

3.10. Accuracy in Rietveld quantitative phase analysis with strictly monochromatic Mo and Cu radiations

L. LEÓN-REINA, A. CUESTA, M. GARCÍA-MATÉ, G. ÁLVAREZ-PINAZO, I. SANTACRUZ, O. VALLCORBA,
A. G. DE LA TORRE AND M. A. G. ARANDA

3.10.1. Introduction

Most industrial materials are multiphase systems and the accurate determination of their phase assemblage is key to understanding their performances. There are different approaches to carrying out quantitative phase analysis (QPA; see Chapter 3.9); however, nowadays, the Rietveld method is the most widely employed methodology for QPA of crystalline materials (Madsen *et al.*, 2001; Scarlett *et al.*, 2002), including cements (Stutzman, 2005; León-Reina *et al.*, 2009; Chapter 7.12).

The factors affecting the accuracy and precision of Rietveld quantitative phase analysis (RQPA) results can be gathered into three main groups: (i) instrument related, (ii) sample-preparation related and (iii) data-analysis protocol(s). The Rietveld method is a standardless methodology which uses the crystal-structure descriptions of each crystalline component to calculate its powder pattern. For this reason, the correct choice of crystal-structure description for each phase in multiphase materials is key (Zevin & Kimmel, 1995; Madsen *et al.*, 2001, 2011). The

influence of the instrument type on RQPA has previously been evaluated (Madsen *et al.*, 2001) and the main conclusion was that neutron and synchrotron powder diffraction yielded the best results owing to larger irradiated volumes and also to the minimization of microabsorption effects.

High-energy (short-wavelength) X-rays contribute (i) to minimize absorption and microabsorption effects, (ii) to the measurement of a higher number of Bragg peaks and (iii) to increase the irradiated volume of the specimen. Figs. 3.10.1(a) and 3.10.1(b) show the irradiated volumes bathed by X-rays when using flat samples for Mo and Cu radiations in transmission geometry, and Fig. 3.10.1(c) shows the irradiated volume for Cu in reflection mode (Cuesta *et al.*, 2015). Mo radiation combined with a flat sample in transmission geometry allows an irradiated volume of close to 100 mm³; meanwhile, for Cu radiation (flat samples in reflection and transmission geometries) the irradiated volumes are close to 5 mm³ (Cuesta *et al.*, 2015). In this context, it is worth mentioning that the absorption correction for flat-

