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Rietveld Refinement

The Rietveld Method

Based on the idea suggested in the middle 1960s by Rietveld

Aim of the method

All structural and instrumental parameters are refined by fitting a calculated profile to the observed data without extraction of the individual integrated intensities

- Nonlinear least squares method
- Requires a model of a crystal structure

Fundamentals of the Rietveld Method

The minimized function is given by:

$$\chi^{2} = \sum_{i=1}^{N} w_{i} [y_{i,obs} - y_{i,calc}]^{2}$$

 $y_{i,obs}$ is the observed intensity at the *i*th data point

 $y_{i,calc}$ is the calculated intensity at the *i*th data point

The weight is given by $w_i = rac{1}{y_{i,obs}}$

Peak-Shape Functions

The diffracted profile is expressed by the equation:

$$y_{i,calc} = b_i + S \sum_{k=1}^m I_k y_k(x_k)$$

 $y_{i,calc}$ is the total intensity calculated at the point *i*

k=1

- b_i is the background intensity
- S is the phase scale factor
- y_{ik} is the contribution from the *k*th individual Bragg peak
- I_k is the intensity of the *k*th Bragg reflection and the sum is extended over all *m* reflections contributing the intensity to point *i*

$$x_k = 2\theta_i - 2\theta_k$$

$$y_{i,calc} = b_i + S \sum_{k=1}^{m} I_k [y_k(x_k) + 0.5y_k(x_k + \Delta x_k)]$$

wavelength 1.54059 1.54443 0.5



Intensity

Fundamentals of the Rietveld Method

The intensity I_k is given by the expression:

$$I_k = M_k L_k |F_k|^2 P_k$$

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 M_k is the multiplicity

 L_k is the Lorentz-polarisation factor

- F_k is the structure factor
- P_k is the preferred orientation

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Single phase crystalline material:

$$y_{i,calc} = b_i + S \sum_{k=1}^m I_k y_{ik}$$

Mixture of several N_p phases:

$$y_{i,calc} = b_i + \sum_{p=1}^{N_p} S_p \sum_{k=1}^m I_k^p y_{ik}^p$$

For mixture of several phases, the contribution from every crystalline phase is accounted in the expression of y_{ci} .

Quantitative analysis of a multiple phase crystalline material

Multiple phase powder diffraction patterns

<pre>%job Sample_ID_1e (Corundu 15.25%)</pre>	m 55.12%, Fluorite 29.62%, Zincite
<pre>%structure Sample_ID_1e</pre>	
<pre>%data pattern cpd-1e.dat wave 1.54056 1.54439 0.5</pre>	
<pre>%crystal Corundum-Al2O3.cif</pre>	Rietveld Refinement _ C ×
<pre>%crystal Fluorite-CaF2.cif</pre>	General Powder Data Corundum-Al2O3 Fluorite-CaF2 Zincite-ZnO
<pre>%crystal Zincite-ZnO.cif</pre>	Automatic Procedures Print Options Automatic refinement of profile Image: start/end cycle
%rietveld	Automatic refinement of structure correlation matrix LSQ matrix Number of Cycles: 3 - + CIF
	LSQ Options Number of Cycles: 30 - + Weighting Scheme: # 2: W=1.0/Count Criterium of Convergence: 4 - + Refine non-structural parameters with Le Bail method
J. Appl. Cryst. (2001). 34, 409-426	Info Rp = 37.335 Rwp = 45.840 Refine Quit BLP

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Fundamentals of the Rietveld Method

$$\chi^2 = \sum_{i=1}^{N} w_i [y_{i,obs} - y_{i,calc}]^2$$
$$y_{i,calc} = b_i + S \sum_{k=1}^{m} I_k y_{ik}$$

$$I_k = M_k L_k |F_k|^2 P_k$$

The Rietveld method is similar to the full pattern decomposition using:

- **Pawley algorithms**: the integrated intensities are treated as free least squares variables. We minimize χ^2 respect to $|F_k|$ (non linear least-squares) or $|F_k|^2$ (linear least-squares).
- Le Bail algorithms: the integrated intensities are determined iteratively after each refinement cycle

