RIETVELD REFINEMENT: GOLD STANDARD OF QUANTITATIVE ANALYSIS

ASHNA JOYSON*[1], ASWATHY. S[1], RENI.M[1], JOSNA JOHNSON[1], VIPIN R[1],

ANNAMMA BABY[2]

[1]Fourth year B. Pharm, Mar Dioscorus College of Pharmacy, Trivandrum, Kerala, India
[2]Assistant professor, Department of Pharmaceutical Analysis, Mar Dioscorus College of Pharmacy, Trivandrum, Kerala, India

* ASHNA JOYSON

ABSTRACT:

The Rietveld refinement is a popular analytical technique for the quantitative phase analysis of various natural and synthetic materials. It can be used for both fully crystalline multiphase systems as well as for materials containing even an amorphous fraction. This method involves the analysis of XRPD data and utilizes the Rietveld refinement technique to determine the relative proportions of each phase present in the sample. Overall, the Rietveld method offers a reliable and accurate means of characterizing materials and is essential for various scientific and industrial applications. A modified version of the Rietveld computer program has been used to perform quantitative phase analysis of multicomponent mixtures using X-ray powder diffraction data. The improved program was successful in determining composition of mixtures with high accuracy and precision. Quantitative information was obtained through refined individual scale factors and unit cell volumes using Rietveld refinement program. The analytical report of quantitative phase analysis using Rietveld refinement method specify the details of the instrument used for data collection as well as software and databases employed for the Rietveld refinement. To correct the preferred orientation, we processed the XRPD patterns using commonly available program Rietveld refinement. It allows for accurate determination of crystal structure, lattice parameter and atomic positions.

Key words: Rietveld refinement, XRPD, Quantitative phase analysis, preferred orientation

INTRODUCTION:

Rietveld refinement is a multiparameter curve fitting methodology to refine X Ray diffraction result [1,2,3]. Rietveld refinement technique was developed for the refinement of crystal structure, it is also very efficient in quantitative phase analysis [4]. It was first introduced and implemented full profile refinement method in powder diffraction by professor Hugo Rietveld [1,5,6]. In modern crystallography it is treated as a black box [7]. Crystal structure data having physical constants used for calculating reflection intensities eliminates the errors associated with the procedures [4]. The Rietveld refinement is mainly developed for refinement of crystal structure from neutron powder diffraction data. The physical origins affect diffraction lines, the diffraction angle have high degree of correlation between the refinable parameters [8].

Quantitative phase analysis is capable of determining the proportion of each crystalline phase in a multiphase sample, as well as identifying the presence and quantity of amorphous phases. This technique utilizes diffraction patterns to measure the intensities of diffraction peaks from each phase and compares them to reference standards. By accurately quantifying the amount of each phase present, quantitative phase analysis provides crucial information for material characterization and optimizing manufacturing processes. The technique is widely used

in fields such as materials science, geology, and pharmaceuticals [9]. Rietveld refinement based quantitative phase analysis is more accurate and precise than methods based on chemical extraction [10]. The precision of the method was tested by independent replicate sample preparation and analysis. The analysis yielded information on the proportions of different phases and the refined substitutions of elements. These findings provide insight into the composition and structure of the material being analysed [11]. This technique refines user selected parameters to minimise the difference between experimental (observed) pattern and model based on hypothesised crystal structure and instrument parameters (calculated pattern) [1] by least square method [12,13].

Rietveld analysis is a complex process, since it must fit structural, sample, instrumental terms. It can also provide result that cannot be obtained in other ways or results at their ultimate precision. With the availability of appropriate specimen, structural determination from single crystal diffraction is preferred, sometimes measurement condition preferred powder diffraction. For this reason, use of Rietveld refinement technique is increasing [14].

Application

- microstructural information
- Crystalline size distribution
- Average domain size
- Crystalline defect concentration [8]
- Texture analysis
- Standardless Quantitative phase analysis [12]
- Percentage crystallinity
- Quantitative phase analysis
- Characterization of substitution
- Unit cell determination and shape
- Atomic coordinates/bond length
- Micro strain in crystal lattice- texture effects [15]

