Quantitative Phase Analysis for Titanium Dioxide From X-Ray Powder Diffraction Data Using The Rietveld Method

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Abstract :

In this study, we report the quantitative phase analysis which is performed by Rietveld X-ray diffraction using "fullprof"(fullprof.2k,Version 5.00 - Jan2011-ILL JRC) program to four different samples of TiO_2 . Titanium dioxide is formed of two phases, Anatase and Rutile with different weight percentage. Four samples under study , first is a nanopowder , second is thin a film ,third is the micropowder while the fourth is formed of 50:50 Anatase and Rutile TiO_2 which is considered as standard.

Retiveld refinement on X-ray data for the samples is performed . The obtained results have a good optimization between the observed x-ray diffraction pattern and that calculated by Retiveld. This optimization is determined according to R_p, R_{wp} and GOF . The accuracy check was done by examining the fourth sample by X-ray. Then, quantitative phases were calculated by comparing method which needs pure phases mixture. The final result shows that Retiveld refinement is more accurate than comparing method.

Key words: Rietveld method, Quantitative analysis , XRD, TiO_2

Introduction

Titanium dioxide or titania (TiO_2) was first produced commercially in 1923. It is obtained from a variety of ores. The bulk material of TiO_2 is widely nominated for three main phases of Anatase , Rutile, and Brookite [1]. Among them, the TiO_2 exists mostly as Rutile and Anatase phases which both of them have the tetragonal structures. However, Rutile is a high-temperature stable phase and Anatase is formed at a lower temperature.The phase and particle size are the important parameters that influence physical properties of material .TiO_2 is mainly applied as pigments, adsorbents, catalyst supports, filters, coatings, photoconductors, and dielectric materials. In recent years, TiO_2 has been well known as a semiconductor with photocatalytic activities and has a great potential for applications such as environmental purification, decomposition of carbonic acid gas. [2]

Qualitative analysis usually involves the identification of a phase or phases in a specimen by comparison with "standard" patterns (i.e., data collected or calculated by someone else), and relative estimation of proportions of different phases in multiphase

specimens by comparing peak intensities attributed to the identified phases. Quantitative analysis of diffraction data usually refers to the determination of amounts of different phases in multi-phase samples. Quantitative analysis may also be thought of in terms of the determination of particular characteristics of single phases including precise determination of crystal structure or crystallite size and shape. In quantitative analysis, an attempt is made to determine structural characteristics and phase proportions with quantifiable numerical precision from the experimental data itself. Though "standard" patterns and structural data are used as a starting point, the most successful quantitative analysis usually involves modeling the diffraction pattern such that the calculated pattern(s) duplicates the experimental one. All quantitative analysis require precise and accurate determination of the diffraction pattern for a sample both in terms of peak positions and intensities. Diffraction data are generally very dependent on the systematics of diffractometer and its data collection system, application of quantitative methods that involves ratios of peak intensities requires careful calibration with well-known standards before a quantitative analysis is attempted. [3]

X-ray diffraction is the most useful technique for quantitative analysis of phases in multi component mixtures. Quantification is possible because the intensity of the diffraction pattern of a phase in a mixture depends on its concentration [4]. There are several methods of X-ray diffraction to quantify phases, but the Rietveld method has been perhaps the most useful tool in recent years as it accounts for the factors that affect the reproducibility of the intensity peaks: the peak overlapping, the presence of amorphous phases, and the preferred orientation of crystallites. This is possible because the totality of the diffraction pattern is used to calculate the phase amount. [5]

Rietveld method holds several advantages over other peak intensity-based methods:

Differences between the experimental standard and the phase in the unknown are minimized. Compositionally variable phases are vari 2 the software , Pure-phase standards are not required for the analysis, Overlapped lines and patterns may be used successfully. An accurate assessment of the amorphous phase content is very important to obtain correct absolute weight fractions. Lattice parameters for each phase are automatically produced, allowing for the evaluation of solid solution effects in the phase.[3,6]

The use of the whole pattern rather than a few select lines produces accuracy and precision much better than traditional methods . Preferred orientation effects are averaged over all of the crystallographic directions, and may be modeled during the refinement. [5, 7]

The aim of the present work is the analysis of quantitative phase of TiO_2 by Rietveld refinement , because it is important to understand that this method , because of the whole-pattern fitting approach, is capable of much greater accuracy and precision in quantitative analysis than any peak-intensity based method .