Mathematical procedure*

$$\chi^{2} = \sum_{i=1}^{N} w_{i} [y_{i,obs} - y_{i,calc}]^{2}$$

 $y_{i,calc}$ is a non linear function with respect to the unknown parameters, $x_1, x_2, ..., x_m$ and a system of equations can be assumed:

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$$y_{1,calc} = M_1(x_1, x_2, ..., x_m)$$

$$y_{2,calc} = M_2(x_1, x_2, ..., x_m)$$

$$y_{N,calc} = M_N(x_1, x_2, ..., x_m)$$

In the matrix form:

$$\chi^2 = [\mathbf{y} - \mathbf{M}(\mathbf{x})]^T \mathbf{W} [\mathbf{y} - \mathbf{M}(\mathbf{x})]$$

* Chapter 3 of the monograph The Rietveld method, R.A. Young, Ed., Oxford University Press, Oxford, New York (1993)

Linear Least Squares

$$\chi^2 = [\mathbf{y} - \mathbf{M}(\mathbf{x})]^T \mathbf{W}[\mathbf{y} - \mathbf{M}(\mathbf{x})]$$

 ${f y}$ is the set of observable quantities $y_{1,obs},y_{2,obs},...,y_{N,obs}$ ${f W}$ is a diagonal matrix whose diagonal elements are $w_1,w_2,...,w_N$

If the model function is linear

$$\mathbf{M}(\mathbf{x}) = \mathbf{A}\mathbf{x} + \mathbf{b}$$

The set of parameters ${f x}$ that minimizes $~\chi^2$ is the solution of normal equations

$$\mathbf{J}^T \mathbf{W} \mathbf{J} \mathbf{x} = \mathbf{J}^T \mathbf{W} (\mathbf{y} - \mathbf{b})$$

J(x) is the Jacobian matrix
$$J(x)_{ij} = \frac{\partial M_i(x)}{\partial x_j}$$
 $1 < i < N$
 $1 < j < m$

Example of linear least squares: background in a polynomial approximation, phase scale, are linear, $|F_{\mu}|^2$ in the Pawley full pattern decomposition

Nonlinear Least Squares

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Expanding the model function M(x) around the starting point x_0 in Taylor's series and retaining only the linear terms we obtain the equation:

$$M(x) \approx M(x_0) + J(x_0)(x - x_0)$$

Gauss Newton algorithm for each *k* iteration

(1) Compute the search direction d as the solution of the linear system $\mathbf{J}^T \mathbf{W} \mathbf{J} \mathbf{d} = \mathbf{J}^T \mathbf{W} [\mathbf{y} - \mathbf{M}(\mathbf{x})]$ (2) Set $\mathbf{x}_k = \mathbf{x}_{k-1} + \mathbf{d}$

(3) If not converged go to (1), else stop.

Gauss-Newton-Type Methods

Gauss-Newton method with a line search

Set $\mathbf{x}_{k-1} = \mathbf{x}_k + \alpha \mathbf{d}$

where called step length, is such that the algorithm is in descendant condition:

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$$\chi^2(\mathbf{x}_k + \alpha \mathbf{d}) < \chi^2(\mathbf{x}_k)$$

is chosen by a line-search procedure

Levenberg–Marquardt algorithm modify the normal equations in

$$(\mathbf{J}^T \mathbf{W} \mathbf{J} + \lambda \mathbf{I}) \mathbf{d} = \mathbf{J}^T \mathbf{W} [\mathbf{y} - \mathbf{M}(\mathbf{x})]$$

where I is the identity matrix, λ is a damping factor

Standard deviations

Variance-covariance matrix: $\mathbf{V}_x = (\mathbf{J}^T \mathbf{W} \mathbf{J})^{-1}$

$$\sigma(x_j) = \sqrt{\frac{(V_x)_{jj}\chi^2}{n-m}}$$

n is the number of observations

m is the number of unknown parameters

 $(V_x)_{jj}$ is the corresponding diagonal element of the variance-covariance matrix

General Powder Data cime	
Automatic Procedures Print Options Automatic refinement of profile If start/end cycle Automatic refinement of structure If conclusion matrix Number of Cycles: 3	
LSQ Options Number of Cycles: 30 - + Weighting Scheme: # 2 : W=1.0/Count Criterium of Convergence: 4 - +	
Refine non-structural parameters with Le Bail method	
Info Rp = 31.854 Rwp = 43.076	
🗞 Refine 🛃 Quit	

