

UNCERTAINTY ESTIMATION OF LATTICE PARAMETERS MEASURED BY X-RAY DIFFRACTION

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Abstract: The uncertainties in lattice parameters determination, for X-Ray Diffractometers with Bragg-Brentano geometry, were estimated according GUM recommendations using the Monte Carlo simulation approach. The analyzed specimen was a Corundum NIST 1976 SRM Standard. Misalignment of instrument (zero 2theta offset and peak position) is an important error source, and should be kept $(2\theta) < 0.015^\circ$ to be able to perform lattice parameters measurements with an accuracy ≥ 0.0001 Angstroms. Sample displacement is in general the main source of error, and the above mentioned misalignment of instrument (0.015°) only becomes dominant as error source if the sample displacement is very small ($< 10 \mu\text{m}$). The analysis showed that sample absorption (Corundum) is negligible as error source, if compared with sample displacement and equipment misalignment. Other possible sources of systematic error are discussed.

Keywords: lattice parameters, X-Ray Diffraction, error estimative, GUM, Diffractometers.

1. INTRODUCTION

Measurement with exactitude of 1/1000 Angstroms is possible by the X-Ray Diffraction technique. Accuracy of 0.02° for the 2 theta angle in the Bragg-Brentano geometry, which is obtained in state-of-art equipments, allows an accuracy of 0.001 \AA or 0.0001 nm [1]. This means the possibility of measuring a quantity of the order of 10^{-13} m , corresponding to 0.1 pm or 10^{-4} nm , i.e., much below the nanometric scale.

Thus, X-Ray Diffraction is a very powerful method, offering the possibility of measuring distances that could not be detected by other experimental methods.

For example, X-Ray Diffraction is the better technique for determination of the variation of the amount of a given element in solid solution inside a given phase. As consequence, lattice parameters determination is essential for the assessment of phase diagrams. An example of previous application of this method for Phase Diagram

evaluation – the CoSm phase Diagram -was shown in Ref. [2,3].

It has been mentioned that correct positioning of the sample is fundamental: the sample should be positioned exactly parallel to the surface of the sample holder. The error in the positioning should be less than 0.1 mm [1] for attaining the above mentioned accuracy of 0.1 pm .

Cohen method [1] is the least squares refinement of the peaks position (2 theta), which is also the refinement of d - the interplanar distance - by means of the Bragg law, the equation $\lambda = 2d \sin \theta$ (where d is interplanar distance, λ is wavelength, and θ is the Bragg angle, or diffraction angle).

The objective of this work is to use Monte-Carlo simulation [4] for determination of the uncertainty due to the systematic errors, when estimating the lattice parameters by the Cohen method. A corundum (Al_2O_3) standard (NIST SRM 1976) [5] was used for this purpose.

2. SYSTEMATIC ERRORS IN DIFFRACTOMETERS WITH BRAGG-BRENTANO GEOMETRY

i) Misalignment of the equipment

One of the possible systematic errors is just the error of the “zero” 2theta position, i.e., the offset of the instrument. This leads to an error for the peak position that is proportional to 2θ .

ii) Sample displacement

The error generally considered as the most significant error in Diffractometers [1,6] is the specimen displacement in relation to Diffractometer axis.

$$\frac{\Delta d}{d} = \frac{-D \cos^2 \theta}{R \sin \theta} \quad (1)$$

where D is the displacement (positive when ahead of the axis) and R is the radius of the Diffractometer.

iii) Absorption

According Jenkins and Snyder [6], the transparency error (case of thick specimen) is (where μ is the absorption coefficient):

$$\Delta 2\theta = \frac{\sin 2\theta}{2\mu R} \quad (2)$$

Differentiating the Bragg law:

$$\frac{\Delta d}{d} = -\frac{1}{\operatorname{tg}\theta} \Delta\theta \quad (3)$$

