A QUARTER CENTURY OF ROUND ROBIN TESTS ON XRD

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ABSTRACT
This paper reports on some Round Robins conducted over the past twenty-five years. Although this review is not exhaustive, it outlines the objectives and the most frequent conclusions derived from the analysis of results. As the general follow up from these conclusions a proposal is here launched to establish an international network for the "Calibration Monitoring of the Diffractometers".

INTRODUCTION
X-rays were discovered in Germany more than one century ago. Since half a century Conferences are being called annually in Colorado (“The Denver X-ray Conference”) to state the art and the evolution of the many topics involving X-ray Diffraction. Round Robins tests on powder diffraction measurements have been organised in the world since a quarter of a century. It is now probably timely to promote a world-wide network for monitoring the calibration of diffractometers. Round Robins conducted in the past showed a general low comparability of data although the diffraction patterns showed high internal consistence. The general low capability of reproducing the diffraction measurements suggests a new articulation of the Round Robins where in addition to the purposes of the Round Robins the following should be taken into account:

• the repeatability, reproducibility of the diffraction measurements,
• the repeatability of the accurate determination of the lattice parameters of the calibrant specimen,
• the traceable history of the diffractometers,
• the adequacy of the evaluation of the effective values of the instrumental parameters of the diffractometers under “running conditions” and the performance of the adopted processing system.

The paper presents a short not exhaustive review of some Round Robin tests and their pioneering aspects; by referring a few technical and scientific reasonings on the Calibration Monitoring of Diffractometers (Berti and D'Acunto 2001), the paper outlines the reasons why the proposal of establishing an international network is probably timely. This network should be designed mainly for reaching the following targets:
(a) To monitor the calibration of diffractometers,
(b) To establish protocols of use for the evaluation criteria of the quality of the diffraction measurements,
(c) To set forth rules for harmonised protocols of use of diffraction measurements in various fields of applications and types of analysis.

PROGRESSES AND NEW STANDARDISATION PROCESSES OF X-RAY DIFFRACTION
Recent advances in currently available XRPD methods suggest the possibility of extending XRPD techniques to material diagnosis, which can be carried out without destroying the physical
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properties of the specimens under investigation. The potential exists, for example, of using XRPD as a diagnostic tool for controlling processes where failure analysis and life expectancy play a key role in checking instrumentation and the safety of industrial components. Other foreseeable application fields of interest are chemistry and physics of new materials (micro and nano materials), where the effective properties of substances with low degrees of crystallinity or dimensionality are still difficult to detect reliably via XRPD. Due to such a wide spectrum of potential applications, it is necessary to set forth guidelines on non-destructive testing to develop written Standards which concern the intrinsic features of XRPD. The appropriate definitions and utilisation of such features will render the techniques well-suited to many specific applications within expected limits.

In this sense, the Standard Method of the modern XRPD shall consider at least three distinct levels of the many aspects of XRPD. The first collects all the items, which are necessary to set forth the general aspects of the technique and the various fields of its application. The second level defines the specific standards for each individual field of application. The third one is the level where the procedures and protocols of use are stated to set forth the Standard of individual products. From the discovery to the present time the XRPD has found a great important place in so many applications, all of which have generated separate methods, procedures, routines and even languages. Now, a certain level of harmonisation of use is expected. This harmonisation will improve the understanding of many diffraction-related effects and will extend the application sphere of the technique to new fields.

A SHORT NOT EXHAUSTIVE HISTORY OF ROUND ROBINS OF LAST 25 YEARS
Several Round Robins have been carried out in the last twenty-five years by researchers faced with the need of exchanging data and experiments. These Round Robins involved several researchers and laboratories; the Round Robins provided us with a range of data which can be used in principle to quantify the quality of the standards and the procedures adopted. A not exhaustive list of some of these Round Robins has been summarised here.