It can apply only when the cell dimensions and space group are known and when a reasonable model exists for the structure and allows extraction of the maximum amount of information contained in the powder pattern. The refinement technique allows calculation of shift in the parameters which improve the fit of calculated powder pattern to the observed one [16]. It is able to refine whole profile with parameters including half-width, zero shift, cell parameters [17], preferred orientation correction [18,19], overall asymmetry correction, overall scale factor, overall isotropic temperature factor, fractional coordinates of the atoms, atomic isotropic temperature and the components of the magnetic vectors of each atom [20,21].
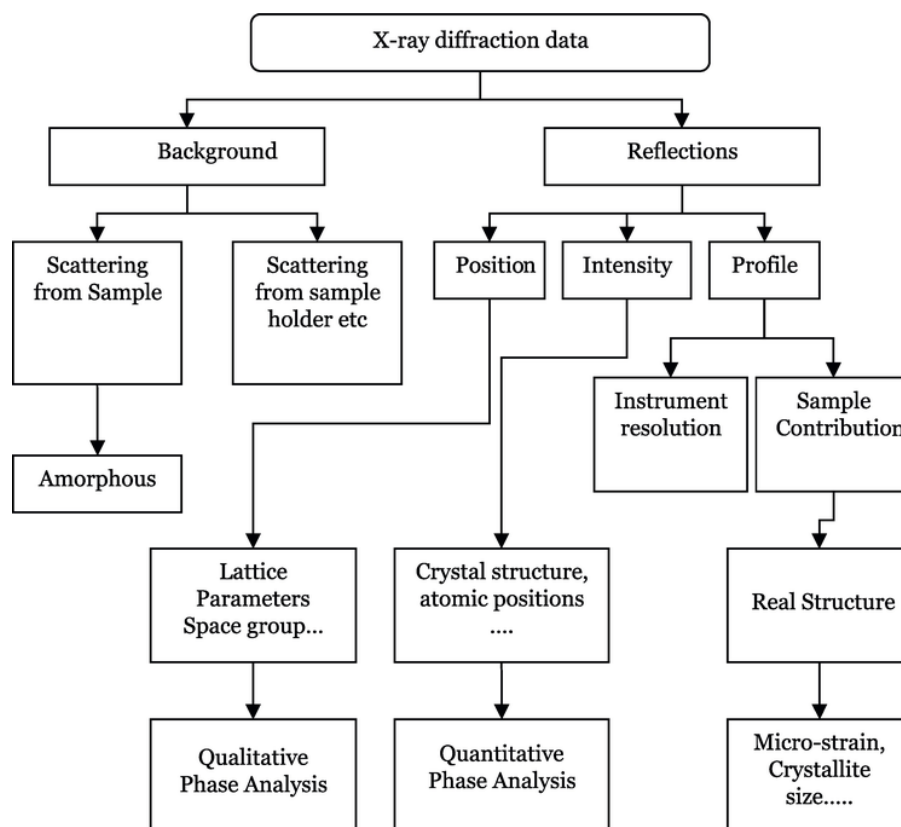
Fig: The algorithm of whole profile refinement program developed by Hugo M Rietveld [reconstructed from the IUCr newsletter no. 26, Dec 2001].

For performing Rietveld refinement, it is essential that powder diffraction data be collected approximately. There are so many factors to be consider prior to data collection, quality of diffractometer, quality of the instrument alignment, and calibration, suitable radiation, wavelength, appropriate sample preparation and thickness. Structure refinement does not yield sensible result, if the relative intensities are not correct. The peak describes the both sample and instrument function. Single peak is selected for the diffraction pattern as a standard peak. The percentage depends on the peak shape. The peak is fitted to some criteria and this curve is divided into symmetric and asymmetric part; values are stored in tabulated form. Before refinement the structural parameters and the position of the peak should be matched well [6]. Peak shape depends on crystallite/domain size, stress/strain, defects/vacancies, source/geometry, slit-size/detector resolution and 2θ/hkl indices [22].

Two approaches are used in powder diffraction pattern. One is linear interpolation between the peak or it can be modelled by empirically. Both these methods work well and fit easily with a plot. Most of the peak not resolved in the baseline so the estimation of background is difficult. In this condition background subtraction approach is used, the background is re-estimated and re-subtracted in the refinement [23].
The refinement decreases the uncertainties in cell-parameter determination. Cell parameters are influenced by sample height, instrumental and sample factors, sample absorption, peak shape and instrumental calibration. On heating material undergoes a phase transition to simple cubic structure [24].
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Rietveld refinement analysis is an effective tool for determining the magnetic structure of materials using powder diffraction data.

The GSAS (The General Structure and Analysis System) software is commonly used and it has the ability to compute magnetic scattering [3].

For n diffraction peaks n-1 parameters can refine

Accurate structural information from powder diffraction data is enhance by combination of Rietveld refinement and Maximum Entropy Methods (MEM) [12]. It is done in sets of two to five cycles at a time but for effective refinements hundreds of cycles will be required and thousands for complex systems. The GSAS (The General Structure and Analysis System) software is commonly used and it has the ability to compute magnetic scattering [3].

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R value

Reliability factors or residual values or Rietveld refinement indiced or R values by Rietveld enabled us to visualize profile fit between observed and calculated patterns more effectively [3,25,26,27].

The weighted profile R value, $R_{wp}{}^2 = \sum_i w_i (y_{C,i} - y_{O,i})^2 / \sum_i w_i (y_{O,i})^2$

Where, w_i the weight at i^{th} step, $y_{C,I}$ is the observed intensity and y_{oi} is the calculated intensity. [28]

MATERIALS AND METHODS:

Requirements for Rietveld refinement
- Experimental diffraction pattern
- Suitable peak and background functions
- A stricture method that makes physical and chemical sense [12]

Crystal structure information get from

- Publications
- Commercial Databases
  - ✓ ICSD (International Crystal Structure Database)
  - ✓ LPF (Linus Pauling File)
  - ✓ NIST Structural Database
- Free Online Databases
  - ✓ ICDD (International Centre for Diffraction Data)
  - ✓ CCDC
  - ✓ Crystallographic open data base
  - ✓ Webmineral
  - ✓ Mincryst
  - ✓ American Mineralogist
  - ✓ Protein data bank
  - ✓ Nucleic acid Database [28]

Rietveld programs
- Fullprof
- GSAS
- Bruker TOPAS
- MDI Jade or Ruby
- Rietica
- PSSP
- Powder cell
- Panalytical X'Pert highscore Plus v3.0d [29]
- EDINP
- XRS-82[30]

Challenges

- Lack of 100 % representative specimen especially powder sample- Differences in grain size, preferred orientation, inhomogeneous grain boundary and other microscopic difference cause limitations
- Porosity of sample- I case of nanomaterial the increase in surface area to volume ratio cause apparent amorphicity in crystalline sample.
- Continues motion of either or both detector and sours of goniometer and recording transit timer of cameras [31]
- Errors in input file, can corrected by converting filer into suitable format using software's [32].

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