

ASSESSING THE PERFORMANCE OF A PORTABLE POWDER DIFFRACTOMETER

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Abstract

Three powder standard specimens (Si, Y₂O₃ and LiF) were studied with the recently acquired Fatec-SP's Rigaku MiniFlex II Desktop X-ray Diffractometer. The patterns were obtained with a copper tube in step by step mode (0.05 °2θ) counting at least three seconds per step (equivalent speed of 1 °2θ/minute).

Pawley and *Rietveld* refinements were performed with the help of Accelrys Materials Studio 5.0. The final statistics indicators for *Rietveld* (expressed in %) R_{wp} , R_{wp} w/o background and R_p (9.0, 12.2 and 7.2 for Si; 3.0, 2.0, and 6.5 for Y₂O₃; 4.0, 5.2 and 2.9 for LiF) did indicate excellent agreements between experimental and calculated profiles.

1. Introduction

In recent years the performance of laboratory powder X-ray diffractometers has notoriously improved. On one side the detection systems have increased their efficiency with better signal/noise ratios and capture time. On the other side the electronics controlling the power source and ultimately the current of the anticathode have reached optimal performance. Today commercial equipments allow collecting exploitable diffraction patterns in a matter of a few minutes. The CCD (charge-coupled device) detectors have opened new venues for time-resolved studies rivaling, in some cases, with the instruments of dedicated X-ray synchrotron sources. Also the evolution of the technology has propitiated the manufacture of smaller and more compact apparatus. The miniaturization has reached such extremes that a really ultra-portable device for the exploration of Mars [1] has been designed for ESA (European Space Agency). Certainly the technical solutions proposed for such device are different from the commercial devices, but the path has been indicated for the construction of portable devices that could be useful for geologists working *in situ*. Without going to those extremes of portability, some more conventional equipments still of a size that could be transported by car have been developed. One of such apparatus acquired by the *Departamento de Ensino Geral da Fatec-SP* and installed at the *Laboratório de Processamento e Caracterização de Materiais* is available for researchers and students. In this article we intend to show that the performance of this diffractometer is very adequate, being able to provide decent service for both teaching and research. To demonstrate that, a few standard

specimens have been scanned, the data collected, and analyzed by a technique initially proposed by H. M. Rietveld [2]. This popular method applied in both X-ray and neutron powder diffraction, essentially calculates the statistics between experimental and calculated diffraction patterns according to a plausible crystal model and finds better solutions in an iterative fashion. These computations are made by a least-squares method but with an essential key feature; they are performed by matching point by point, the calculated and experimental diffraction patterns. Former methods, derived from single crystal data treatments, used integrated intensities of peaks rather than single points. The obvious advantages of *Rietveld* method is that allows crystal refinements of experimental patterns with severe overlap of diffraction peaks and also that the whole information contained in diffraction patterns can be extracted.

2. Experimental

The standard specimens were silicon (Si), yttrium oxide (Y₂O₃) and lithium fluoride (LiF), prepared by L. Gallego according to the procedure described in [3]. A Rigaku MiniFlex II Desktop X-ray Diffractometer with a copper anticathode operating at 30 KV and 15 mA was used. A beta filter was used without secondary monochromator, therefore $K\alpha_1$ and $K\alpha_2$ wavelengths were used. The beam was confined with the standard set of slits, *i.e.* divergence slits of 1.25° and 0.625°, scatter slit of 1.25° and receiving slit of 0.3 mm. The detector of the diffractometer is a scintillator of NaI. The standard materials were placed in flat glass sample holders that allowed to analyzing powder specimens of approximately 1 mm in thickness. The basic setup of the apparatus does not permit rotating the sample. In most of the cases, the recording speed was of 1 °2θ per minute and the data collection in step-by-step mode, with steps of 0.05 °2θ. The 2θ angular range varied: 25° to 90° for silicon, 20° to 90° for Y₂O₃ and 35° to 85° for LiF.