1. Rietveld Analysis

The Rietveld method is a full-profile approach that was initially introduced for refinement of crystalline structures using neutron diffraction. [8] but has been expanded over the last ten to fifteen years for application in quantitative phase-analysis. The method is based on a least-squares fit between step-scan data of a measured diffraction pattern and a simulated X-ray-diffraction pattern.[9] The simulated XRD pattern is calculated from a large number of parameters, including crystal-structure parameters of each component phase, a scale factor for each constituent phase to adjust the relative intensities of the reflections, parameters describing the peak profile and the background, and parameters simulating the instrumental aberrations as well as effects resulting from size-related strain, preferred orientation, and particle size. A key feature of the quantitative analysis of phase proportions by the Rietveld method is that the phase abundances of the constituent phases can be directly calculated from the refined scale-factors. Therefore, quantitative analysis can be performed without the need of experiments undertaken on standard samples to calibrate the method. [10-12]

In the refinement procedure, a calculated pattern is fitted to an observed diffraction pattern by the least-squares method, until the best fit is obtained. The least-squares refinement leads to a minimal residual quantity S_y:

[12] $S_y = \Sigma_i W_i (y_{oi} - y_{ci})^2$ .....(1)

where $w_i = 1/y_{ci}$, y_{oi} = observed intensity at the i^{th} step, and y_{ci} = calculated intensity at the i^{th} step.

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The calculated profile of X-ray powder pattern can be well described by the equation:[12]

$y_{ci} = S \Sigma_k L_k |F_k|^2 \phi(2\theta_i - 2\theta_k) O_k A + y_{bi}$ .....(2) Where

S : is the scale factor,
K :represents the Miller indices (hkl) for the Bragg reflection,
L_k :contains the Lorentz, polarization and multiplicity factors,
ϕ :is the reflection profile function,
O_k: is the preferred orientation function ,
A: is an absorption factor ,
F_k : is the structure factor for the K^{th} Bragg reflection
y_{bi} : is the background intensity at the i^{th} step . where the symbol is a polynomial

The diffraction pattern is calculated by the simultaneous refinement of the unit cell and structural parameters, then other parameters are introduced to compensate the effects of

preferred orientation, angular shifts, surface roughness, etc. Among the refined parameters, the scale factor S_α permits calculating the relative weighted fractions w_α of the phases :[13]

$$W_\alpha = \left(\frac{S_\alpha (ZMV)_\alpha}{\sum_{i=1}^{n} S_i (ZMV)_i}\right) * 100\% \qquad \text{.....(3)}$$

Where S_α is Rietveld scale factor of phase α, w_α is the relative weight fraction of phase α in the mixture of n phases (wt. %), M_α is the molecular weight (in atomic mass units), Z_α is the number of molecules in a cell of unit ,V_α is unit cell volume (in $Å^3$) .

The fit must be evaluated by visual comparison between the observed and calculated pattern; however, some numerical criteria are necessary in order to judge whether the refinement is proceeding satisfactorily and when it can be stopped . There are several R values that can be used to evaluate the fit : R-structure factor R_F, R-Bragg factor R_B, R-pattern factor R_p and the weighted-profile factor R_{wp}. The R_{wp} value is defined as:[11-13]

$$R_{wp} = \sum_i W_i (y_{oi} - y_{ci})^2 / \sum_i W_i (y_{oi})^2 \qquad \text{.....(4)}$$

