CALIBRATION OF DIFFRACTOMETERS II:
INTERNAL CONSISTENCY AND THE BALANCE

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ABSTRACT

The paper outlines recent results from experiments devoted to evaluate the instrumental performance of Bragg-Brentano geometry based diffractometers. Reproducibility, repeatability, and accuracy increased when calibration procedures are taken into account. The evaluation of internal consistency is required for a good quality calibration process, a good check of the optical alignment, and accurate preparation of specimen as well. The results discussed here refer in particular to the contribution given by the asymmetric component of peaks on the short wavelength side of the main diffraction lines. An appropriate evaluation of this asymmetric component increases the accuracy of data processing.

INTRODUCTION

In spite of high internal consistency of data, there is often some difficulty to reliably compare data deriving from diffraction measurements. Three aspects seem to have a great importance for data comparison: i) performance of instruments and the optional devices, ii) inhomogeneity of the experimental set up and its variation in time, iii) specimen characteristics, preparation, and positioning. A new point now shall be considered as one of the most critical one: the data processing. A good calibration procedure shall consider all the variables evaluating the residual systematic effects (not removable) after instrument alignment and may be expressed in terms of the dispersion characteristics of the diffraction angles $\Delta 2\theta$ vs. the expected Bragg angle ($2\theta^B$).

The “calibration curve” and/or “practical calibration curve”, representing optimum alignment, was proposed by Jenkins and Jenkins and Snyder [1,2]. Significant differences between experimental and expected positions of the diffraction lines may be revealed in due course of measurements because of the differences between the effective values of parameters and the nominal ones of each experimental item involved in the diffraction measurement. These differences have the potential to introduce artefacts and ambiguities in the data interpretation process.

The evaluation of the residual systematic effects, still present after the instrument alignment, becomes important when data have to be compared with others taken before by us or taken by others elsewhere. This evaluation is carried out by calculating the effective values of the parameters involved during the measurements. The “correction curve” and the verification of the goodness of the correction are essential steps in the aim of rendering data truly comparable [3,4].
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CALIBRATION, CORRECTION, AND CHARACTERISTIC CURVES

Calibration of a single diffractometer is able in general to ensure that the instrument is working under known “optimum” conditions [1]. Starting from the Bragg’s law, which gives the theoretical locations of the peaks, the “calibration curve” is determined over the full 20 range as a function of the deviations $\Delta 2\theta$, i.e. the separation of the processed (or observed) peak locations from the theoretical locations given by the Bragg’s law. Mallory and Snyder, first had the intuition and proposed the development of curves by aiming to check the instrument alignment by means of an external standard specimen [5]. By fitting the discrete deviations $\Delta 2\theta$, which includes all peak shifts caused by the instrument aberrations and including even other related experiment factors, one obtains the “correction curve” [3]. It is common practice to limit the analysis of the peak shift to few major effects (axial divergence, flat specimen, and transparency). In this case one obtains the “practical calibration curve” [1]. Calibration curves can be predicted from the geometric forms of the aberrations, nevertheless, the control process requires the optimization of a series of parameters referring to: a) geometric set up of diffractometer, b) characteristics of optical devices, by making distinction between instrumental and experiment related factors, c) data processing, [6,7]. In this work the modelling optimization process is implemented by Diffraction Instrumental Monitoring (DIM) code [8,9], which uses modelling constraints and variable restraints on the parameters.

![Figure 1. Optimised calibration curves, (■ Exp-Bragg, Δ Exp-Wilson, — characteristic curve, -- zero line)](image)

Parameters values are thereby made to vary within limits that depend on the physics of the diffraction experiment and the significance of the measurements. Recently, the Calibration Monitoring of Diffractometers project, which has been carried out in Italy from 1997 to 2002, outlined some new properties of the correction curve [10,7]. The most important one is the time invariance; when the calibration process is performed iteratively (usually, each six month) and an appropriate protocol is adopted, the shape of the correction curve is invariant. The shape invariance (or near-invariance) gives helpful suggestions to the user on how to intervene to make lower and lower the systematic contributions (i.e. to improve the general experimental set up). The invariance of the correction curve allows for establishing the characteristic role (the “characteristic calibration curve”) of the curve to define measurement performance, and not only
the diffractometer instrumental performance. Due to the many parameters involved, the type of the adopted model and the limits of any constrained and restrained optimisation modelling, it is essential the interactive role of the skilled operator, who decides if the calculation of the correction curve is satisfactorily reached. To help this operator decision, it is helpful to plot the “optimised calibration curves”. Figure 1 reports: the zero line (dashed), which describes the ideal situation (the null deviation from the expected Bragg angle); the solid line, which is calculated from the inherent not-removable instrument contribution and other experiment related factors.