3. Data Treatment

The diffraction data files were converted to a format, readable by Materials Studio 5, with the help of PowDLL converter. The strategy for refinement was similar in all cases. Prior to doing *Rietveld* [2] refinement, a *Pawley* [4] treatment was carried out testing different peak shapes and schemes of asymmetry, retaining the ones that yielded lower values

for the reliability factors. In addition to peak shapes, geometric displacements for the specimen were allowed to be fitted, according to the equation,

$$2\Theta_{corr} = 2\Theta + T_o + T_1 \cos \Theta + T_2 \sin 2\Theta \quad (1)$$

where:

T_o is the zero displacement point,

T_1 is the displacement parameter expressed as

$$\frac{180(t-s)}{\pi R}$$

T_2 is the transparency parameter expressed as

$$\frac{180}{2\pi\mu R}$$

t is the thickness of the specimen diffracting volume, which does not necessarily coincide with the actual thickness of the sample, except in the case of a very thin one,

s is the displacement of the sample surface with respect to the axis of the diffractometer,

R is the radius of the goniometer circle,

μ is the linear absorption coefficient of the sample.

The Bérar-Baldinozzi [5] asymmetry correction scheme was used, with four refineable parameters: P1, P2, P3 and P4. The function to describe the peak shape that gave better results in all cases was the one proposed by Thompson *et al.* [6]. As in most peak shape functions, the U, V, W, X and Y parameters are included to define the full width at half maximum [7].

Peak broadening due to crystallite size and residual stress/strain was not taken into account. The background refinement was done with a 20th degree polynomial [8]. The crystal structure descriptions were downloaded from the Crystallographic Open Database (COD) as CIF formatted files. When possible (case of Y_2O_3) atomic positions were refined and also the Debye-Waller factors. Cell parameters were also refined except in the case of silicon, where it was kept constant and the zero-shift was refined instead.

4. Results and Discussion

The statistics indicators (also known as reliability factors) employed to assess the goodness of fitting were R_{wp} , $R_{wpwoback}$, without background and R_p . As it is customary they are defined by the following expressions:

$$R_{wp} = \left(\frac{\sum w_i (cY_i^{sim} - I_i^{exp} + Y_i^{back})^2}{\sum w_i (I_i^{exp})^2} \right)^{1/2} \quad (2)$$

$$R_{wpwoback} = \left(\frac{\sum w_i (cY_i^{sim} - I_i^{exp} + Y_i^{back})^2}{\sum w_i (I_i^{exp} - Y_i^{back})^2} \right)^{1/2} \quad (3)$$

$$R_p = \frac{\sum |cY_i^{sim} - I_i^{exp} + Y_i^{back}|}{\sum I_i^{exp}} \quad (4)$$

where:

w_i is a weighting factor defined by $1/I_i^{exp}$,

c is the scale factor optimized to get the lowest value

of R_{wp} ,

I_i^{exp} the measured experimental intensity at i th point,

Y_i^{back} the background intensity at i th point, calculated by fitting experimental data,

Y_i^{sim} the calculated diffraction intensity at i th point without background contribution.

In all cases the values were acceptable, the best ones being for yttrium oxide. Acceptable values for the statistics indicators have to be lower than 10 % for R_{wp} and R_p . R_{wp} w/o back has to be lower than 15%.

Silicon

The crystal structure was refined in Space Group Fd-3m (227), $Z=8$ with Si atoms in 8(a) Wyckoff position. The final statistics indicators, gathered in Table I, are within expected limits. For the refinements the cell constant was not set free, allowing instead the zero shift to be fitted. The Debye-Waller factor found was 0.90 \AA^2 , slightly high, most probably due to the fact that the highest angle attained was $90^\circ 2\theta$ only. To obtain more realistic values it would be necessary to scan to higher angles and at lower speeds, since more precise information on temperature factors can be found in the high angle range. Otherwise the parameters found for other variables were correct. It is worth mentioning that the zero-shift affecting the goniometer was less than a tenth of two-theta degree. The plot of experimental, refined patterns and the difference between them can be seen in Figure 1. The visual impression of the refinement is quite good.

Yttrium Oxide

The atomic positions were refined within Space Group Ia-3 (206), $Z=16$ with Y1 atoms in 8(b), Y2 in 24(d) and oxygen atoms in 48(c). The atoms are located in more generic positions, therefore its diffraction pattern exhibits more diffraction peaks than the other phases analysed. It was considered worth paying more attention to this specimen. Consequently, two diffraction data sets were collected in different days. The first diffraction pattern was acquired in the $20-90^\circ 2\theta$ range at one degree per minute, the second between 18 and 90 but at lower speed ($0.5^\circ 2\theta/\text{minute}$.) The two data sets were independently refined and then the sum of both was treated as well. The list of the parameters after refinement together with statistics indicators can be found in Table 1.