Substituting Eq. (2) in Eq. (3), we obtain:

$$\frac{\Delta d}{d} = -\frac{1}{2\mu R} \cos^2 \theta \quad (4)$$

Concerning alignment, powder reference materials usually are not very reliable standards. There is a systematic error due to specimen transparency effects. In fact, high absorption samples and bulk samples are more suitable for avoiding this error. It has been recognized nowadays that the powder standards made of low atomic number elements like NIST SRM 640c -Silicon - or NIST SRM676 - Al_2O_3 - are not the most adequate for checking alignment [7]. It is very difficult to pack the powder assuring that the surface level is the same of the surface holder. Moreover, the surface of powder specimen is typically quite irregular. However, high absorption standards like NIST SRM660a - LaB_6 , have been recommended for evaluating instrument alignment [7].

iv) Other error sources

Ideally, the sample should be curved, according the Diffractometer geometry. But this is rarely done in practice and a systematic error $\propto \cos^2\theta$ appears as consequence [1]. Small irradiated area reduces this error source.

The Nelson-Riley Function [8], Eq. (5), was originally proposed for Debye-Scherrer cameras (i.e. a geometry different of Diffractometers), however applies very well for Diffractometers, because the first term ($\cos^2\theta/\sin\theta$) corrects for sample displacement, typically the main error source [1,6]. The reasoning behind the second term ($\cos^2\theta/\theta$) is not well understood but it may correct for vertical divergence of the incident beam [1]. Decreasing the window of the detector slit reduces the error due to vertical divergence [1].

$$\frac{\Delta d}{d} = k \left(\frac{\cos^2 \theta}{\operatorname{sen} \theta} + \frac{\cos^2 \theta}{\theta} \right) \quad (5)$$

where k is a constant

3. THEORY – LEAST SQUARE DETERMINATION OF LATTICE PARAMETERS

The employed theory is, essentially, the Cohen method, adapted for the systematic errors we decided to check: sample displacement and specimen absorption.

Cohen method is the extrapolation, according the least squares method, for $2\theta \rightarrow 180^\circ$. As most of the systematic errors are proportional to $\cos^2\theta$, they should vanish when $\theta=\pi/2$.

Rhombohedral or Hexagonal lattices can be evaluated with the expression (6), which makes use of the experimentally observed $\sin^2\theta$:

$$\sin^2 \theta = \frac{\lambda^2}{4} \left[\frac{4}{3} \times \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \right] \quad (6)$$

Eq. (7) is obtained after including the term due to systematic error (ii) sample displacement, which is given by Eq. (1). Others systematic errors, like sample absorption (Eq. 2), can be included in similar way.

$$\sin^2 \theta = \frac{\lambda^2}{4} \left[\frac{4}{3} \times \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \right] + \frac{2D}{R} \cos^2 \theta \sin \theta \quad (7)$$

Eq. (7) can be rewritten:

$$A = C\alpha + B\gamma \quad (8)$$

where:

$$A = \frac{1}{\lambda^2} \left(\sin^2 \theta - \frac{2D}{R} \cos^2 \theta \sin \theta \right) \quad (9a)$$

$$C = \frac{1}{a^2} \quad (9b)$$

$$B = \frac{1}{c^2} \quad (9c)$$

$$\alpha = \frac{(h^2 + hk + k^2)}{3} \quad (9d)$$

$$\gamma = \frac{l^2}{4} \quad (9e)$$

The lattice parameters a and c were determined from the following system of equations:

$$\sum \alpha A = C \sum \alpha^2 + B \sum \alpha \gamma \quad (10a)$$

$$\sum \gamma A = C \sum \alpha \gamma + B \sum \gamma^2 \quad (10b)$$

4. MONTE-CARLO SIMULATION

The ‘‘Guide to the Expression of Uncertainty in Measurement’’, more known as ISO-GUM [4], was elaborated by the International Organization for Standardization in order to establish a harmonized methodology for uncertainty estimation. Recently, ISO has been developing a supplemental guide [4] on numerical methods for the propagation of distributions, including Monte-Carlo simulations.

In order to overcome some limitations of ISO-GUM, the Monte-Carlo simulation approach can be applied to the evaluation of measurement uncertainties. This methodology is a numerical procedure that uses the generation of random numbers to simulate the values of the uncertainty sources, combining distributions instead of statistically propagating errors. The Monte-Carlo simulation is therefore a generalization of the law of propagation of uncertainties, providing uncertainty evaluations that are more valid than those provided by the use of the law of propagation of uncertainties in circumstances where the conditions for the application of that law are not fulfilled. These simulations can be easily performed due to the large availability of high-speed personal computers in the present day.