Classes of Rietveld Refinement Parameters

$$\chi^2 = \sum_{i=1}^{N} w_i (y_{i,obs} - [b_i + S \sum_{k=1}^{m} I_k y_k (x_k)])^2$$

- Background coefficients
- Sample displacement, sample transparency or zero-shift corrections
- Peak-shape function parameters
- Unit cell dimensions
- Preferred orientation
- Scale factors
- Positional parameters
- Atomic site occupancies
- Atomic displacement parameters

Background Functions

Polynomial function

$$b_i = \sum_{j=1}^m B_j (\frac{2\theta_i}{2\theta_0} - 1)^{j-1}$$

where $2\theta_0$ is the the origin of the background polynomial and B_j are the parameters to be refined

Chebyshev polynomial

$$b_i = \sum_{j=1}^m B_j T_{j-1}(x)$$

Cosine Fourier series

j=1

$$b_i = \sum_{j=1}^{m} B_j \cos(2(j-1)2\theta_i)$$

where

$$x = \frac{2(2\theta_i - 2\theta_{min})}{2\theta_{max} - 2\theta_{min}}$$

and $T_{j-1}(x)$ are the Chebyshev polynomials:

 $T_0(x) = 0$ $T_1(x) = x$ $T_{n+1}(x) = 2xT_n(x) - T_{n-1}(x)$

Background function

File Dattern View Solve Define Infe	Modify Function
Intervals Background	Function type Polynomial Chebyshev Cosine Fourier series
Modify Peaks > Indexing >	20 C Automatic
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Function type: Chebyshev; Number of coefficients: 16	Modify
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Peak shape functions

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Pseudo-Voigt profile function

$$y(x) = \eta \frac{C_G^{1/2}}{\sqrt{\pi}H} e^{(-C_G x^2)} + (1 - \eta) \frac{C_L^{1/2}}{\pi H} (1 + C_L x^2)^{-1}$$

$$x = \frac{(2\theta_i - 2\theta_k)}{H_k}$$

$$C_G = 4\ln 2, C_L = 4, C_G^{1/2} / \sqrt{\pi}H \text{ with } \int_{-\infty}^{\infty} y(x)dx = 1$$

 $\eta = \eta_0 + \eta_1 2\theta + \eta_2 2\theta^2$, where $0 \le \eta \le 1$

 $H = \sqrt{Utan^2\theta + Vtan\theta} + W \qquad \text{Caglioti formula}$

 $\eta_0, \eta_1, \eta_2, U, V$ and W are refined variables

Modified Thompson-Cox-Hastings pseudo-Voigt

$$y(x) = \eta \frac{C_G^{1/2}}{\sqrt{\pi}H} e^{(-C_G x^2)} + (1-\eta) \frac{C_L^{1/2}}{\pi H} (1+C_L x^2)^{-1}$$

$$H = \sum_{i=0}^{5} a_i H_G^{5-i} H_L^i$$
$$H_G = \sqrt{Utan^2\theta + Vtan\theta + W + Z/cos^2\theta}$$

$$H_L = X/\cos\theta + Y \tan\theta$$

$$\eta = \sum_{i=1}^{3} b_i \left(\frac{H_L}{H}\right)$$

U, V, W, Z, X and Y are refined variables

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Pearson-VII profile function

$$y(x) = \frac{\Gamma(\beta)}{\Gamma(\beta - 1/2)} \frac{C_p^{1/2}}{\sqrt{\pi}H} (1 - C_p x^2)^{-\beta}$$

$$\beta = \beta_0 + \beta_1 / 2\theta + \beta_2$$

 $\begin{array}{l} \beta = 1 \ {\rm Cauchy \ function} \\ \beta = 2 \ {\rm Lorentz \ function} \\ \beta = \infty \ {\rm Gauss \ function} \end{array}$

The FWHM (H) is modeled by using the Caglioti formula as in the case of the pseudo-Voigt function