In Table II the positions of atoms after refinement with their Debye-Waller factors can be seen. The value found for the oxygen temperature factor was zero, obviously unrealistic, and did not improve with data

acquired at lower speed. This is the only problematic parameter, but it could be argued, as in the case of silicon, that a correct value would be found by counting longer at higher angles. Otherwise, the figures indicate that the relevant parameters are not different, if the deviation error ranges are considered. There are some minor discrepancies with the Debye-Waller factors for yttrium that could be attributed to the different

acquisition speeds, the values found for the data sets acquired at lower speed being closer to the real ones. In Figure 2, the diffraction of experimental and calculated patterns can be seen; also the difference is shown.

Again the visual inspection of these graphs indicates good agreement between calculated and experimental data. Furthermore, the inter-atomic Y-O distances found

Table I - Parameters found after refinement. Statistics indicators (R_s) are expressed in %, the shifts in 2Θ degrees, cell parameters in Å. The rest of refined parameters, Caglioti (U, V, W, X and Y) and Bérar-Baldinozzi (P1, P2, P3 and P4) are dimensionless. The numerical values are displayed to the last certain figure.

	Si	Y ₂ O ₃ (1)	Y ₂ O ₃ (2)	Y ₂ O ₃ (sum)	LiF
R_{wp}	8.98	2.97	3.16	3.03	5.01
R_{wp} w/o back	12.23	6.53	6.55	6.35	6.54
R_p	7.22	2.08	2.11	2.02	3.55
zero shift	-0.09	-	-	-	-
shift 1	-0.05	0.12	0.13	0.13	-0.25
shift 2	0.04	0.19	0.19	0.19	0.27
a_0	5.43119	10.620	10.620	10.620	4.035
U	-0.003	0.041	0.040	0.039	-0.218
V	0.001	-0.039	-0.037	-0.037	0.246
W	0.021	0.025	0.025	0.025	0.007
X	0.01	-0.060	-0.066	-0.063	0.02
Y	0.04	0.075	0.079	0.077	0.04
P ₁	0.6	0.8	0.9	0.8	-1.6
P ₂	0.01	0.05	0.06	0.05	-0,28
P ₃	-1.4	-2.1	-2.1	-1.9	3.0
P ₄	-0.09	-0.18	-0.20	-0.18	0.46