For the measurement of the lattice constants shown in this paper, Monte-Carlo simulations were used by programming Microsoft Excel® to generate pseudo-random probabilities for the distributions of the involved quantities. In this way, possible random values are generated for each quantity, according to their distribution functions. Uniform pseudo-random numbers were generated using the Hill-Wichmann algorithm [10], which was implemented in Excel® by adding new macro functions. This algorithm is recommended by the ISO-GUM supplement on numerical simulations as suitable for metrology calculations [9]. The simulations were performed using 50,000 iterations each.

5. EXPERIMENT

The accurate measurement of lattice parameters is function of the proper experimental conditions.

For better results, the slits should be of minimum size, whereas the maximum angle 2θ should be near 180° . The maximum intensity is not very relevant, since it can be controlled by increasing the exposition time, if necessary. Nevertheless, the accuracy of the 2θ position is very important. The equipment (Bruker D8 Focus) has 2θ accuracy better than 0.015° , according to the manufacturer (Bruker). It also can be mentioned that the option “step scan” allows better X-Ray Diffraction Spectra than the option “continuous scan”.

The conditions chosen for the Spectrum shown in Fig. 1 were Bragg-Brentano geometry, with emission slits 0.6 mm, receiving slit 0.1 mm, time per step 2 seconds, 2θ step = 0.01° . The 2θ range was between $25-140^\circ$.

(Note: the name of manufacturers and used software are mentioned with informative purposes only, and do not represent an endorsement).

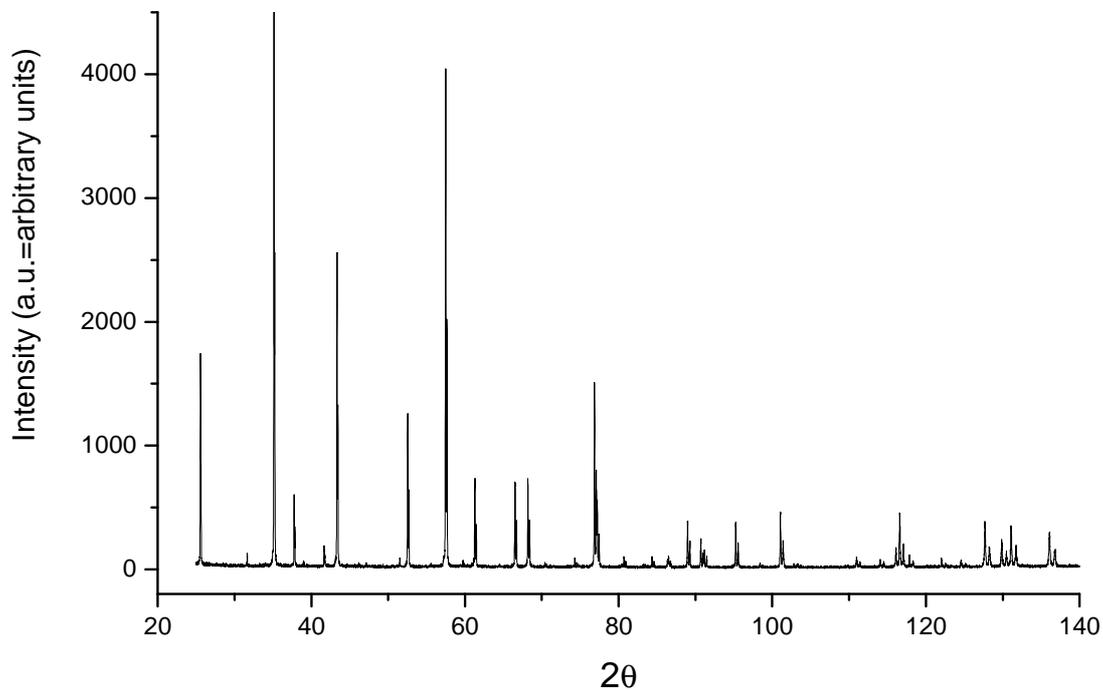


Fig. 1 X-Ray Diffraction Pattern used for estimation of the lattice parameters of Corundum (SRM 1976)