The expression in the numerator of the R_{wp} is the minimal residual quantity being minimized; therefore, this is the most expressive of the R's, and it is the one that best reflects the fit of the calculated pattern diffraction. The R_F and R_B are based on the intensities calculated, thus they are biased towards the model being used . The ''goodness of fit (GOF)'' is another numerical criterion frequently used for evaluation of the success of the fit: [11-13]

$$\text{GOF} = \left[\frac{S_y}{(N-P)}\right]^{1/2} = R_{wp} / R_{\exp} \qquad \text{.....(5)}$$

where N is the number of observations (peaks), P is the number of parameters and R_{exp} is the expected R value which reflects the quality of the data, R_{exp} is defined as: [11,12,13]

$$R_{\exp} = [(N-P) / \sum_i^N W_i y_{oi}^2]^{1/2} \qquad \text{.....(6)}$$

For comparison ; quantitative phase analysis is carried out with Direct comparison method[3]:

$$\frac{W_A}{W_R} = K \frac{I_A}{I_R} \qquad \text{.....(7)}$$

Where I_A: intensity for Anatase phase in the mixture for [101] ($I\backslash I_{max}$=100%),

I_R: intensity for Rutile phase in the mixture for [110]. ($I\backslash I_{max}$=100%)

W_A: weight percentage for Anatase phase, W_R: weight percentage for Rutile phase.

Where:[3]

$$K = \frac{I_{RP}}{I_{AP}} \qquad \text{.....(8)}$$

I_{RP}: intensity for pure Rutile phase , I_{AP}: intensity for pure Anatase phase

2. Experimental details

Materials

The selection of starting materials was based on a quantitative analysis samples. All investigated samples are Titanium dioxide in two phases (Anatase + Rutile) with nuknown weight percentage.

The present study investigates the accuracy and reliability of the quantitative Rietveld analysis at various weight fractions of four samples data of Titanium dioxide collected from different methods .

1. Commercial Nano powder (Np)
2. Thin film (Tf)
3. Commercial Micro powder (Mp) [5]
4. Commercial Micro powder (standard sample) (Msp) (mixture of 50% Anatase +50% Rutile)

Quantitative phase analysis were calculated by comparing method which is needed for pure phases mixture .

1. Pure Anatase (A)
2. Pure Rutile (R)

Experimental conditions

The X-ray diffraction patterns were obtained in a (Shimadzu XRD-6000) goniometer using copper target (Cu K_α, 1.5418 Å), (40 kV, 30 mA). The samples were mounted in an aluminum sample holder. Step-scan data were collected from different ranges with a step width of 0.02° and a counting time of 5 sec/step. The divergence, scattering , and receiving slits are 1.0° , 1.0° and 0.30 (mm) respectively with monochromator was used.

X-ray diffraction patterns of pure Anatase (A) and pure Rutile (R) are shown in Figures – (1 a,1b) respectively.

XRD patterns exhibited strong diffraction peaks at (25.2591°, 48.0060° , 37.7633°) and (27.4158°, 54.3002°, 36.0592°) indicating TiO_2 in the Anatase and Rutile phase respectively.

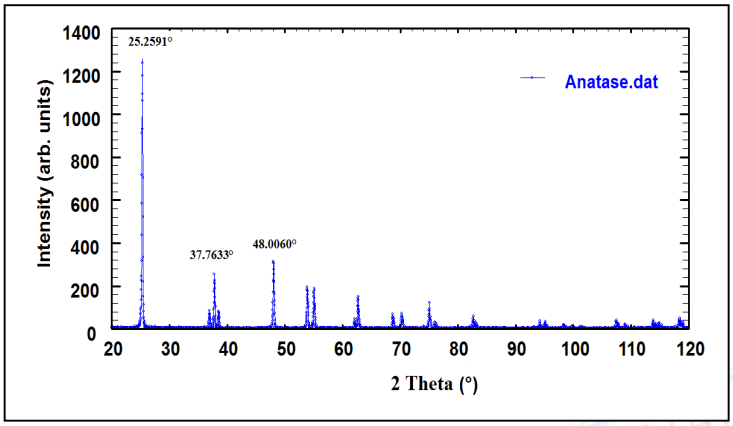

Fig. 1a X-ray diffraction pattern of TiO_2 Anatase phase.