 $\beta_0, \beta_1, \beta_2, U, V, W$ are refined variables

Default choice

Peak Asymmetry

The correction for the peak asymmetry is applied by using as multiplier the semi-empirical function given in Bérar & Baldinozzi, (1993). J. Appl. Cryst. 26, 128-129

$$A_{ik} = 1 + P_1(\theta_k)F_a(z) + P_2(\theta_k)F_b(z)$$

$$P_1(\theta_k) = A_0/tan(\theta_k) + A_1/tan(2\theta_k)$$
$$P_2(\theta_k) = B_0/tan(\theta_k) + B_1/tan(2\theta_k)$$

$$F_a(z) = 2ze^{-z^2} F_b(z) = (8z^3 - 12z)e^{-z^2} z = \frac{\theta_i - \theta_k - S}{H_k}$$

 A_0, A_1, B_1 , and B_2 are refined variables

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Preferred orientation

The preferred orientation P_k is calculated using the March-Dollase function (Dollase, 1986):

$$P_k = \frac{1}{N} \sum_{i=1}^{N} (G^2 \cos^2 \phi_k^i + \frac{1}{G} \sin^2 \phi_k^i)^{-3/2}$$

where Φ_k is the angle between the reciprocal lattice vector $\mathbf{d_k}^*$ corresponding to a Bragg reflection k and the reciprocal lattice vector parallel to the preferred orientation axis.

G is the refined parameter

Line-shifts corrections

$$2\theta_{obs} = 2\theta_{calc} + \Delta 2\theta$$

$$\Delta 2\theta_s = -2s\frac{\cos\theta}{R} = S\cos\theta$$

Sample displacement error in Bragg-Brentano geometry

$$\Delta 2\theta_t = \frac{1}{2\mu R} \sin 2\theta = T \sin 2\theta$$

Transparency correction in Bragg-Brentano geometry

$$\Delta 2\theta = S\cos\theta + T\sin2\theta + Z$$

The constant term Z is the zero-shift error

S, T, and Z are refined variables

Profile parameters

The Le Bail technique can be adopted to perform a full pattern decomposition prior to Rietveld refinement

	Rietveld Refinement _ C X
General Profile Crystal Structure	
Automatic Procedures	Print Options Image: Start/end cycle Image: correlation matrix Image: Standard deviation
LSQ Options Number of Cycles: 30 🗘 W Criterium of Convergence: 4 2 Refine non-structural parameters with Le Ba	/eighting Scheme: # 2 : W=1.0/Count v
lfo	
Rg	p = 8.222 Rwp = 13.351 Image: Constraint of the second s

This strategy is suggested especially if the available structure model is not completed (Rietveld refinement guidelines, L.B. McCusker, R.B. Von Dreele, D.E. Cox, D. Louer, P. Scardi, *J. Appl. Cryst.* **32** (1999) 36)

Refinement strategies

The refinement can be carried out by following two alternative approaches:

- The user can decide the refinement strategy via graphical interface
- An automatic refinement schedule can be applied
 - Scale
 - 20 correction
 - Background coefficients
 - W
 - U, V, other profile parameters
 - Coordinates of atoms
 - Isotropic displacements

Restraints

$$\Phi = \sum_{i=1}^{n} w_i \cdot (y_{i,obs} - y_{i,calc})^2 + w_{dist} \sum_{i=1}^{n} w_i \cdot (dist_i^{exp} - dist_i^{calc})^2 + w_{dist} \sum_{i=1}^{n} w_i \cdot (dist_i^{exp} - dist_i^{exp} - dist_i^{exp})^2 + w_{dist} \sum_{i=1}^{n} w_i \cdot (dist_i^{exp} - dist_i^{exp} - dist_i^{exp} - dist_i^{exp})^2 + w_{dist} \sum_{i=1}^{n} w_i \cdot (dist_i^{exp} - dist_i^{exp} - di$$

$$w_{ang} \sum_{i=1} w_i \cdot (a_i^{exp} - a_i^{calc})^2 + w_{plane} \sum_{i=1} w_i \cdot (p_i^{exp} - p_i^{calc})^2$$

Each type of restraints is included in the refinement as a set of observations, in addition to the main set