1. The Round Robin on computer search-match methods for qualitative analysis (R. Jenkins, 1976) has been carried out with the objective to quantitate the success of computer search/match techniques in the analysis of unknown specimen under routine laboratory conditions. The conclusion the author arrived to was that “hand searching” and “computer” searching are equally efficient for inorganic and mineral analysis, not for organics, where the “hand searching” resulted vastly superior. Principally for the first time, it was realised the overall generality of data was rather poor. It was then decided to design a new R.R. in which three mixtures and three carefully recorded d/I data sets should be submitted to as wide as possible range of diffractionists.

2. The Round Robin on systematic errors found in routine analysis (W.N. Schreiner and T.G. Fawcett, 1984) had the following objectives:
   - study type and extent of systematic errors in routine powder works;
   - study variability of measured 2\(\theta\) values in raw data;
   - obtain raw data for peak hunting round robins etc.;
   - allow participant to compare instrument alignment etc.

The conclusions were that the routine powder diffractometer data is probably 3-5 times worse on the average than most workers are willing to admit (primarily because of displacement errors). The suggestion launched was that the internal standard shall become more widespread.
3. The Intensity Round Robin Report (W.N. Schreiner and R. Jenkins, 1987; R. Jenkins and W.N. Schreiner, 1989) pursued the following objectives:
   - to study measured intensities obtained from modern computer controlled powder diffractometers (performance of data treatment of software packages).
   The conclusions, and the suggestions were:
   - intensity measurement precision in a single person/single laboratory is nearly limited by counting statistics (e.g.: high repeatability).
   - among distinct laboratories systematic errors were observed (e.g.: low reproducibility).
   - an intensity calibration standard would be very useful in improving the intensity reproducibility.
   - expansion of intensity calculation programs to include additional terms associated with the geometric arrangement of the diffractometers.
   - an external standard could be used (alternatively to the above point) to convert between calculated and measured intensity values.
   - a new Round Robin should be designed to explore diffractometer alignment and to identify the calibration standard.

4. The Round Robin on Rietveld Refinement (R.J. Hill, 1992; R.J. Hill and L.M.D.Cranswick, 1994) was intended to reach the following objectives:
   - to evaluate a cross section of currently used Rietveld refinement software
   - to examine the range and effects of various strategies of Rietveld Refinement
   - to assess the precision and spread of the model parameters derived by Rietveld analysis
   - to compare and contrast various methods of step-scan data collection.
   The work provided the following conclusions and outlined a preliminary guideline for using the Rietveld method:
   - the "forgiving" nature of Rietveld analysis allows errors to remain undetected for extended periods (see incorrect calculation of reflection multiplicity)
   - test and tutorials guidelines are required to make users familiar with the refinement strategies on the results of analysis
   - standardisation of use is necessary to uniform the meaning and the process of the agreement indices, the signal/noise ratio, the proportions of the background-only regions.
   The provisional protocol for Rietveld data collection and analysis provided by the authors is summarised as follows:
   • Collect and include in the refinement the maximum reasonable range of d-spacing (obs./struct.param. >10:1)
   • Maximise the instrumental resolution and peak to background ratio
   • Ensure adequate counting statistics at the small d-spacing end of the pattern
   • Provide sufficiently flexible models for the background and the peak shape and width
   • Include an adequate range of steps on either side of the peak centre (0.1% of the intensity)
   • Refine the model to convergence (parameter shifts should be less than 10%) of the associated e.s.d.'s in the final cycle
   • For accurate unit-cell dimensions include an internal standard
   • Specify the type of agreement index used.

5. The Round Robin on Powder Diffraction Sensitivity is also known as the "Instrument Parameters Round Robin" (R. Jenkins, 1992; V. Valvoda. D. Rafaja, L. Dobiasova, R. Kuzel, 1995). The objectives are to study the effects of instrument parameters on the precision of the
d-spacing, the Intensity, the background level, the signal to noise ratio, the resolution. Conclusions and recommendations are summarised here following:

- the differences of the relative intensities are too large and contain some errors
- to use appropriate current (mA) and Voltage (KV), and appropriate receiving slit, step size, divergence slit, secondary collimator, the count time etc.
- to check the instrument alignment and the instrument sensitivity by the Standard Reference Specimen
- to use the $\Delta 2\theta$ correction curve
- the use of the sensitive curve.