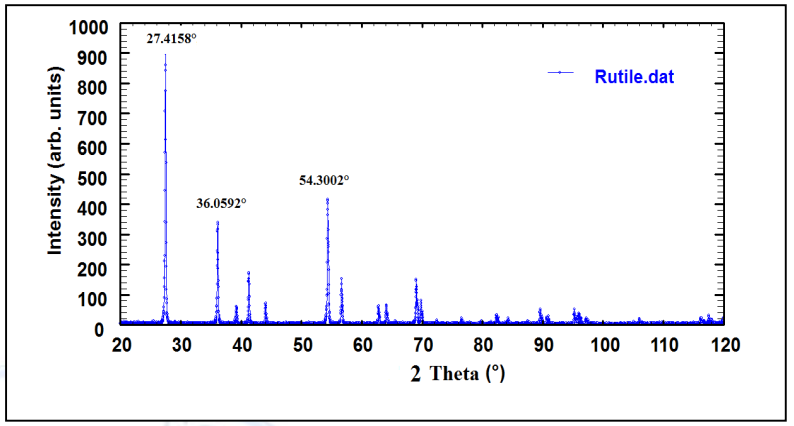

Fig. 1b X-ray diffraction pattern of TiO_2 Rutile phase.

X-ray diffraction patterns of nano-TiO_2(Np), micro-TiO_2(Mp) ,Thin film (Tf) and standard micro- TiO_2(Msp) Anatase50%+Rutile%50 , are shown in Figures (2a,2b,2c,2d) respectively . Analysis of the X-ray diffraction patterns of TiO_2 reveals the presence of two phases Anatase and Rutile in different weight percentage.

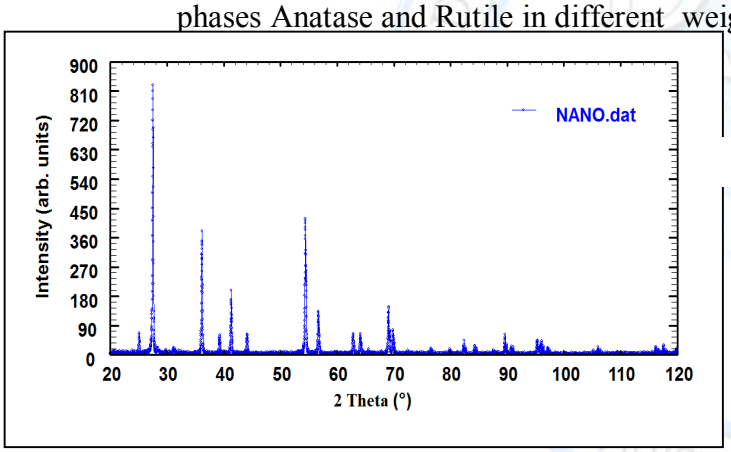

Fig. 2a X-ray diffraction pattern of nano TiO_2 mixture of two phases Anatase+Rutile.

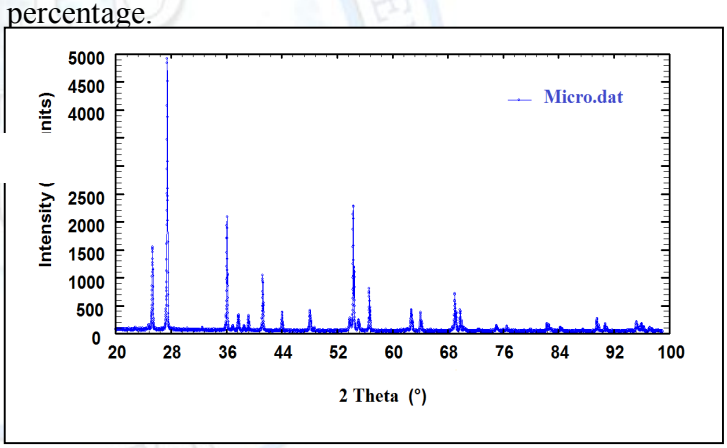

Fig. 2b X-ray diffraction pattern of micro TiO_2 mixture of two phases Anatase+Rutile.

