

A simplified rietveld code for quantitative phase analysis: development, test and application to uranium mineral So

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As part of a team project about geological sampling in the environment of the city of Chihuahua, x-ray diffraction (XRD) phase analysis of different rock types is required. The most accepted technique to perform quantitative XRD phase analysis is the well-known Rietveld method. Rietveld codes (Fullprof, Rietan, Rietica, DBWS, Topas, . . .), oriented to a complete characterization of the diffraction pattern (from crystal structure to texture and crystal size investigation) have been developed by several authors. The majority of these codes show a high level of automation, but application may be long and troublesome anyway. False minima and instabilities during software running are recognized problems and represent current working lines of specialized groups. As the samples considered in the present geological investigation are particularly difficult for the Rietveld technique, it was decided to develop a program that performs phase analysis by an alternative route, with a degree of automation between Rietveld and the so-called Direct Comparison Method. The Basic Rietveld-ENhanced Diffraction Analysis (BRENDA) code has been developed and tested. BRENDA uses structure-factor (and other theoretical parameters) calculations from well-established diffraction codes (Fullprof, PowderCell), refines experimental diffraction peaks' profiles and intensities by means of a robust algorithm and determines phases' concentrations. Application of BRENDA code to computer-simulated problems, NIST standards and geological samples is divulged. Discrepancies with calibration figures are of the order of declared uncertainties. The advantages and disadvantages of the considered diffraction methods are discussed. In practice, being only half-automated gives the user more control of the refinement process and leads to an overall economy of time and higher reliability.

Keywords: Quantitative phase analysis; Rietveld; uranium minerals.

Como parte de un proyecto en equipo de muestreo geológico en los alrededores de la ciudad de Chihuahua, se realiza análisis de fases por difracción de rayos x (DRX) de diferentes rocas, las cuales presentan particularidades respecto de las fases existentes en las bases de datos cristalográficos. Por ejemplo, los feldespatos muchas veces vienen como soluciones sólidas de diferentes tipos, en lugar de fases de un feldespato único y definido. La técnica más aceptada para realizar análisis de fases por DRX es el conocido método de Rietveld, cuya aplicación puede ser larga y engorrosa, y del cual se profundizará más adelante. El programa más empleado para este tipo de trabajo es el Fullprof, de Juan Rodríguez Carvajal. Debido a que nuestras muestras son particularmente difíciles para hacerles Rietveld y a que el Fullprof, con frecuencia, da problemas de estabilidad, se decidió hacer un programa que realiza análisis de fases por una vía alternativa, intermedia entre Rietveld y Comparación Directa, más rápida y estable que el primero y más versátil que el segundo. Se desarrolló y se puso a prueba el programa Brenda (Basic Rietveld ENhanced Diffraction Analysis) el cual hace análisis de fases siguiendo los criterios recién descritos. Se presenta la aplicación de BRENDA a muestras virtuales, estándares NIST y materiales geológicos. Las discrepancias están en el orden de las incertidumbres declaradas. Se discuten las ventajas y desventajas de los métodos considerados. En la práctica, ser sólo parcialmente automatizado permite al usuario llevar un mejor control del proceso de refinamiento y conduce a un balance global favorable en cuanto a economía de tiempo y confiabilidad.

Descriptores: Análisis cuantitativo de fases; Rietveld; minerales de uranio.

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1. Introduction

Practically everywhere in materials research and development the necessity for quantitative phase analysis appears. X-ray diffraction (XRD), with its computer-aided tool –the Rietveld Method–, is nowadays of common use in academy and industry for general characterization of polycrystalline materials, including phase analysis. The present paper deals with the development, proof and application of a simplified Rietveld-inspired code specially designed for quantitative phase analysis. The goal of the work is to develop friendly software that facilitates the rapid determination of concentrations in complex multi-phase samples, avoiding complicated files' handling, instabilities and false minima. Mentioned difficulties are recognized drawbacks of the majority of available Rietveld codes.

2. Background

2.1. Historical

Quantitative x-ray diffraction (XRD) phase analysis was invented more than 50 years ago by Leroy E. Alexander and Harold P. Klug [1]. The first determinations of quartz-cristobalite concentrations in artificial mixtures were performed by means of Debye-Scherrer experiments and subsequent intensity measurements in photographic films.

