Basics of Rietveld refinement

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The last step in the pathway of the solution process by powder diffraction data is the structure model refinement by the Rietveld method (Rietveld, 1967, 1969) whose fundamentals are thereinafter given. For more details about this topic see specialized books [*e.g.* by Young (1993)] and papers (*e.g.,* McCusker *et al.*, 1999).
The main features and an example of application of the Rietveld refinement by *EXPO2014* (Altomare *et. al.*, 2013) are also briefly described.

The Rietveld Method: an overview
The Rietveld method is a whole-pattern-fitting technique based on cycles of non-linear least squares, whose aim it to refine both structure and profile parameters. The method, firstly proposed and applied to neutron diffraction data, revealed itself effective also in case of X-ray diffraction data. Other useful applications of the Rietveld method are: i) microstructure analysis; ii) quantitative phase analysis.
Let us consider the experimental profile $\{y_i(obs)\}$ and the calculated profile $\{y_i(calc)\}$, where $y_i(calc)$ is a function of *n* refinable parameters $\{x_1,..., x_j,...., x_n\}$. The basic idea of the Rietveld method is to obtain the best estimate of the refinable parameter x_j by minimizing, *via* least-squares technique, the following quantity (*i.e.*, the residual function *S*):

$$S = \sum_i w_i [y_i(obs) - y_i(calc)]^2 , \qquad (1)$$

where the summation is overall data points; $w_i = 1/y_i(obs)$ is a weight associated to the *i*-th observed count. Structure model and profile parameters (*i.e.*, atomic coordinates, isotropic and anisotropic thermal factors, site occupancies, unit cell, 2θ zero, asymmetry, background coefficients, scale factor, peak shape, ...) are refinable parameters as well as preferred orientation, absorption correction, specimen displacement, specimen transparency, crystallite size and microstrain.
The residual function *S* is a non-linear function [being $y_i(calc)$ a non-linear function], consequently, the minimization procedure is carried out in an iterative way: approximate values for all parameters are used for the first refinement cycle, then the next refinement cycles are applied to the updated parameters up to a convergence criterion has been reached.
Due to the non-linearity of the relationships between the refinable parameters and the calculated profile, the starting model to be refined has to be close to the true one; if this condition is not satisfied the refinement procedure may diverge or converge to false minima. The trap of false minima is particularly critical in case of powder data, due to the correlation between the several refined parameters (*e.g.*, site occupancy and thermal factor) and the loss of information related to the collapse of the three-dimensional reciprocal space into the one-dimensional powder diffraction profile.
The reliability of the Rietveld refinement outcome depends not only on the starting model to be refined but also on the data quality, on the goodness of the description of the

observed profile by analytical function, and on the refinement strategy (see, *e.g.*, the refinement guidelines described by McCusker *et al.*, 1999).
Several criteria of fit are used to monitor the progress of the Rietveld refinement, among them the profile agreement factors R_p and R_{wp}, able to check the difference between the observed and calculated pattern:

$$R_p = \sum_i | y_i(obs) - y_i(calc) | / \sum_i y_i(obs), \quad (2)$$

$$R_{wp} = \{ \sum_i w_i [y_i(obs) - y_i(calc)]^2 / \sum_i w_i [y_i(obs)]^2 \}^{1/2}. \quad (3)$$

Among the different criteria of fit R_{wp} is the most meaningful, being the numerator in (3) the residual S to be minimized.
Other useful criteria for judging the goodness of a Rietveld refinement are based on the experience and suggested by i) an inspection of the difference profile, giving insights on the parameters that need to be further refined (*e.g.*, cell parameters and/or 2θ zero, in case of errors on reflections positions); ii) the chemical sense of the refined structure model (*e.g.*, reliable bond distances, bond angles, …)
To reduce problems due to the loss of experimental information, additional observations can be exploited at the least-squares refinement process. They can be included as constraints (*i.e.*, rigorous or hard constraints) or as restraints (*i.e.*, soft or slack constraints).
Constraints are imposed so that the related conditions are exactly fulfilled, *e.g.*, in case of constraints on symmetry involving atoms on special positions. Other examples of constraints concern the atomic displacement parameter (ADP), *e.g.*, the assignment of the same value to all the atoms belonging to the same species, or, in case of H-atom, the riding model approximation, according to which the position of H-atom in X-H bond is recalculated from the current refined position of the atom X (*i.e.*, X-H distances, as well as, if present, H-X-H angles are constraint to fixed values); also the ADP of H-atom is recalculated by multiplying by a constant the ADP of the atom X in X-H bond.
Restraints are relationships imposed approximately. Restraints, *e.g.*, on bond distances, bond angles, planarity, can be managed as a second data-set compensating for the loss of information and increasing the ratio 'Observations/Number of parameters to be refined'.
The quantity to be minimized in the refinement is (McCusker *et al.*, 1999)