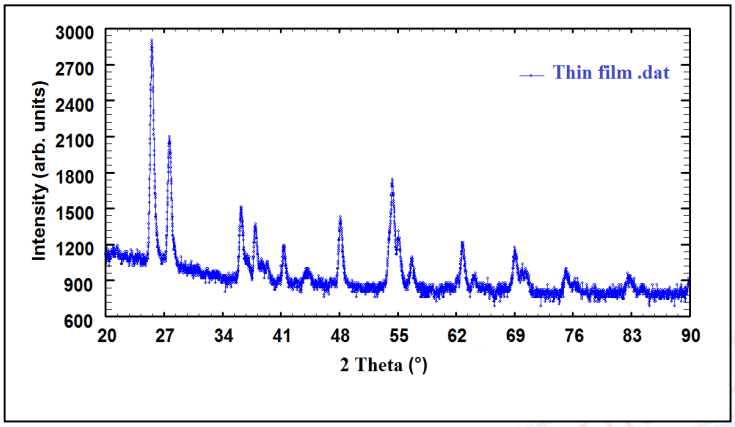

Fig. 2c X-ray diffraction pattern of thin film TiO_2 mixture of two phases Anatase+Rutile.

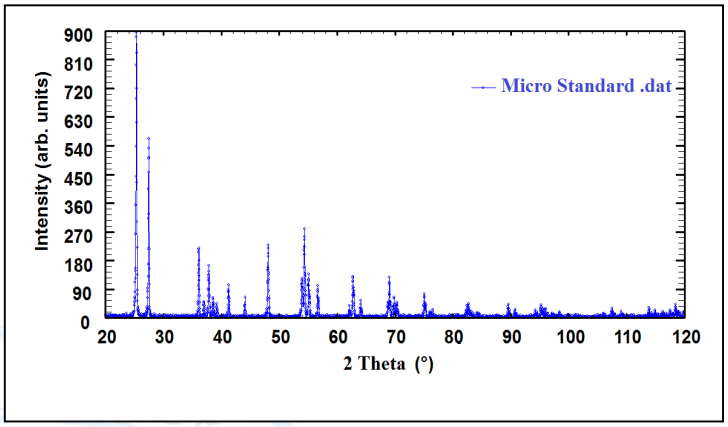

Fig. 2d X-ray diffraction pattern of micro standard TiO_2 mixture of two phases Anatase 50%+Rutile 50%.

X-ray diffraction – Rietveld refinement was carried out with the method supplied by the fullprof software [14] to (Np) , (Mp) ,(Tf) and (Msp) samples . All the samples consist of two phases (Anatase+Rutile) and Rietveld refinement are shown in Figures 3a,3b,3c and 3d respectively. The experimental points are given as dot (.) and theoretical data(calculated by eq. 2) are shown as solid line. Difference between theoretical and experimental data is shown as bottom line. The vertical lines represent the Bragg's allowed peaks. The results of crystsl system , cell parameters(a,b,c) and atomic position(x,y,z) are presented in Table -1.

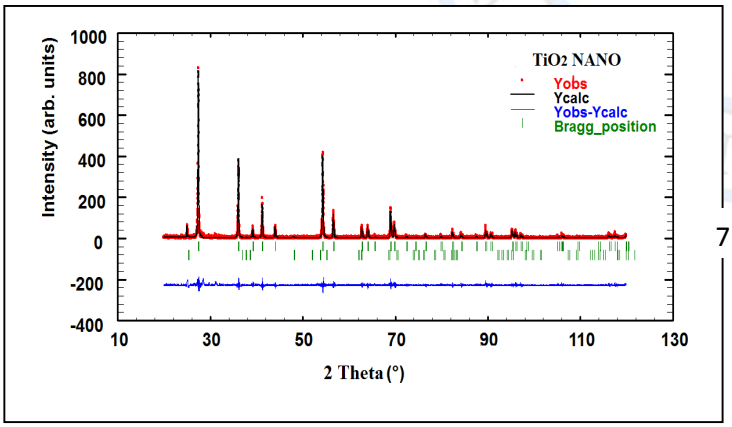

Fig. 3a Rietveld refinement pattern of nano TiO_2 mixture of two phases Anatase+Rutile.