In the 50's, diffractometers began to replace the photographic technique, and intensity measurements significantly gained in precision and exactitude. Alexander and Klug (AK) introduced a high level of reliability in the quantitative XRD phase analysis.

The analyses of AK and contemporaries were limited to 2–3 phases. A calibration diffraction pattern from each phase was used and concentrations reliable to about 5 % were obtained. The habitual method consisted of comparing the integrated diffracted intensity of one peak from the problem sample with the corresponding intensity in a calibration pattern. The AK treatment [2] considered in proper detail the difficulties implied by x-ray absorption.

At the considered time period, for the solution of a steel metallurgy problem (the determination of residual austenite), the *direct comparison* method was introduced. In this technique, the intensities of selected peaks from the experimental pattern were compared with the corresponding *calculated* peaks. This method satisfactorily solved the lack of pure materials for martensite-austenite calibrations.

Quantitative phase analysis in the cement industry faces the same problem of single-phased standards availability. Several variants of the direct comparison method are consequently used in the cement activity.

The 60s, favored by the introduction of computational resources, opened a new period.

The work of Karlak and Burnet (KB) [3] is representative of the methodologies oriented to take advantage of the information contained in *all the peaks* of a diffraction pattern, and so perform the quantitative analysis of multi-peak and multi-phase systems. During the second half of the 60s, and more intensively during the 70s, methods and programs for the analysis of up to 10 phases with errors of the order of a few % were published. The computer was used basically to solve two problems: a) to separate overlapped peaks (by modeling or by deconvolution) and b) to apply the KB matrix algorithm for the calculation of concentrations on the basis of the measured integrated intensities (overlapped or not). An article by Szabo and Fuentes [4] illustrates the use of the KB method.

The use of all the peaks of a pattern allowed to diminish such effects as texture, solid solutions and superposition of peaks, among other difficulties of the previous methods.

This period coincides with the parallel development of two important diffractometric tools: a) the establishment by Hugo Rietveld of the method that is associated with his name [5] and b) the development by Hans J. Bunge of the Mathematical Texture Analysis [6]. None of these disciplines was created as a support for quantitative phase analysis, but both have become decisive frames for the solution of serious problems in this branch of Crystallography.

The fingerprint of powder diffraction investigations during the last two decades of the 20th Century has been the Rietveld Method (RM). Not only the information in all the peaks of a pattern, but data from *all the points* in the spectrum are used in the RM. Any detail in the form of a peak, the smallest variation in the background curve, everything that is registered in a diffraction pattern must be quantitatively characterized for a Rietveld refinement to be considered as satisfactory. For example, in AK texture is avoided, in KB it is averaged and in Rietveld it is measured.

Characterizing quantitatively every detail of a diffraction pattern is an essential characteristic of the Rietveld method. In general it is an advantage of the technique. But, if the determination of the concentrations is the unique objective of the diffractometric measurement, then this requisite may turn down into a drawback. A full Rietveld refinement of a complex sample may require much more time than the application of simpler quantitative phase analysis methods.

2.2. Mathematical

2.2.1. Direct comparison

Theoretically, the contribution J_{ki} of phase k to the integrated intensity of peak i is:

$$J_{ki} = K_0 |F_{ki}|^2 p L T C_i / (\mu_s V^2) = K_0 R_{ki} C_k / \mu_s \quad (1)$$

K_0 : instrumental constant.

$|F_{ki}|^2$: structure factor.

P: multiplicity factor.

L: Lorentz-polarization factor.

T: Temperature factor.

C_k : Volume fraction of phase k .