6. RESULTS AND DISCUSSION

Table 1 shows the quantities, uncertainties and the respective distributions considered in the simulations as sources of errors. The wavelength is the CuK α_1 radiation. Sample displacement represents the error of sample misplacement in relation to the plane normal to the plane of incidence. The diffractometer radius is given by the manufacturer as (200.5 ± 0.5) mm. The absorption coefficient μ was considered as $1.21 \text{ mm}^{-1} \pm 5\%$. In the simulations, the uncertainties of θ were generated considering an offset error for all spectrum (Offset 2θ), an individual peak position error (given by the manufacturer) and an absorption correction factor, as follows (see Eq. 11):

$$\theta = \theta_m + \theta_o + \theta_p + \theta_{abs} \quad (11)$$

where θ_{abs} is given by Eq. 12:

$$\theta_{abs} = \frac{\sin 2\theta_m}{4\mu R} \quad (12)$$

where θ is the final considered angle, θ_m is the measured angle, θ_o is the offset error, θ_p is the individual peak error, μ is the absorption coefficient and R is the diffractometer radius. Table 2 shows the results obtained for the simulations. As one can observe, the obtained values are in agreement with the values of the lattice parameters given by the standard reference material certificate [5]: $a = (4.758846 \pm 0.000109)$ Angstroms and $c = (12.99306 \pm 0.000238)$ Angstroms.

Table 1. Parameters, uncertainties and distributions used in the lattice parameters measurement uncertainty evaluations (“well aligned instrument” scenario).

Quantity	Estimate	Distribution	Dispersion
Wavelength (Angstroms)	1.54056	Uniform	0.00001
Sample displacement (mm)	0	Uniform	0.1
Diffractometer radius (mm)	200.5	Uniform	0.5
Absorption coefficient (mm^{-1})	1.21	Uniform	0.06
Offset 2θ (degrees)	0	Uniform	0.005
Individual peak position (degrees)	Varies for each peak	Triangular	0.015

Table 2. Results obtained for the estimation of the lattice parameters (“well aligned instrument” scenario).

Parameter	Estimate (Angstroms)	Expanded uncertainty (Angstroms)
a	4.7586	0.00099
c	12.9938	0.0031

Figures 2a and 2b show analysis of the uncertainty contributions for the lattice parameters. These results were obtained by performing simulations considering each source of uncertainty individually, excluding the other sources. The indicated value of the lattice parameter is estimated considering all the contributions. As it can be seen, the sample displacement presents a major contribution to the expanded uncertainty of the lattice parameters.

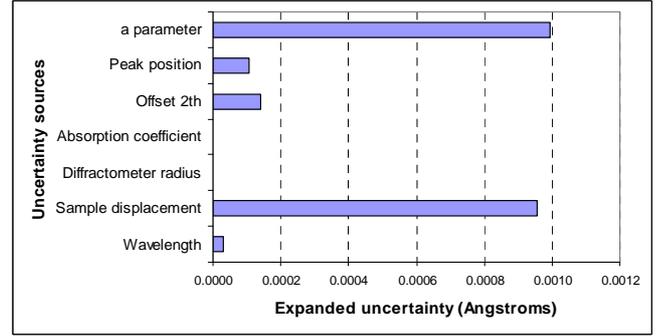


Fig. 2a. Uncertainty contribution analysis for the estimated a lattice parameter (“well alignment instrument” scenario, with $100\mu\text{m}$ of sample displacement uncertainty).

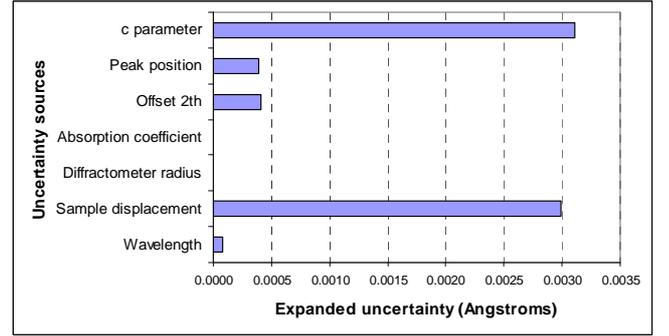


Fig. 2b. Uncertainty contribution analysis for the estimated c lattice parameter (“well aligned instrument” scenario, with $100\mu\text{m}$ of sample displacement uncertainty).