$$S = S_y + c_w S_G, \quad (4)$$

where S_y is given by (1), $S_G = \sum w[G_{obs} - G_{calc}]^2$, G_{obs} and G_{calc} are the expected and calculated geometric restraints, respectively; c_w is a suitable weight of the geometric observations data-set with respect to the diffraction data-set.
Restraints are useful for stabilizing the refinement procedure, avoiding false minima, opening the door to the structure refinement of challenging structures. It is worth noting that the use of restraints has made possible protein powder refinement (Von Dreele, 1999, 2007; Margiolaki *et al.*, 2013).

The Rietveld refinement by EXPO2014

EXPO2014 is able to carry out a user-friendly Rietveld refinement thanks to an effective graphic interface. Among the refinable parameters: Unit cell, Background coefficients, Profile shape function coefficients, Asymmetry parameter, Preferred orientation [by March-Dollase function (Dollase, 1986)], 2θ-zero correction, Scale factor, Atomic positions, thermal factors and site occupancy.

The most commonly adopted criteria of fit can be applied (among them R_p and R_{wp}). Restraints on bond distances and/or bond angles and/or planes can be applied as well as constraints (*e.g.*, in case of riding model approximation and ADP). In Fig. 1 the graphic interface of *EXPO2014* enabling to manage restraints and constraints is shown.

H atom(s) can be located and added to the structure model by using geometrical criteria. The H-atom generation can be carried out in automatic way or selecting the carbon type (*e.g.*, tertiary C-H, secondary CH2, primary CH3, ethylenic=CH2, acetylenic ≡ CH, aromatic C-H).

The starting values of the parameters to be refined are automatically assigned by *EXPO2014*. The strategy of refinement can be automatic or user defined. The user intervention is minimal.

Not always the automatic refinement of profile and crystal structure is advisable and successful, particularly in case of poor quality data and/or complex structure. Thereinafter an example of successful automatic refinement of *EXPO2014* on 2-(4-Hydroxy-2-oxo-2,3-dihydro-1,3-benzothiazol-7-yl)-ethyl-ammonium chloride (Florence *et al.*, 2005), with code name AMMONIUM (Chemical Formula: $C_9H_{11}N_2O_2S{\cdot}Cl$), is described.

The starting model of AMMONIUM consists of 15 non-H atoms correctly located (within a distance from the true atoms less than 0.6 Å). Their average distance from the published structure is 0.149 Å; the corresponding R_p and R_{wp} values are 11.937% and 21.06%, respectively.

By using a graphic tool of *EXPO2014* it is possible to place at calculated positions all the 11 H atoms in the asymmetric unit. If an automatic refinement of crystal structure and profile is carried out (in case of H atoms the riding approximation is adopted) R_p, R_{wp} and the distance of non-H atoms lower to 2.723%, 3.573% and 0.082 Å, respectively.

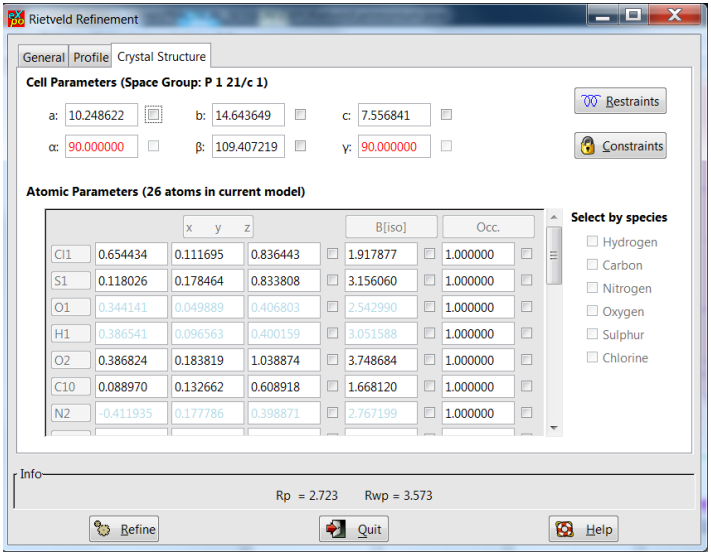

Figure 1. Dialog window of *EXPO2014* enabling to manage restraints and constraints at the Rietveld refinement step.

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