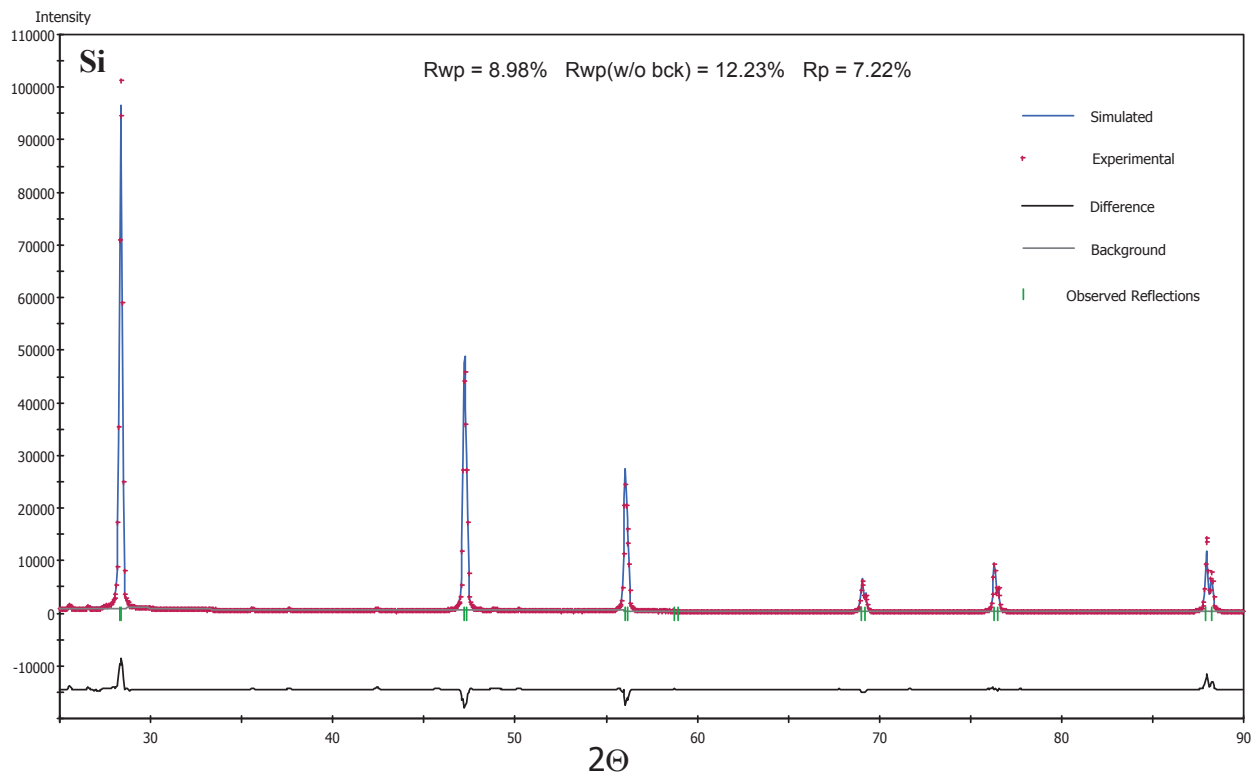


Figure 1 - Experimental and calculated diffraction patterns for Si after *Rietveld* refinement.

Table II - Atomic positions and temperature factors in Y_2O_3 found after *Rietveld* refinement.

	x	y	Z	$B_{iso}(\text{\AA}^2)$
O	0.6201 ± 0.0005	0.8907 ± 0.0004	0.3471 ± 0.0004	-
Y1	1/4	1/4	1/4	0.36 ± 0.01
Y2	0.5328 ± 0.0001	1/2	1/4	0.36 ± 0.01
O	0.6201 ± 0.0005	0.8904 ± 0.0004	0.3474 ± 0.0004	-
Y1	1/4	1/4	1/4	0.31 ± 0.01
Y2	0.5328 ± 0.0001	1/2	1/4	0.36 ± 0.01
O	0.6200 ± 0.0005	0.8906 ± 0.0004	0.3473 ± 0.0004	-
Y1	1/4	1/4	1/4	0.31 ± 0.01
Y2	0.5328 ± 0.0001	1/2	1/4	0.36 ± 0.01

are physically meaningful. Basically the crystal structure consists of two sets of octahedra: One set of regular ones (Y-O distance of 2.28 Å), and another of irregular ones with three different distances for Y-O (2.34, 2.25 and 2.28 Å.) A detail of this arrangement can be found in Figure 3.

Lithium Fluoride

The crystal structure of LiF is of NaCl type, *i.e.* S.G. Fm-3m (225) and Z=4. Li atoms are located in 4(a) and fluorine atoms in 4(b). As in the case of silicon the crystal structure of this phase is very simple and the diffraction pattern exhibits a few peaks. The reliability

factors can be seen in Table 1. They are correct. As in the previous case, two sets of data were acquired at 1 °2θ/minute and 2 °2θ/minute in the 35-85 °2θ range. The cell parameter found for both scans is the same (within statistics deviation errors.) However, the temperature factors for the first set were unrealistically high (3.94 and 2.85 Å² for Li and F respectively.) The second data set provided better values still though a bit higher (1.46 and 0.96 Å².) This stresses again the need of collecting diffraction data at higher angles, same as in the case of silicon. Finally the graphs showing the agreement between refined and experimental data can be seen in Figure 4.