The “experimental” points (■) are the deviation from the zero line of the diffraction line position, calculated by a fitting process (Lorentzian and pseudo Voigt are the representing function) of the diffraction pattern. In Figure 1 they have been named “EXP-Bragg” to emphasise that the deviations from the Bragg angles contain systematic displacements, which are related to the measurements. The points (Δ) are the deviation from the zero line of the Wilson angles [9]. The Wilson angle 2θW identifies the position of the diffraction line calculated by using a model which is more complete than the Bragg law:

\[ 2\theta^W = 2\theta^B + \sum_{i=1}^{8} T_i(2\theta^B) \]

where the first term is the Bragg angle and the second one is the correction term calculating each individual contribution to the diffraction line shift. The casual straddling of these Wilson angles around the zero line demonstrate that deviations from the Bragg angles are still remaining and they have an accidental origin.

Figure 2 reports the correction curves of three different tests of the optimised calibration on the same diffractometer (diffractometer “A”). The invariance (or near invariance) of the curves in time suggests that such a shape is characteristic of that set of measurements and may be used as a helpful tool for calibration purposes.

The participants to the Calibration Monitoring of Diffractometers program have made available diffractometers and assured that the diffractometer configuration were in compliance with the agreed protocol for data collection at the data collection time (each six months). In the interval between the biannual checks the diffractometer operates according to the laboratory necessities.

In Figure 3 two different series of correction curves are shown for the diffractometer “B” and “C”. In most cases the characteristic shape of the correction curve is time invariant (apart for a
significant translation) for three intentionally repeated tests occurred each six months for the Diffractometers “A”, “B”, and “C”.

![Graph showing repeated measurements on diffractometers B and C](image)

Figure 3. Three repeated measurements on the diffractometers “B” (a) and “C” (b) respectively and obtained from three distinct tests: “line” = 1° cycle; “dash” = 2° cycle; “dots” = third cycle.

When (as in the case shown by Figure 3(b)) the curves are not time invariant, a chance exists that the systematic effects have not been completely calculated. On passing from the first to the third cycle, through the second one, the suggestions obtained by the effective values have been considered to intervene on the instrument re-alignment and on the whole experimental set up.

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<tr>
<th>Table I. Balance “quadrature” of the Calibration of Diffractometers</th>
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<td><strong>Parameters</strong></td>
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<td>χ² = 0.06</td>
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<td>χ² = 0.08</td>
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The result is reported in the Figure 3b (third cycle), where the shape of the correction curve is conserved as in the second cycle, apart from a significant translation effect. It is worthwhile to note that in the case of Diffractometer “C” the effects are of one order greater than “A” and “B”
respectively. Table I reports the effective values obtained as the output of DIM. The balance squaring (or “quadrature”) is obtainable by following three steps: a) by checking the effective values, the $\chi^2$, the values of the cell parameters, which are close to the PDF 10-10173 used as a reference for the calibration purposes; b) by checking the physical significance of the individual parameters; c) by checking the values of each parameter across time (repeatability) and involved diffractometers “A”, “B”, “C” (reproducibility).