			Manage	e restraints						
Select Restraint Type and weight										
Distance re	straints	✓ Weight	on distances	: 10000.00	Save restra	ints Coad				
List of rest	raints					Active restraints				
C Active	Atoms	Current	Target	esd						
	C1-N1	1.355	1.321	0.030						
	C1-01	1.233	1.221	0.030						
	C1-S1	1.785	1.751	0.030						
	C2-C3	1.388	1.380	0.030						
	C2-C7	1.401	1.380	0.030						
	C2-S1	1.758	1.751	0.030						
	C3-C4	1.398	1.380	0.030		:				
	C3-N1	1.397	1.443	0.030		:				
	C4-C5	1.388	1.380	0.030						
	C4-02	1.372	1.395	0.030						
	C5-C6	1.399	1.380	0.030						
	C6-C7	1.393	1.380	0.030						
	C7-C8	1.512	1.530	0.030						
	C8-C9	1.521	1.530	0.030						
	C9-N2	1.498	1.443	0.030						

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Constraints

Constraints are mathematical relationships between parameters

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Symmetry constraints are mandatory and automatically imposed by the program

- Special position

 e.g., atom on special position (¹/₂, ¹/₂, ¹/₂) should non be refined,
 atom on special position (x, x, x) in space group P23 should have equal shift on x,y,z
- Unit cell dimension

e.g., a=b=c and $\alpha = \beta = \gamma$ in cubic crystal system

Constraints

Constraints imposed by the user to reduce the number of parameters

Riding model (move H atoms synchronously with the C atoms)

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- Constraints on ADPs (ADPs are made to shift synchronously)
- Occupation factor
 e.g., A,B atoms in same site: occA + occB = 1

Statistical measures of a refinement

Unweighted profile R-factor

$$R_p = \frac{\sum_{i}^{N} |y_{i,obs} - y_{i,calc}|}{\sum_{i}^{N} y_{i,obs}} \times 100$$

Weighted profile R-factor

$$R_{wp} = \sqrt{\frac{\sum_{i}^{N} w_i \cdot (y_{i,obs} - y_{i,calc})^2}{\sum_{i}^{N} w_i \cdot (y_{i,obs})^2}} \times 100$$

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Profile residual with the background subtracted

$$R'_{p} = \frac{\sum_{i}^{N} |y_{i,obs} - y_{i,calc}| \cdot \frac{|y_{i,obs} - b_{i}|}{y_{i,obs}}}{\sum_{i}^{N} y_{i,obs} - b_{i}} \times 100$$

$$R'_{wp} = \sqrt{\frac{\sum_{i}^{N} w_{i} \cdot \left((y_{i,obs} - y_{i,calc}) \frac{(y_{i,obs} - b_{i})}{y_{i,obs}}\right)^{2}}{\sum_{i}^{N} w_{i} \cdot (y_{i,obs} - b_{i})^{2}}} \times 100$$

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Statistical measures of a refinement

Expected R value

$$R_{exp} = \sqrt{\frac{N-p}{\sum_{i}^{N} w_i \cdot (y_{i,obs})^2}} \times 100$$

Goodness-of-fit

$$\chi^2 = \frac{\sum_{i}^{N} w_i \cdot (y_{i,obs} - y_{i,calc})^2}{N - P} = \left[\frac{R_{wp}}{R_{exp}}\right]^2$$

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Other residual on F or F²:

$$R_F = \frac{\sum_{j}^{m} |F_{j,obs} - F_{j,calc}|}{\sum_{j}^{m} F_{j,obs}} \times 100 \qquad R_B = \frac{\sum_{j}^{m} |I_{j,obs} - I_{j,calc}|}{\sum_{j}^{m} I_{j,obs}} \times 100$$

Quality of refinement

Important criteria for the quality of the refinement:

the fit of the calculated pattern to the observed data and

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the chemical sense of the structural model



Structure refinement of C₉H₁₁N₂O₂S·CI

Input file for Rietveld refinement:

%Structure ammonium
%Job ethylammonium chloride (C9H11N2O2SC1)
%Data

Pattern ammonium.xy Wavelength 1.54056 %crystal ammonium_riet.cif %rietveld



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2-(4-Hydroxy-2-oxo-2,3-dihydro-1,3-benzothiazol-7-yl) ethylammonium chloride

 $\mathrm{C_9H_{11}N_2O_2S}{\cdot}\mathrm{CI}$

From graphical interface:

- File > Import Diffraction Pattern
- File > Import Structure
- Refine > Rietveld

Contact, software download and info http://www.ba.ic.cnr.it/softwareic/expo/

Acknowledgements

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