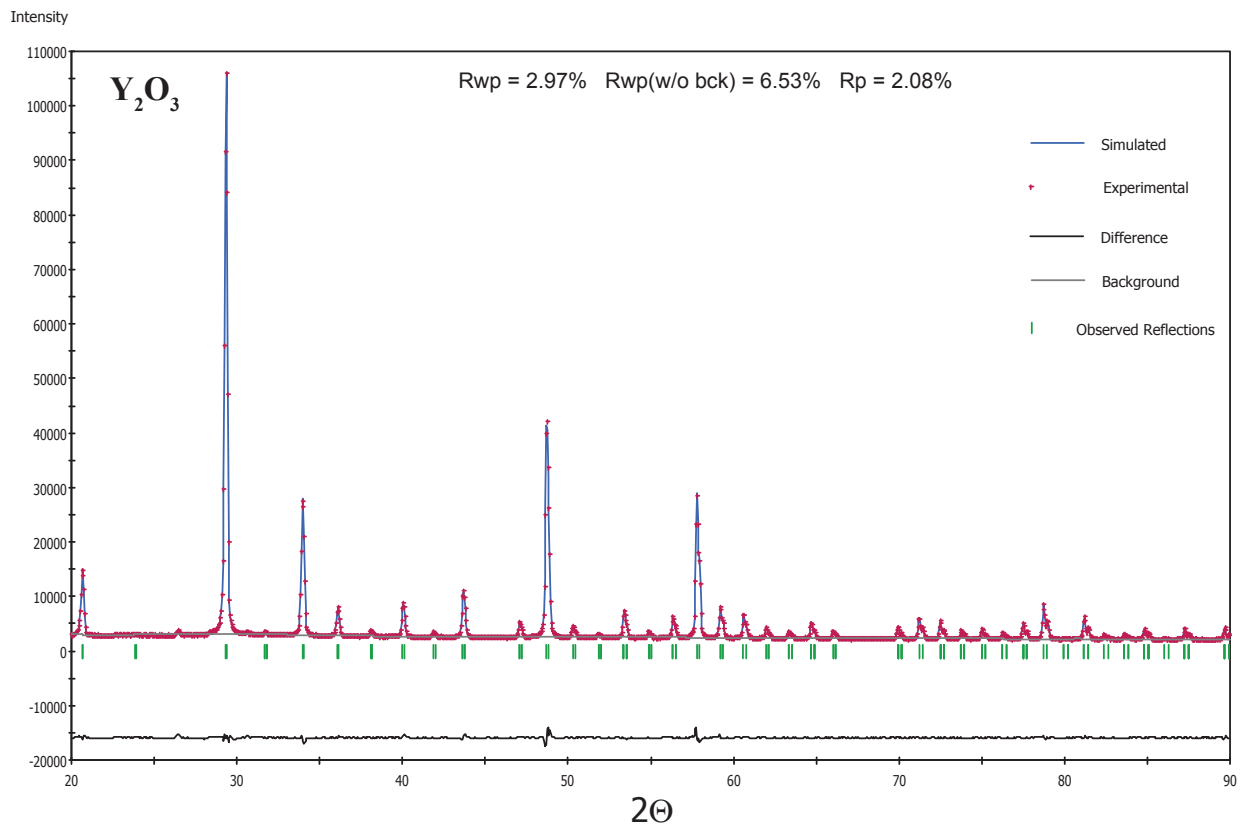


Figure 2 - Experimental and calculated diffraction patterns for Y_2O_3 after *Rietveld* refinement.

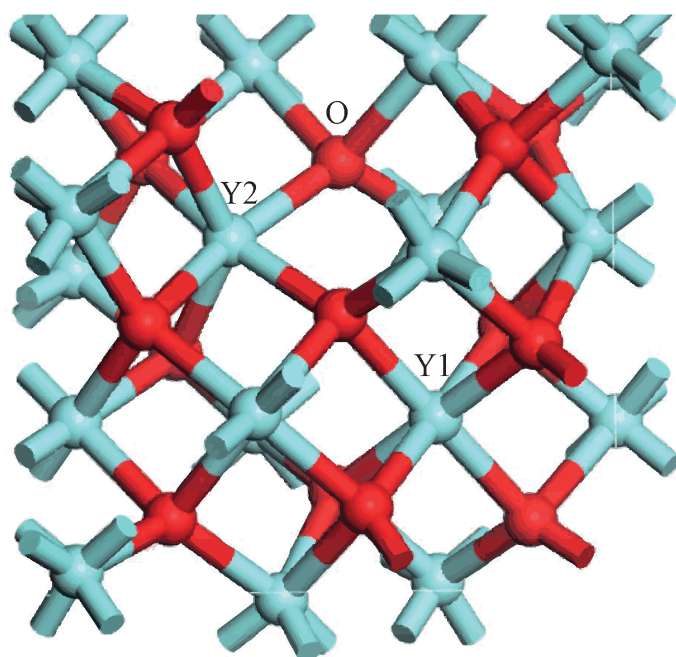


Figure 3 - Detail of the crystal structure of Y_2O_3 , showing the neighbourhood of yttrium (light) and oxygen (dark) atoms. The Y1 atom is equidistant to six oxygen atoms (regular octahedron), and Y2 is in an irregular environment (distorted octahedron.)

