



Lab Report XRD 79

Accuracy in quantitative X-ray mineralogy - Part 1: Fe-ore certified reference materials

X-ray diffraction (XRD) is a method for determining the mineralogy of ore. The combination of a fast detector integrated in the XRD instrument with TOPAS quantitative phase analysis (QPA) allows standard-less analysis within minutes even with a desktop instruments.

Basic results in iron ore analysis are amount and type of the iron bearing species for general quality and grade control of the run-off mine material. Knowing the gangue minerals and their composition determines the necessary steps of beneficiation before further processing of the ore. The oxidation state of iron can easily be calculated from the quantitative XRD result this determines the CO₂ footprint of iron plants.

The typical accuracy of QPA for well crystalline samples can be better 1 wt-%. This is proved by comparing the QPA result to traditional chemical analysis.

Why X-ray diffraction in mining

Quantitative phase analysis is frequently applied to the study of geologic materials in research and service laboratories, but also in quality control of mining operations. Understanding the properties of ore (minerals from which metals are extracted) and gangue (deleterious minerals that need to be separated from the ore) is of tremendous economic importance for the process mineralogy.

Physical properties that determine the processability of the material such as hardness, solubility, magnetism, or density are directly related to the crystal structure of the minerals and not to their chemical composition. Therefore, those properties directly influence processing conditions such as the method of separation (gravity, magnetic or dissolution), the method of metals extraction (leaching, flotation, smelting), costs of the operation through e.g. acid and other chemicals consumption, transport of material between the mine and different facilities in a processing plant, or simply the choice of the right mill and its energy consumption.

QPA using the Rietveld method and X-ray diffraction data is one of the few direct methods for obtaining the relative or

absolute phase abundances of crystalline and non-crystalline (amorphous or nano-crystalline) components in a mixture. The frequently asked question: “How accurate is this method?” is answered here for certified reference materials from Dillinger Hütte as an example for well crystallized ore.

How to assess accuracy

Accuracy is considered as closeness of the analytical result to the true value. The assessment of the accuracy of QPA is neither a simple nor a straightforward task. The true result of the analysis is a priori unknown. Even expected concentrations of synthetic mixtures are prone to experimental uncertainties e.g. errors of weighing. In general it is impossible to assess the accuracy of a single sample QPA analysis without having further information on composition or phase content.

The accuracy of the QPA result may be evaluated by comparing to traditional chemical analysis. The XRD based chemical analysis of a multi-phase mixture follows from the phase abundances and the known stoichiometry of the crystalline phases. This method requires the composition of the crystalline phases to be well defined. A complication – in particular for minerals – is that frequently idealized compositions are known only and the true composition of the species present in the specimen is not known. Furthermore, one needs to bear in mind that traditional elemental analysis does not distinguish between crystalline phase abundances and amorphous content. The composition of amorphous phases may be unknown or only partly known. Even well crystalline material may contain amorphous components due to non-diffracting surface layers of the grains.

Results and Discussion

Figures 1 and 2 show iron ores as typical examples of moderately complex materials. The samples are the commercially available reference materials SX11-12 and SX11-14 certified by Dillinger Hütte. XRD data were measured with Co radiation and the LYNXEYE detector on a D2 PHASER desktop diffractometer. The scan conditions were a step width of 0.02° at 0.2 sec measuring time per step. The total scan time was about 12 min.

Table 1 summarizes what minerals were identified for the two samples. The phase abundances from Rietveld QPA are presented in Tables 2 and 3. The sample SX11-12 is a predominantly hematitic high-grade iron ore with only very little amounts of gangue. SX11-14 is magnetite rich ore with more complex gangue mineralogy.

According to the nominal chemical formulae of the minerals the phase abundances were split into the total metallic iron

TOPAS quantitative phase analysis

Quantitative phase analysis (QPA) using the Rietveld [1] method was performed using the TOPAS [2] software. It is based on the calculation of the full powder pattern from crystal structure information. Therefore, it does not rely on calibration curves and also tube ageing does not need consideration.

Quantitative phase analysis in the TOPAS software is based on the method first described by Hill and Howard in 1987 [3]. This method is based on the assumption that (i) all phases in the specimen are identified, (ii) all phases are crystalline, and (iii) the crystal structures of all phases are known. The weight-% w_u of a phase u in a mixture of n phases is

$$w_u = S_u (ZMV)_u / \sum_{k=1}^n S_k (ZMV)_k$$

with S the scale factor of the Rietveld calculation, Z the number of formula units in the unit cell, M the mass of one formula unit, and V the unit cell volume. The factor (ZMV) is a phase specific scaling parameter that is solely defined by the usually well-known crystal structure of the mineral.

- [1] Rietveld, H.M. (1969) Journal of Applied Crystallography, 2:65–71.
- [2] TOPAS: Total Pattern Analysis Solution, Bruker AXS GmbH, Karlsruhe, Germany, (2003 – 2014).
- [3] Hill, R.J. and Howard, C.J. (1987). Journal of Applied Crystallography, 20: 467-74

Table 1: Minerals species identified in iron ore certified reference materials SX11-12 and 14.

Minerals	Formula	SX11-12	SX11-14
Hematite	Fe ₂ O ₃	x	x
Goethite	FeOOH	x	x
Magnetite	Fe ₃ O ₂	x	x
Quartz	SiO ₂	x	x
Gibbsite	Al(OH) ₃	x	x
Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	-	x
Orthoclase	KAlSi ₃ O ₈	-	x
Albite	NaAlSi ₃ O ₈	-	x
Calcite	CaCO ₃	-	x

content and individual oxide based chemical compositions of the non-iron bearing components. Those fractional concentrations are summarized for all minerals and compared to the well-known chemical analysis of the certified reference materials. The bias between the XRD results and the bulk chemical analysis is small and well below ± 1 wt-% for both samples.

