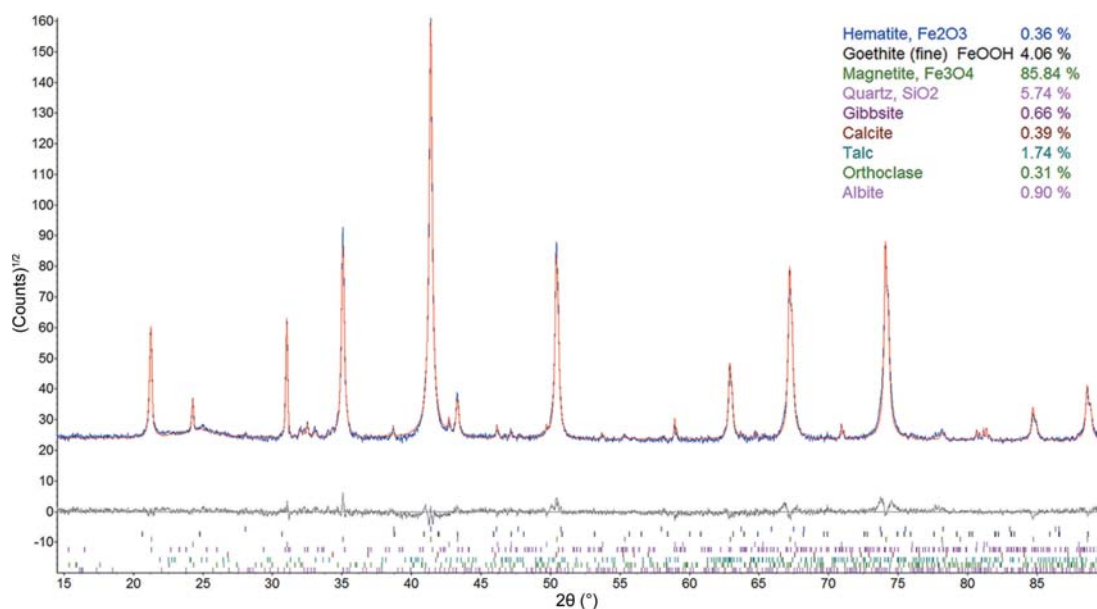


Figure 3.9.22

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.

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