μ_s : Sample linear absorption coefficient.

$$R_{ki} = |F_{ki}|^2 p L T / V^2. \quad (2)$$

The ratio of selected peaks' intensities from two analyzed phases is:

$$\frac{J_{ki}}{J_{jn}} = \frac{C_k R_{ki}}{C_j R_{jn}} \quad (3)$$

This equation, combined with the normalization condition (4), allows the determination of volume fractions.

$$\sum_{i=1}^N w_i = 1 \quad (4)$$

Required input consists of the mentioned theoretical factors and the measured intensities in the problem sample. Final working equation is:

$$C_k = \frac{J_{ki}}{R_{ki} \sum_{j=1}^N \frac{J_{jn}}{R_{jn}}} \quad (5)$$

Volume fractions are converted to weight concentrations by means of formula (6).

$$w_k = \frac{\rho_k C_k}{\sum_{j=1}^N \rho_j C_j} \quad (6)$$

The ρ 's are phases densities.

Precision estimates are given by the standard deviations $\sigma^2(w_i)$:

$$[\sigma(w_i)]^2 = \sum_{k=1}^M \left(\frac{\partial w_i}{\partial I_k} \right)^2 [\sigma(I_k)]^2 \quad (7)$$

$\sigma(I_k)$ is the standard deviation of the experimental intensity I_k (the square root of the number of counts). Another frequently used reliability descriptor is the so-called agreement factor R , given by:

$$R = \frac{\sum |J_k - I_k|}{\sum I_k} \quad (8)$$

2.3. The Rietveld method

The calculated intensity of one point in a diffraction patterns is:

$$y_{ci} = s \sum_k L_k |F_k|^2 \phi(2\theta_i - 2\theta_k) P_k A + y_{bi} \quad (9)$$

Magnitudes in (9) have the following meaning: s is a scale factor; L_k groups Lorentz, polarization and multiplicity; F_k is the structure factor (includes temperature factors); $\phi(2\theta_i - 2\theta_k)$ is the peak shape function (Gaussian, Lorentzian, intermediate), centered at the Bragg angle $2\theta_k$; P_k describes the texture; A is the absorption factor (constant in Bragg-Brentano geometry) and y_{bi} is the background intensity at position $2\theta_i$. Indexes k and i scan, respectively, the diffraction peaks and the pattern points.

The general idea of a refinement is as follows. The residue S_y is calculated:

$$S_y = \sum_i W_i (y_i - y_{ci})^2 \quad (10)$$

In this expression, y_i are the observed intensities and W_i are the respective statistical weights. The criterion $W_i = 1/y_i$ is usually adopted. The refinement problem consists of minimizing S_y . The maths of optimizing S_y may be found in the book by Young[8].

For a mixture of n phases, scale factors (s_j) refinement leads to weight fraction (w_j) determination using Eq. (11):

$$w_j = \frac{s_j Z_j M_j V_j / t_j}{\sum_{i=1}^n (s_i Z_i M_i V_i / t_i)} \quad (11)$$

Indexes i and j refer to the phases in the analyzed mixture. Z_j is the number of molecules per elementary cell; M_j is the molecular mass; V_j is the volume of the elementary cell and t_j is the so-called *Brindley factor* for absorption contrast. This factor is tabulated elsewhere [9] and its numerical value differs significantly from unity if particle sizes are larger than the micrometer range.

FULLPROF software package[9] is a versatile Rietveld code, with wide international acceptance. Among several

other capabilities, Fullprof performs quantitative phase analysis by means of Eq. (11).

Successful application of Rietveld phase analysis depends on the following factors.

Microabsorption must be avoided or quantified. Texture and extinction should be considered as affecting perturbations. Reduction of particle size to the micrometer domain diminishes all three of these possible problems.

All the phase analysis methods, including XRD, are susceptible of non-validity of the used standards (experimental or theoretical) in relation with actual phases in investigated samples.

Specific concerns about Rietveld analyses are:

False minima are not rare. First structural approximation should be relatively close to physically significant model. Eventual trial-and-error (by hand) refinement is required.

Instability also occurs, leading to loss of important volumes of work. The best is to perform calculations patiently, with frequent saving of registered advances.

The majority of available codes are un-friendly. Complicated data files with voluminous information are required. Regarding user training, profitable use of Rietveld programs is time-expensive.