In addition to total metallic iron Fe, the amount of iron bound as bivalent oxide FeO is presented. This is of particular importance for iron producers because they belong to the major pollutants of CO₂, a primary green house gas.

The amount of CO₂ emitted during the production of iron depends on the valence state of Fe in the ore which is defined by the type of mineral that hosts the metal and the concentrations of the minerals. A traditional method for the determination of the FeO content would be titration, which is a time consuming and operator prone procedure.

Both samples show good agreement of the FeO amount with the expected values. This proves XRD to be a useful tool for the fast determination of the valence state of iron ore at a time scale of a few minutes only.

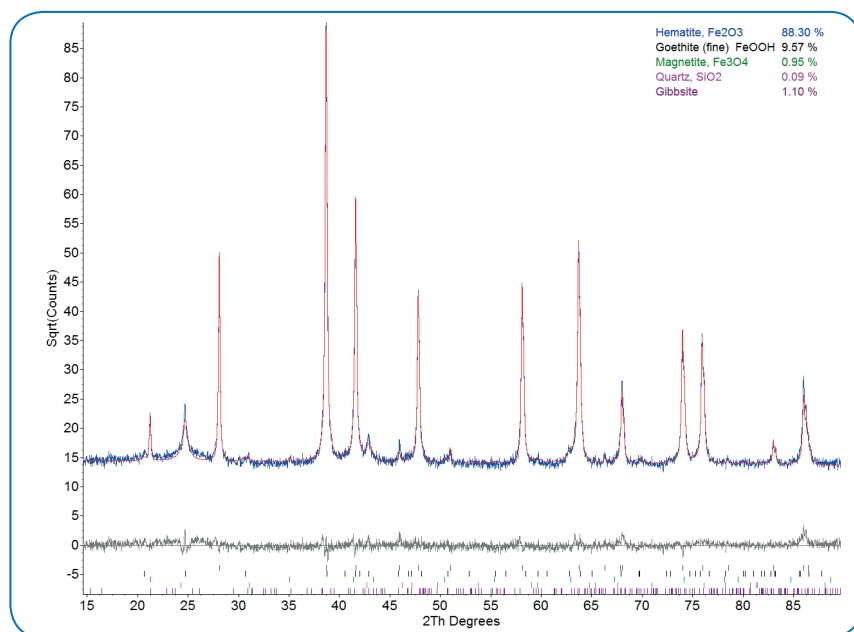


Figure 1: TOPAS QPA of Dillinger Hütte iron ore certified reference material SX11-12.

Table 2: Chemical analysis of the Dillinger Hütte iron ore certified reference material SX11-12, derived from QPA results taking into account the nominal stoichiometry (table 1) of the phases.

	Wt-%	Fe	FeO	SiO ₂	Al ₂ O ₃
Hematite	88.30	61.76	-	-	-
Goethite	9.57	6.02	-	-	-
Magnetite	0.95	0.68	0.29	-	-
Quartz	0.09	-	-	0.09	-
Gibbsite	1.10	-	-	-	0.72
		Fe	FeO	SiO₂	Al₂O₃
	XRD	68.46	0.29	0.09	0.72
	Chem.	67.83	0.41	0.60	0.70
	Bias	0.63	-0.12	-0.51	0.02

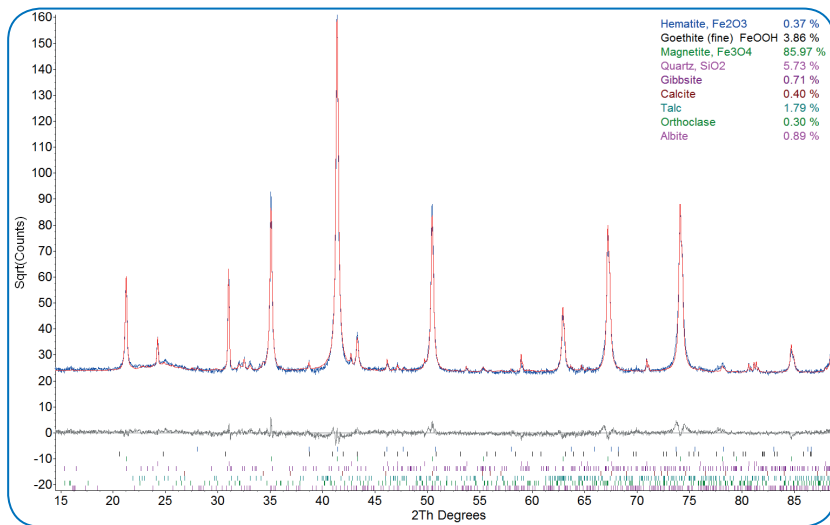


Figure 2: TOPAS QPA of Dillinger Hütte iron ore certified reference material SX11-14.

Table 3: Chemical analysis of the Dillinger Hütte iron ore certified reference material SX11-14, derived from QPA results taking into account the nominal stoichiometry (table 1) of the phases.

	Wt.-%	Fe	FeO	SiO ₂	Al ₂ O ₃	MgO	CaO	K ₂ O	Na ₂ O	C
Hematite	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	SiO₂	Al₂O₃	MgO	CaO	K₂O	Na₂O	C
	XRD	64.89	26.68	7.66	0.70	0.57	0.22	0.05	0.10	0.19
	Chem.	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

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