In order to investigate a more pessimistic scenario, in which the instrument would be “poorly aligned”, new simulations were executed using larger values of offset and individual peak uncertainties, $\pm 0.02^\circ$ and $\pm 0.05^\circ$ respectively. In addition, the distribution of the later was considered as uniform, instead of triangular. Table 3 summarizes the quantities, uncertainties and the respective distributions used in these new simulations and Table 4 shows the obtained results. As it can be seen, the estimated expanded uncertainties for both lattice parameters – 0.0014 \AA for a parameter and 0.0043 \AA for c parameter – were only slightly higher than those estimated for the well aligned instrument scenario – 0.00099 \AA and 0.0031 \AA , respectively.

Table 3. Parameters, uncertainties and distributions used in the lattice parameters measurement uncertainty evaluations (“poorly aligned instrument” scenario).

Quantity	Estimate	Distribution	Dispersion
Wavelength (Angstroms)	1.54056	Uniform	0.00001
Sample displacement (mm)	0	Uniform	0.1
Diffractometer radius (mm)	200.5	Uniform	0.5
Absorption coefficient (mm^{-1})	1.21	Uniform	0.06
Offset 2θ (degrees)	0	Uniform	0.02
Individual peak position (degrees)	Varies for each peak	Uniform	0.05

Table 4. Results obtained for the estimation of the lattice parameters (“poorly aligned instrument” scenario).

Parameter	Estimate (Angstroms)	Expanded uncertainty (Angstroms)
<i>a</i>	4.7586	0.0014
<i>c</i>	12.9938	0.0043

Figures 3a and 3b show the same uncertainty contribution analysis that was applied to the “well aligned instrument” scenario to the “poorly aligned” one, for both lattice parameters. As it can be seen, even with a “not well aligned” instrument, the major contribution for the overall expanded lattice parameter uncertainty is still due to the sample displacement error (supposed as 100 μm).

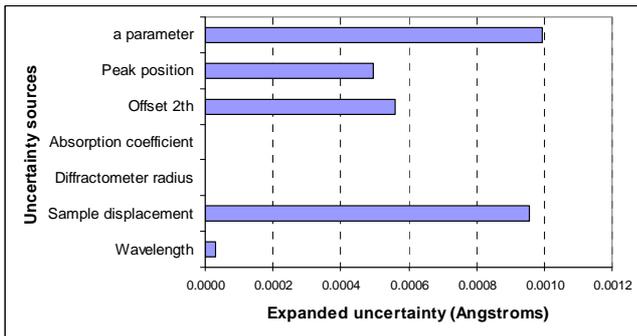


Fig. 3a. Uncertainty contribution analysis for the estimated *a* lattice parameter (“poorly aligned instrument” scenario, with 100 μm of sample displacement uncertainty).

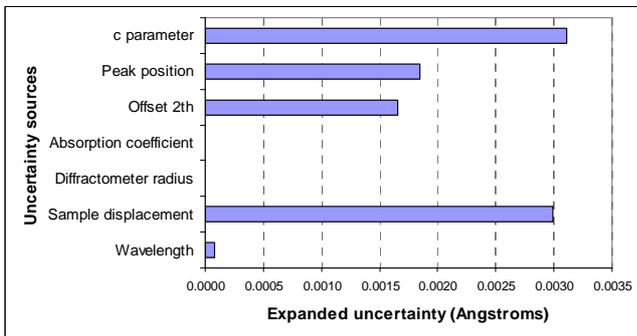


Fig. 3b. Uncertainty contribution analysis for the estimated *c* lattice parameter (“poorly aligned instrument” scenario, with 100 μm of sample displacement uncertainty).

Figure 4 shows the results of the estimated expanded uncertainties for both lattice parameters of a series of simulations (performed supposing the optimistic scenario) made for different values of sample displacement uncertainties (10 to 500 μm). As it can be noted, the overall expanded uncertainties for both lattice parameters increase considerably with the increase of the misplacement error.