3. Proposed method and the Basic Rietveld-Enhanced Diffraction Analysis (BREND) program.

The present method and program is a midpoint between "Rietveld" and "Direct Comparison". From Rietveld it can use whichever peaks by phase are desired and a modeling algorithm. From Direct Comparison, it works with the integral intensities of the peaks. The method is resumed in the following fundamental stages:

1. The measurement of the intensities of the peaks that form the experimental diffractogram.
2. The identification of the theoretical peaks, in each phase, that contributes to each experimental maximum.
3. The calculation of the proper scale factors that lead to calculated-observed patterns fitting, by successive approximations,.
4. To convert the scale factors into "weight concentrations".

To use the program it is necessary to have identified all the phases contributing to the investigated pattern.

A data base is required, with the theoretical diffraction patterns of all the appearing phases.

This data base is obtained, phase by phase, starting from the crystal structures, with the help of the Bragg law and the formula for the intensities of diffraction peaks.

Having the complete data base and the phases that take part in the given diffractogram, the time necessary to finish a

phase analysis with the program BRENDA is approximately 2 ~ 3 hours, depending on the complexity of the sample.

The fundamental advantage of the program is its easiness of use. Everything can be done with the Mouse. The program has two main windows:

1. *The Pattern Analysis Window.* It starts by showing the experimental diffractogram. The user selects interactively, with the mouse, a first approximation to the position and forms of the peaks. The program refines, how many times the user requests it, the positions, forms, widths and intensities of the peaks. When the user is in agreement with the refinement, he commands the program to measure the area under the curve for each peak and the program measures them and saves all the information into a file.
2. *The Phase Quantification Window.* It connects calculated and experimental peaks and solves matrixes to find the concentrations – The user indicates and correlates the experimental peaks with the corresponding theoretical ones. With this information the program creates the suitable matrix equation, solves it by a successive approximations algorithm and determines the concentrations of all the phases. During execution BRENDA shows a dynamic comparison among calculated and observed peaks.

4. Tests and Application:

To verify reliability and practical usefulness, the program was proved with three very different “samples”: a virtual (computer-generated) mixture, a NIST reference material for the cement industry (with certified concentrations) and a real uranium mineral specimen. In all cases, BRENDA results were compared with those obtained with FULLPROF.

4.1. Analysis of a Virtual sample

A simulated mixture of 40% calcite, 30 % cristobalite and 30% quartz was computer-generated with FULLPROF. The diffraction patterns of this virtual sample were analyzed with BRENDA. Obtained results are shown in Table 1. The discrepancies are well inside the uncertainties estimated by BRENDA.

4.2. NIST reference clinker SRM 2686

NIST reference clinker SRM 2686 is a five-phased mixture used as standard in cement industry. Diffraction phase analysis of this material is difficult, because the two major components, alite and belite, overlap their most intense peaks. The third component, ferrite, produces microabsorption. The two minor components, aluminate and periclase, show 2 - 3% concentrations, figures close to their uncertainties. Furthermore, structural models for alite and belite are numerous and significantly different. To assign proper starting models and

TABLE I.

FULLPROF		BRENDA	
Calcite:	40.3 %	Calcite:	42(2) %
Cristobalite:	29.9 %	Critobalite:	29(1) %
Quartz:	29.8 %	Quartz:	29(1) %

to clarify the contributions of the considered phases to the observed overlapped peaks, is a problem that lacks uniqueness in its answer.

The phases' weight percents, with their uncertainties, given by NIST for SRM 2686 are:

Alite 58.6 ± 4.0

Belite 23.3 ± 2.8

Ferrite 14.1 ± 1.4

Aluminate 2.3 ± 2.1

Periclase 3.3 ± 1.9

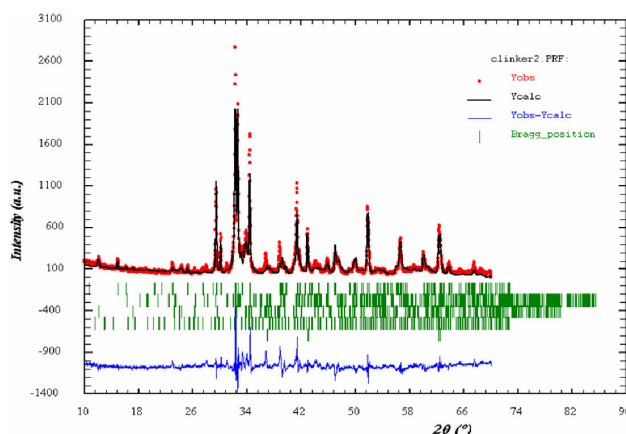


FIGURE 1. Rietveld analysis of NIST clinker SRM 2686

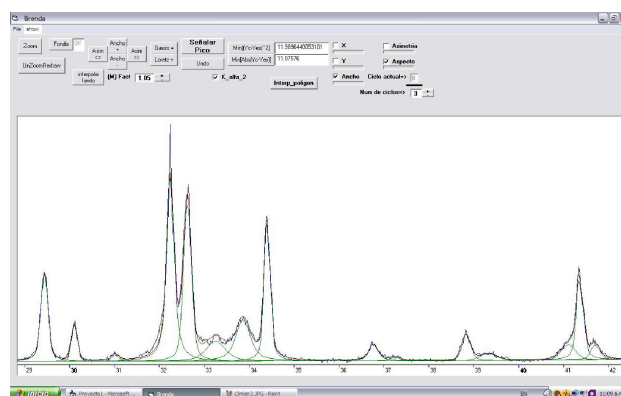


FIGURE 2. Spectrum analysis by software BRENDA. Sample NIST 2686.

TABLE II.

FULLPROF		BRENDA	
Uraninite:	2.0 %	Uraninite:	4 (2) %
Cristobalite:	12.4 %	Cristobalite:	15 (1) %
Quartz:	21.5 %	Quartz:	21 (1) %
Uranophane:	64.1 %	Uranophane:	60 (5) %

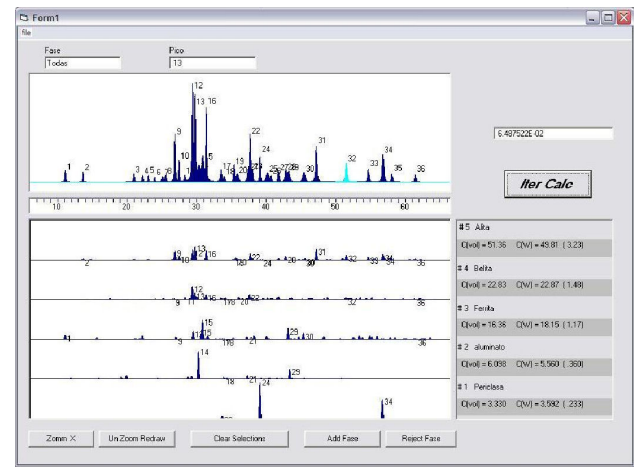


FIGURE 3. Phases' concentrations calculation by BRENDA.

Figure 1 shows the best Rietveld refinement obtained in our laboratory for the considered sample. The agreement factor was $R = 17.6$ and the concentrations (with standard deviations) were as follows:

Alite 47 ± 1
Belite 31 ± 1

Ferrite 15 ± 0.5
Aluminate 1.5 ± 0.2
Periclase 5.1 ± 0.2

Figure 2 shows the diffraction pattern of sample 2686 under BRENDA. A zoom of the angular interval $29 \leq 2\theta \leq 42$, with some (selected) peaks decomposed, is demonstrated.

Figure 3 presents phase quantification of the investigated sample. The upper-left field shows the numbered peaks. Lower-left window displays the theoretical-experimental links and lower-right field gives the concentrations with their estimated uncertainties.

Brenda's results are the following:

Alite 49.8 ± 3
Belite 22.9 ± 2
Ferrite 18.1 ± 1
Aluminate 5.6 ± 0.4
Periclase 3.6 ± 0.2

Results are not ideal, but acceptable. More representative structure models are required to improve the coincidence with the NIST standard. BRENDA's results are better than Rietveld's ones, and uncertainties are more realistic.

4.3. Uranium mineral simple

As a practical exercise, a sample containing uranium minerals was analyzed. A comparison with Rietveld treatment was again performed (see Table II).

Agreement is good. Starting models were suitable for both methods.

As general conclusion, BRENDA's reliability is competitive with internationally accepted codes. Besides, it is a friendly, stable and rapid software.

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