6. Intensity Round Robin (V. Valvoda and D. Rafaja, 1995). The claimed objective was to determine the interplanar spacing and the integral intensity of 11 reflections of Corundum and 12 reflections of Anglesite to use as a comparison with Rietveld analysis. The main conclusion was that the powder sample preparation plays a minor role in comparison with errors caused by a poor diffractometer alignment. Moreover, the claimed standard deviations of each user are 3-6 times lower than the standard deviations of whole data (e.g. each diffraction pattern shows high internal consistency and low reproducibility). Finally the users are solicited to use certified standard sample and to adopt appropriate data collection strategies because these are important to obtain reliable results.

7. The Round Robin on quantitative phase analysis of $\alpha$- and $\beta$- silicon nitrides (H. Toraya, S. Hayashi, T. Nakayasu, 1999). The claimed objective was to test the accuracy, the precision of the results obtained by using the proposed guidelines for the following three methods: the Rietveld method, the Mean Normalized Integrated method and the Peak Intensity method. The conclusion is that the main cause of error occurs during the derivation of the scale factor. The presence of both random numerical error and systematic errors is not negligible. In particular, the Rietveld refinement gives high precision; the scale factors are too sensitive to the choice of a constrained or unconstrained FWHM models.

A PROPOSAL FOR THE INTERNATIONAL NETWORK FOR THE "CALIBRATION MONITORING OF DIFFRACTOMETERS"

A group of participants in the Italian standardisation programme of X-ray Diffraction is aware that a long standing problem exists in X-ray diffraction measurements; they are confident that the way to resolve it is through written procedures and protocols of use. Their goal is to go beyond the observations made on data during the various Round Robins and to overcome the conclusions regarding the results of measurements. If the Round Robins showed the generally low comparability of data despite the great internal consistency, we speculate that this fact is independent of diffractometer technology; it may actually depend on how we practice and train the diffractometry. How to surpass the observation stage and reporting of data, which is typically the main aim of a Round Robin project? New requirements and articulation of the Round Robin activity are the possible answers. The implementation of a continuous Round Robin activity enables controlling the repeatability, the reproducibility and the traceability of the diffraction measurements. According to the "International vocabulary of basic and general terms in metrology" (ISO 1993) these terms mean:

- repeatability is the closeness of the agreement of results obtained under the same conditions (procedures and protocols, observer, measuring instrument, location, repetition over a short time)
- reproducibility is the closeness of the agreement between the results under changed conditions of principle and method of the measurement, observer, measuring instrument, location, condition of use, time.
- traceability is the capability to recover the history of the various diffraction measurements. This activity implies implementation of a “network of Monitoring the Calibration of Diffractometer”.

In this activity, the repeatability and reproducibility are expressed in terms of the deviation from the expected characteristic curve of a diffraction experiment (Berti and D'Acunto, 2001). This deviation indicates the presence of systematic experimental effects which might lead to biased results of the diffraction measurements.

The following “space-time diagram” shows a schematic view of the “Network of Monitoring of the Diffractometer Calibration” (Berti and al. 2000).

![Diagram illustrating the functioning of the proposed international network as it is described in the text.](image)

**Figure 1:** Diagram illustrating the functioning of the proposed international network as it is described in the text.

The evaluation of the local reproducibility is evaluated by checking the data collected by using distinct devices and operators. The repeatability is checked by intentional repeated collection of data at any time and according to the user need. The Coordinator Centre collects the data files and processes them according to a defined protocol. The characteristic curves of the user laboratory and the diffractometers are established and validated by a number of iterations. The repeatability
and the reproducibility are evaluated on the basis of the deviation from the established Characteristic curves.

CONCLUSIONS
Although this project could appear ambitious and very expensive, it costs few percent of the expensed supported to validate the results. Well established results will take probably many years for being reached. It requires establishment of the characteristic curves of the diffraction experiment, the method of analysis and the protocol of use.

REFERENCES