The results (see Fig. 2a, 2b, 3a and 3b) indicate that sample displacement is in general the main source of error in Bragg-Brentano geometry. Even when the situation “poor alignment” of instrument was considered, sample displacement is the dominant error source, and only will be comparable to the typical misalignment of instrument when it is quite small (i.e., when the displacement is of the order of 10-20 μm , see Fig. 4, 5a and 5b).

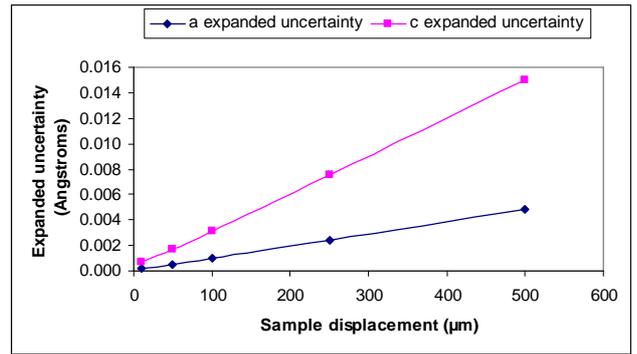


Fig. 4. Estimated expanded uncertainties for the lattice parameters considering different values for the sample displacement error (supposing the “well aligned instrument” scenario).

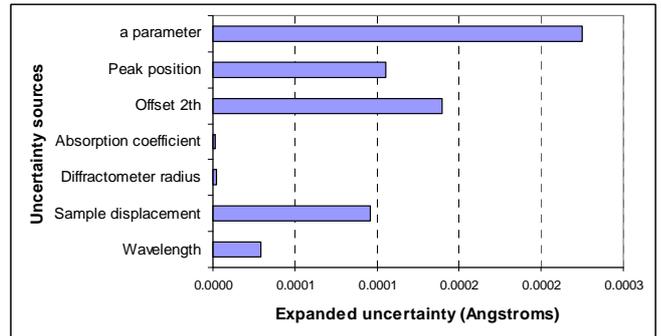


Fig. 5a. Uncertainty contribution analysis for the estimated *a* lattice parameter (“well aligned instrument” scenario, with 10 μm of sample displacement uncertainty).

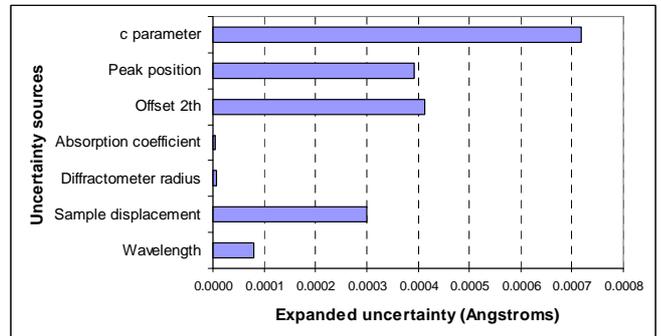


Fig. 5b. Uncertainty contribution analysis for the estimated *c* lattice parameter (“well aligned instrument” scenario, with 10 μm of sample displacement uncertainty).

Figures 5a and 5b show the uncertainty contribution analysis for both lattice parameters considering the “well aligned” scenario but with an uncertainty for the sample displacement of 10 μm . From this value below, this source of uncertainty becomes less important than the 2 theta uncertainties.

7. SOME REMARKS

The values chosen in the present simulation are similar to those admitted by Coelho [11], which considered as the dispersion of zero error (off-set) $\pm 0.03^\circ$ and also tested several different values for $\Delta 2\theta$ dispersion: $\pm 0.005^\circ$ $\pm 0.01^\circ$ $\pm 0.03^\circ$

8. CONCLUSIONS

Several kinds of systematic errors in Diffractometers (assuming Bragg-Brentano geometry) were discussed. Monte Carlo analysis of statistical errors was performed according GUM recommendations. The results have pointed out that specimen displacement is in general the main source of error, and that misalignment of instrument only becomes dominant if the sample displacement is very small ($<10\ \mu\text{m}$).

According to the results, our laboratory is able to perform lattice parameters measurements with an accuracy ≥ 0.0001 Angstroms, since the error due to specimen displacement could be avoided. This will enable Inmetro to produce reference material for X-Ray Diffraction - lattice parameters measurement - in a near future.

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