**THE EVALUATION OF INTERNAL CONSISTENCY OF DATA**

The evaluation of internal consistency of data benefits from considering the “peak asymmetry” rising on the short wavelength side of the main lines. This asymmetry is in general related to the presence of “some fainter companions, generally called K\(\alpha_3\)” of the components of the K\(\alpha\) spectroscopic complex [6]. The overall observed contribution to this asymmetry is in general much higher than expected from considering the K\(\alpha_3\) transition of the ionized atom alone. There is a kind of further undefined instrumental effect, which tends to magnify the K\(\alpha_3\) contribution; the overall representation can be fulfilled by Lorentzian shape (see Figure 4). This approximate shape stems from considering the effects on the Ewald sphere caused by the K\(\alpha_3\) spectroscopic contribution, the beam divergence, the specimen rotation, the detector rotation, the related 2:1 missetting, and the distance of the detector from the specimen. Instead of using here the generic term “asymmetry” we would rather to emphasise the blurring effect of the mentioned experimental contribution on the K\(\alpha_3\) component of the K\(\alpha\) complex (Wilson, 1963, pag.2).

![Figure 4. Decomposition of peak as given by best fitting involving CuK\(\alpha_1\) (dot line), K\(\alpha_2\) (dashed line) and the “blurred $\alpha_3$“ components (continuous line). The picture includes the observed points(*) and the best fit line (double dot dash blue line)](image)

The evaluation of the internal consistency of the data in the pattern is a test carried out in the course of the data processing and aims to reduce to a low level the risk of introducing ambiguities and artefacts during the data processing. In fact one of the first step of the data processing is the separation of signal from the underlying background. Background is considered

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1 This card is related to not calculated data for Corundum syn. specimens, uses a wavelength that is compatible with that used by DIM and not affected by the wavelength dispersion value of parameter a(7) I Table I.
here as a smooth function. The data processing operating code, DISVAR96, applied to the peak [104] of Corundum is shown in Figure 4. The fitting profile has three distinct contributions: the two spectroscopic terms, Kα₁ and Kα₂ [11,12] and the so-called “blurred α₃” term accounting for asymmetric systematic aberrations. The control of internal consistency starts by adopting appropriate representation function (a composition of pseudo-Voigt and Lorentzian functions), and finally, by checking the parameters related to the profile analysis process.

**Figure 5.** Plots of the profile parameters for checking the internal consistency of a X-ray pattern.

The process starts from checking the Kα₁ and Kα₂ components of X-ray incident radiation. The results of this control are in Figure 5 and regard: a) the spread percentage %S (%S =100×(I_{obs}-I_{norm})/I_{norm}), where I_{obs} and I_{norm} are the normalised observed intensities, coming from the measurement and the PDF 10-0173 respectively; b) the FWHM vs. tanθ, c) the Gaussian-Lorentzian shape parameter “P” vs. 2θ, d) the difference between the processed angular values and the correspondent PDF 10-0173 values. In Figure 6 are reported two of the three controls of consistency performed on the “blurred α₃”
CONCLUSIONS

Calibration of diffractometers involves a number of operations devoted to obtain fine information on alignment, alignment verification, specimen preparation and mounting, data processing refinement. All these mentioned points are potential sources of artefacts, aberrations and ambiguous interpretation of patterns. The balance “quadrature” is a powerful tool to reach this information by leading the operator to the right point to find the causes of aberrations. These aberrations may be either removable (mistakes) or not removable (experimental and instrumental contributions). When mistakes are encountered during the calibration process, they can be removed by following the indication given by the effective values of the parameters of the balance quadrature table.

In general mistakes provide optimised calibration curves where the Wilson angles are no longer straddling around the zero line as it happens in Figure 1 and demonstrated in Figures 7a and 7b [13].

Figure 6. Control of internal consistency for the “blurred $\alpha_3$ “ component.

Figure 7. Examples of erroneous optimised calibration for Diffractometer “A” (a) and “B” (b) due to the mistakes intentionally introduced during the optimisation process, (■ Exp-Bragg, △ Exp-Wilson, — characteristic curve, -- zero line)
They refer to the third test of Diffractometers “A” and “B”, where a mistake on the parameters a(3) of Table I has been introduced to force the correction curve to the shape invariance a part from a translation effect. This forcing translate to the systematic effect shown by Figures 7a and 7b. The mistake on parameter a(2) on the test n. 1 of Diffractometer “C” has the power to modify the shape of the correction curve (Figure 3b). It is worthwhile notice that the forced mistakes have propagated their effects on other values of the balance quadrature table.

ACKNOWLEDGMENTS

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REFERENCES