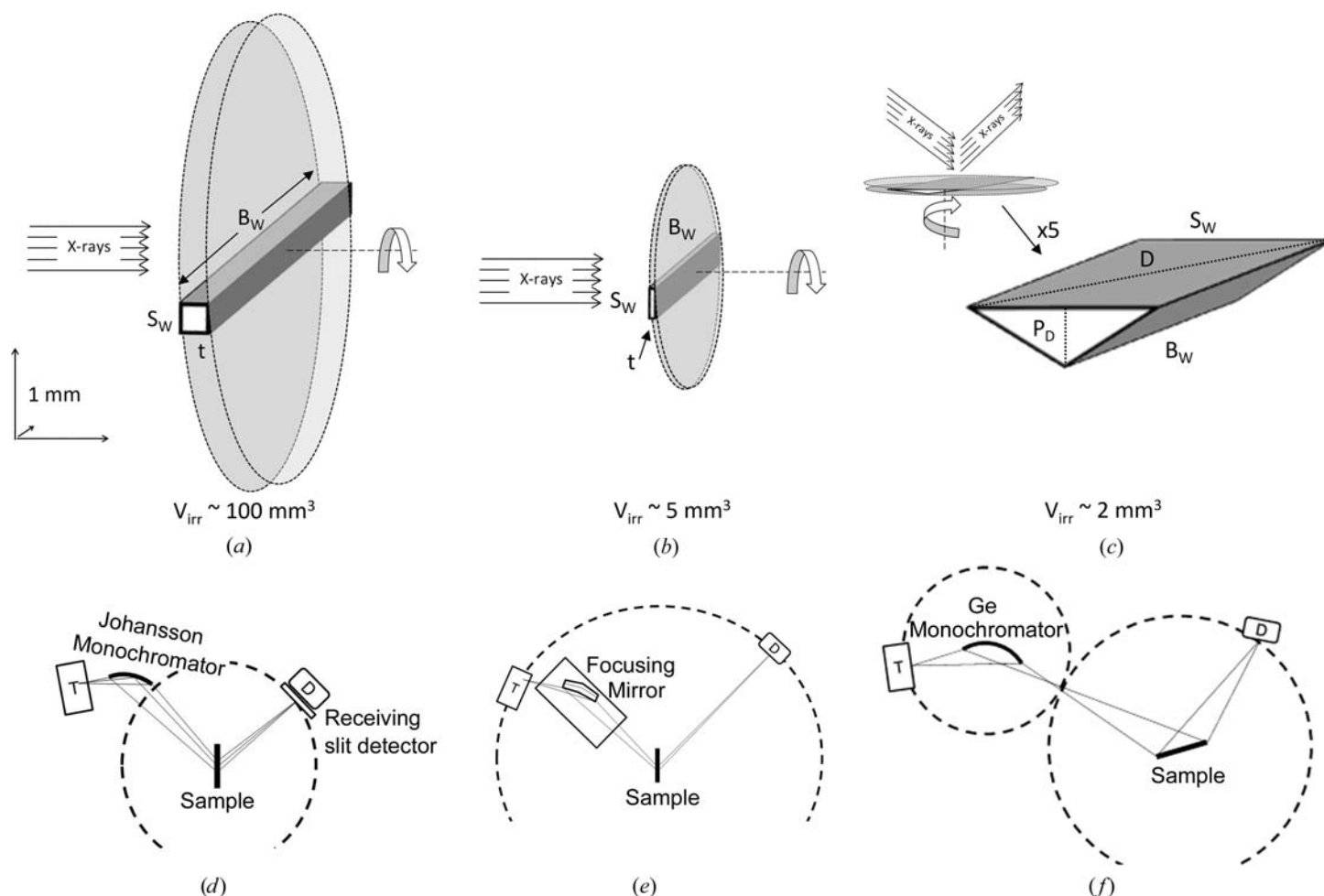


Figure 3.10.1

Irradiated volume for a flat sample holder in transmission mode using (a) Mo radiation and (b) Cu radiation, and (c) reflection mode using Cu radiation. Diffraction-geometry sketches: (d) transmission geometry with primary monochromator, (e) transmission geometry with focusing mirror and (f) reflection geometry with primary monochromator. [Reprinted from Cuesta *et al.* (2015) with permission from Cambridge University Press.]

3.10. ACCURACY IN RIETVELD QUANTITATIVE PHASE ANALYSIS

Table 3.10.1

Cambridge Structural Database (CSD)/Inorganic Crystal Structure Database (ICSD) reference codes for all phases used for Rietveld refinements in this work and the linear absorption coefficients for the wavelengths used

Phase	Chemical formula	CSD/ICSD refcode	μ (cm ⁻¹), Cu $K\alpha_1$, $\lambda = 1.5406 \text{ \AA}$	μ (cm ⁻¹), Mo $K\alpha_1$, $\lambda = 0.7093 \text{ \AA}$	μ (cm ⁻¹), $\lambda = 0.7744/0.4959 \text{ \AA}$	Reference
Glucose	C ₆ H ₁₂ O ₆	Glucsa10	12	1	1.3/—	Brown & Levy (1979)
Fructose	C ₆ H ₁₂ O ₆	Fructo11	12	1	1.3/—	Kanters <i>et al.</i> (1977)
α -Lactose monohydrate	C ₁₂ H ₂₂ O ₁₁ ·H ₂ O	Lactos10	12	1	1.3/—	Fries <i>et al.</i> (1971)
Xylose	C ₅ H ₁₀ O ₅	Xylose	12	1	1.2/—	Hordvik (1971)
Gypsum	CaSO ₄ ·(H ₂ O) ₂	151692	141	16	22/—	De la Torre <i>et al.</i> (2004)
Quartz	SiO ₂	41414	92	10	11/2.9	Will <i>et al.</i> (1988)
s-Anhydrite	CaSO ₄	16382	219	24	31/—	Kirfel & Will (1980)
i-Anhydrite	CaSO ₄	79527	219	24	31/—	Bezou <i>et al.</i> (1995)
Zincite	ZnO	65120	285	244	—/89.1	Albertsson <i>et al.</i> (1989)
Calcite	CaCO ₃	80869	194	22	27/7.3	Maslen <i>et al.</i> (1995)
SrSO ₄	SrSO ₄	22322	299	187	40/—	Garske & Peacor (1965)

sample transmission geometry is conceptually similar to that for flat-plate reflection geometry, but the length of the scattered beam path has to be properly defined. The corresponding equation is given in section A5.2.5 of Egami & Billinge (2003).