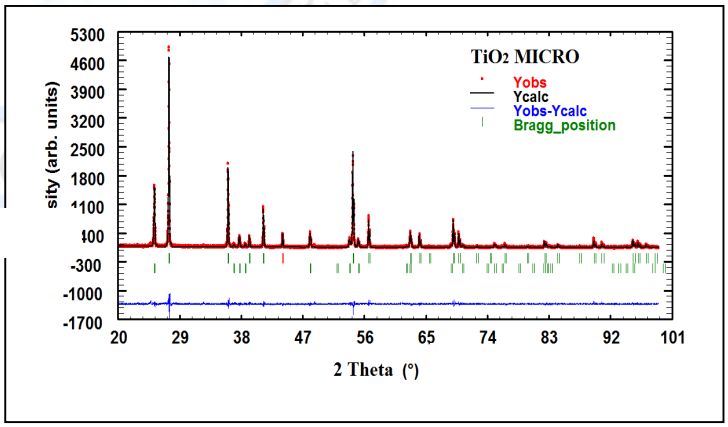

Fig. 3b Rietveld refinement pattern of micro TiO_2 mixture of two phases Anatase+Rutile.

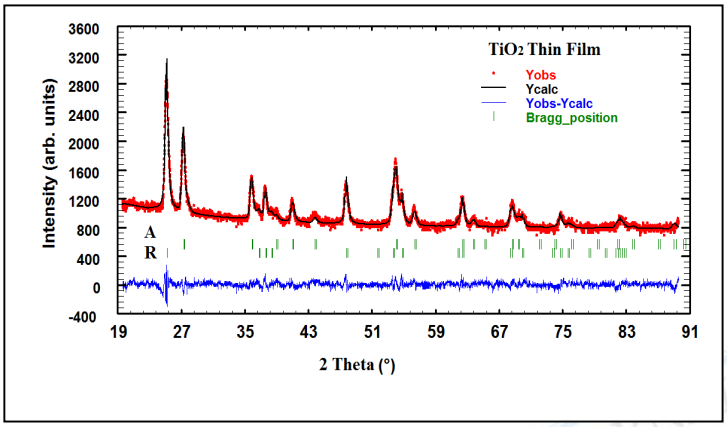

Fig. 3d Rietveld refinement pattern of micro standard TiO_2 mixture of two phases Anatase

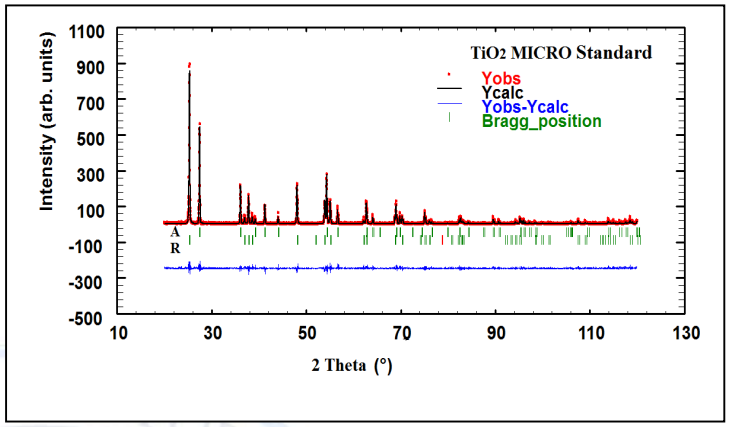

Fig. 3c Rietveld refinement pattern of thin film TiO_2 mixture of two phases Anatase+Rutile.

Table-2: Quantitative phase analysis obtained by Rietveld refinement (Rr) compared with Direct method (Dm) .

Table- 1: X-ray diffraction -Rietveld refinement, cell parameters and atomic position TiO_2 samples.

The weight percentages of the phases were calculated by applying the Rietveld method using the fullprof software.[14]

Quantitative phase analysis obtained by Rietveld refinement compared with those obtained by the Direct method by using Figures 1a , 1b and equations (7),(8) .The results of quantitative phase analysis are presented in Table-2