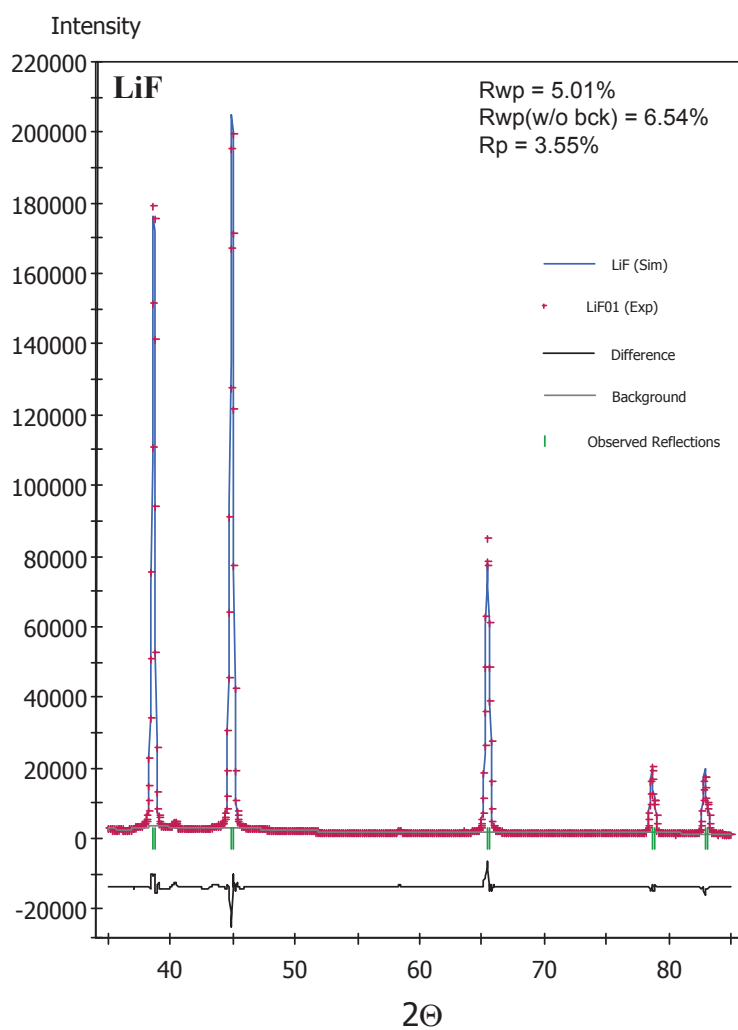


Figure 4: Experimental and calculated diffraction patterns for LiF after *Rietveld* refinement.

5. Conclusions

The goniometer of the device seems to have a good precision. The mechanical bearings do not show signs of lag, since scans taken within a few days of difference match perfectly as it was shown in the test with yttrium oxide. The speed necessary for ordinary work that mainly involves cell parameters determination, at least for very crystalline materials, and with a step of $0.05^\circ 2\theta$, seems to be optimal around 1 deg/min. Lower speeds do not significantly improve the statistics. Smaller steps were not tested, but it seems that 3 seconds of counting per step is reasonable. The set of slits placed by default (divergence slit of 1.25° , receiving slit of 0.3 mm and scattering slit of 1.25°) seem to be adequate for *Rietveld* refinement in the range $18 - 90^\circ 2\theta$. Apparently there are no losses of intensity for the diffracted signal at the lowest angles. However, Debye-Waller factors were overestimated. It would be necessary to scan higher angles and at lower speed to get more realistic figures. Nevertheless the results obtained for temperature factors are acceptable within these limitations. Finally, standard corrections available in *Rietveld* software packages for the goniometer geometry are adequate and help to fit the experimental data.

Next task to test the diffractometer would be to scan specimens with crystal structures of lower symmetry and tendency to exhibit preferred orientation, alumina for instance. Bearing in mind that with the present configuration of the apparatus the sample holder does not allow rotation to minimise orientation, it will be quite instructive to analyse the quality of the diffraction patterns and the possibilities to correct the preferred orientation affecting the intensities, via *Rietveld* refinement.

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