It must also be noted that Mo radiation has a major drawback when compared with Cu radiation. The λ^3 dependence of diffraction intensity favours the use of Cu radiation by a factor of 10.2. Thus, a detector receives approximately ten times as many diffracted X-ray photons with Cu than with Mo (this calculation neglects the different fractions of photons lost in the diffractometer optical paths). This fact can be partially overcome in modern X-ray detectors by increasing the counting time for patterns collected with Mo radiation without reaching prohibitively long times.

As discussed in Chapter 3.9, there are many factors that affect the accuracy and precision of QPA results. It must be recalled that accuracy is the agreement between the analytical result and the true value, and precision is the agreement between results for analyses repeated under the same conditions. Precision may be further divided into repeatability, the agreement between analyses derived from several measurements on the same specimen, and reproducibility, the agreement including re-preparation, re-measurement and data re-analysis of the same sample. Since the largest sources of errors in RQPA are experimental, sample preparation is key, as the reproducibility of peak-intensity measurements is mainly governed by particle statistics (Elton & Salt, 1996). It is generally accepted that the diffraction intensities have to be collected with an accuracy close to $\pm 1\%$ to obtain patterns that are suitable for good RQPA procedures (Von Dreele & Rodriguez-Carvajal, 2008). Milling the sample to reduce the particle size is an approach that should be exercised with care to avoid peak broadening or amorphization (Buhrke *et al.*, 1998). In order to improve particle statistics, a very common practice is to continuously spin the sample during data collection. A much less developed approach is to use high-energy, highly penetrating laboratory X-rays.

Another important issue in the QPA of mixtures is the limit of detection (LoD) and the limit of quantification (LoQ). In this context, the LoD can be defined as the minimal concentration of analyte that can be detected with acceptable reliability (Zevin & Kimmel, 1995), *i.e.* for which its strongest (not overlapped) diffraction peak in the powder pattern has a signal-to-noise ratio larger than 3.0. The 'reliability' criterion is flexible and may be defined by regulatory agencies, as is mainly the case for active pharmaceutical ingredients. Evidently, the LoD can be reduced (improved) by increasing the intensity of the X-ray source, for example using synchrotron radiation. In this context, the LoQ

can be defined as the minimum content of an analyte that can be determined with a value at least three times larger than its standard deviation and determined to an acceptable reliability level. For RQPA, this type of approach can be straightforward, although the accuracy for minor phases may be quite poor.

The main aim of the study described here was to test whether the use of high-energy Mo radiation, combined with high-resolution X-ray optics, could yield more accurate RQPA than well established procedures using Cu radiation. In order to do so, three sets of mixtures with increasing amounts of a given phase (the spiking method) were prepared and the corresponding RQPA results were evaluated with calibration curves (least-squares fits) and quantitatively by statistical analysis based on the Kullback–Leibler distance (KLD; Kullback, 1968). The three series were (i) crystalline inorganic phase mixtures with increasing amounts of an inorganic phase, (ii) crystalline organic phase mixtures with increasing amounts of an organic compound and (iii) a series with an increasing content of amorphous ground glass. This last series is the most challenging case because the amorphous content is derived from a small overestimation of the internal standard employed. Amorphous content determination is important for many industries, including cements, glasses, pharmaceuticals and alloys.

3.10.2. Compounds and series

3.10.2.1. Single phases

Table 3.10.1 provides information about the phases used in this work. Further details can be found in the original publication (León-Reina *et al.*, 2016). All of the mixtures were prepared by grinding the weighed phases by hand in an agate pestle and mortar for 20 min to ensure homogeneity.

3.10.2.2. Crystalline inorganic series

A constant matrix of calcite (C), gypsum (Gp) and quartz (Q) was prepared. Six samples with known increasing amounts of insoluble anhydrite (i-A) were then produced and were labelled CGpQ_xA, where *x* represents the target i-A content: 0.00, 0.125, 0.25, 0.50, 1.0, 2.0 or 4.0 wt%.

3.10.2.3. Crystalline organic series

A constant matrix of glucose (G), fructose (F) and lactose (L) was prepared. Six samples with known increasing amounts of xylose (X) were then produced and labelled GFL_xX, where *x* represents the target X content: 0.00, 0.125, 0.25, 0.50, 1.0, 2.0 or 4.0 wt%.