Sample	Phase	a=b (Å)	c (Å)	Atom	x	y	z
(Np)	Anatase	3.7819	9.5271	Ti^{+4}	0.00	0.25	0.3750
				O^{-2}	0.00	0.25	0.1679
	Rutile	4.5925	2.9589	Ti^{+4}	0.00	0.00	0.00
				O^{-2}	0.3052	0.3052	0.00
(Mp)	Anatase	3.7845	9.5111	Ti^{+4}	0.00	0.25	0.3750
				O^{-2}	0.00	0.25	0.1686
	Rutile	4.5928	2.9590	Ti^{+4}	0.00	0.00	0.00
				O^{-2}	0.3067	0.3067	0.00
(Tf)	Anatase	3.8015	9.5503	Ti^{+4}	0.00	0.25	0.3750
				O^{-2}	0.00	0.25	0.1649
	Rutile	4.6125	2.9738	Ti^{+4}	0.00	0.00	0.00
				O^{-2}	0.3019	0.3019	0.00
(Msp)	Anatase	3.7818	9.5275	Ti^{+4}	0.00	0.25	0.3750
				O^{-2}	0.00	0.25	0.1678
	Rutile	4.5926	4.5926	Ti^{+4}	0.00	0.00	0.00
				O^{-2}	0.3052	0.3052	0.00

Sample	Method	Phase (%)		R_P(%)	R_{WP}(%)	R_{exp}(%)	GOF
		A	R				
(Np)	Rr	4.72	95. 28	21.0	23.6	18.73	1.26
	Dm	5.93	94.07				
(Mp)	Rr	21.92	78.08	8.82	11.8	10.26	1.15
	Dm	18.83	81.17				
(Tf)	Rr	57.22	42.78	20.4	23.3	17.78	1.31
	Dm	53.04	46.96				
(Msp)	Rr	49.81	50.19	17.3	20.8	17.62	1.18
	Dm	49.08	50.92				

4. Conclusions

The Rietveld method showed good precision for the quantitative analysis of phases present in TiO_2. The characterization and sampling method employed revealed good precision taking into account the reproducibility of results from samples of each set. A careful sample preparation to obtain representative results with the totality of the material is very important.

With the Rietveld method, it is possible to quantify the amounts of all phases present in the sample simultaneously .The phase quantification procedure involved the identification of major and minor phases . In other methods each phase must be quantified independently.

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Compared with other X-ray diffraction methods, such as the internal standard and direct method, the Rietveld method has numerous advantages: having better accuracy, and requiring neither an additional internal standard nor calibration curve and sample homogenization, in addition to that, Pure-phase standards are not required for the Rietveld method analysis.

In our opinion, the Rietveld method offers some new and powerful tools in quantitative phase analysis of complex composed samples.

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Quantitative Phase Analysis for Titanium Dioxide From X-Ray Powder Diffraction Data Using The Rietveld Method

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تحليلات الطور الكمية لثاني أوكسيد التيتانيوم بطريقة ريتفيلد من بيانات حيود الأشعة السينية

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الخلاصة :

تم في هذه الدراسة إجراء التحليلات الكمية بطريقة ريتفيلد بإستخدام برنامج "fullprof" لأربع عينات مختلفة من TiO_2 المتكون من طوري الأنتيز والروتايل وبنسب وزنية مختلفة ،الأولى مسحوق نانوي والثانية غشاء رقيق والثالثة والرابعة مسحوق مايكروي .

أجريت تصفية ريتفيلد على البيانات المأخوذة من حيود الأشعة السينية، حيث دلت النتائج على الموائمة الجيدة بين مخطط الحيود الملاحظ المأخوذ مباشرة من حيود الأشعة السينية ومخطط الحيود المحسوب بطريقة ريتفيلد على نجاح عملية التصفية حيث تم ذلك من خلال عوامل الموثوقية GOF, R_{wp} R_p ., للتحقق من دقة نتائج التحليل الكمي بهذه الطريقة تم إعتبار العينة الرابعة كمقياس لذلك حيث تم تحضيرها بخلط طوري الأنتيز والروتايل بنسبة وزنية متساوية 50:50 لكل منهما، ثم فحصت العينة بالأشعة السينية .ولإجراء المقارنة تم إجراء التحليل الكمي بطريقة المقارنة المباشرة حيث تحتاج هذه الطريقة الى الأطوار النقية من العينة التي يجرى التحليل الكمي لها ،على خلاف طريقة ريتفيلد ، وقد كان التحليل الكمي بطريقة ريتفيلد أكثر دقة من طريقة المقارنة المباشرة .

الكلمات المفتاحية: طريقة ريتفيلد، تحليلات الطور الكمية، حيود الاشعة السينية ،ثاني اوكسيد التيتانيوم.