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Anatase/rutile mass fraction determination in TiO_2 nanoparticles using Rietveld refinement aiming applications in water purification

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Abstract
Given the growing demand for sanitation solutions, various techniques of wastewater treatment have been proposed. Among them, we highlight the use of photocatalysts. Among all alternative materials proposed for using in the photocatalytic process, crystalline titania has been one of the most used because it can be easily sensitized by ultraviolet light. However, studies indicate that its efficiency is dependent on the mass fraction of anatase and rutile phases present in the titania composition. This paper aims at the use of the Rietveld refinement for quantifying the mass fraction present in titania nanoparticles obtained by the flame aerosol method. X-Ray diffraction patterns were obtained from synthesized samples and compared with the analysis of a commercial sample (Degussa P-25). We observed that the methodology of flame aerosol is effective for controlling the growth of anatase and rutile phases by just controlling the gas flow in the burner. Fraction of anatase / rutile with relative errors smaller than 10% was obtained by Rietveld refinement.

Keywords
Photocatalysis, Titanium dioxide, X-Ray diffraction, Rietveld refinement, Water purification.

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Introduction

One of the characteristics of developing countries is the gap between economic growth and the fulfillment of the population basic needs, as sanitation (MENDES, 1992; HELLER, 1998). As we discuss public policies to meet those sanitation needs, innovative technologies have been developed for treating water and wastewater in a safe and environmentally friendly way. In this context, we highlight the research based on the principle of photocatalysis for such purposes (POZZO et al., 1997; LJUBAS, 2005; CHATZISYMEON, et al., 2011).

Photocatalysis can be defined as increasing the speed of a chemical reaction due to the presence of a catalyst sensitive to light (GAYA et al., 2008). These catalysts, when absorbing light energy, produce highly reactive substances which generate high degradation capacity of chemically stable compounds. Thus, it is possible, for example, to degrade polluting elements or eliminate pathogenic microorganisms using a photocatalyst at some stage of the process of water treatment (GAMAGE; ZHANG, 2010; BARNES et al., 2013).

Among the various photocatalyst materials, titanium dioxide (TiO_2), or titania, is very promising, and it has already been successfully used in several experiments (FERREIRA, 2004). The reason TiO_2 has excelled relies on the fact that this material has a non-toxic nature, being chemically stable, allowing its use at room temperature and pressure. In addition, it dispenses with the use of supporting reagents, and it has a relatively low cost, being also able to be sensitized by light in the ultraviolet range present in sunlight (CHATZISYMEON et al., 2011). However, studies show that the efficiency of this material for this application is closely linked to its microstructure (OHNO et al., 2001; DI PAOLA et al., 2008).

Titania has three allotropic crystalline forms: anatase, rutile and brookite. Brookite is a metastable orthorhombic structure, and it is difficult to be synthesized. The anatase and rutile crystals are tetragonal: anatase is metastable and rutile has a more compact and stable structure (DASSLER et al., 1988). Studies indicate that the optimun titanium dioxide efficiency as a photocatalyst system is achieved when a mixture of 70% anatase / 30% rutile is obtained (BACSA; KIWI, 1998). This 70-30 ratio can be present in powders and nanostructured materials, the latter being the most effective (OHNO et al., 2001). This emerges the need to quantify the phases present in TiO_2 powders and nanopowders in a fast, efficient and reliable approach.

In this context, this paper aims at using the Rietveld refinement (YOUNG, 1993) applied to X-ray powder diffraction patterns of various samples of titania nanoparticles obtained through the process of flame aerosol in the Laboratory of Photonic Materials and Devices (LIQC), FEM/UNICAMP. It also compares obtained quantifications to those calculated using conventional quantitative analysis. The Rietveld refinement is a mathematical method based on the least squares method, and it calculates the best fitting curve to the powder diffraction pattern obtained experimentally after certain initial conditions are established and parameters are set. As a consequence, it is possible to correlate the adjusted parameters to the material microstructure.

Despite the need of high numeric calculation efforts by this method, the capabilities of the current computing hardware makes the analysis quick and efficient, especially regarding to the quantitative phase.

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Titanium dioxide and the process of heterogeneous photocatalysis

Titanium dioxide is a semiconductor material of great interest in the process of heterogeneous photocatalysis. The principle of heterogeneous photocatalysis involves the activation of a semiconductor material by sunlight or artificial light. A semiconductor material can be defined as crystalline solids with electrical conductivity between conductors and insulators, being characterized by a valence band (VB) and an empty conduction band (CB) with an in-between gap.

The valence and the conduction bands are energy bands that the electrons from crystalline solids may assume. In semiconductors, the valence electrons of the covalent bonds fill the entire valence band. When a photon with energy greater than or equal to the "band gap" is absorbed, the excitation of an electron (e^-) occurs and, consequently, it is promoted to the conduction band (and so this electron can be considered a free electron) generating a gap (h^+) in the valence band. These gaps have enough positive potential to generate hydroxyl radicals (HO•) from water molecules adsorbed on the surface of TiO_2. These radicals are highly reactive and have a high oxidation potential. On the other hand, the conduction band electrons migrate to the surface of the semiconductor, participating in the reduction/oxidation (redox) of organic compounds in contact with the surface of the photocatalyst (GAYA; ABDULLAH, 2008). Figure 1 illustrates that phenomenon.

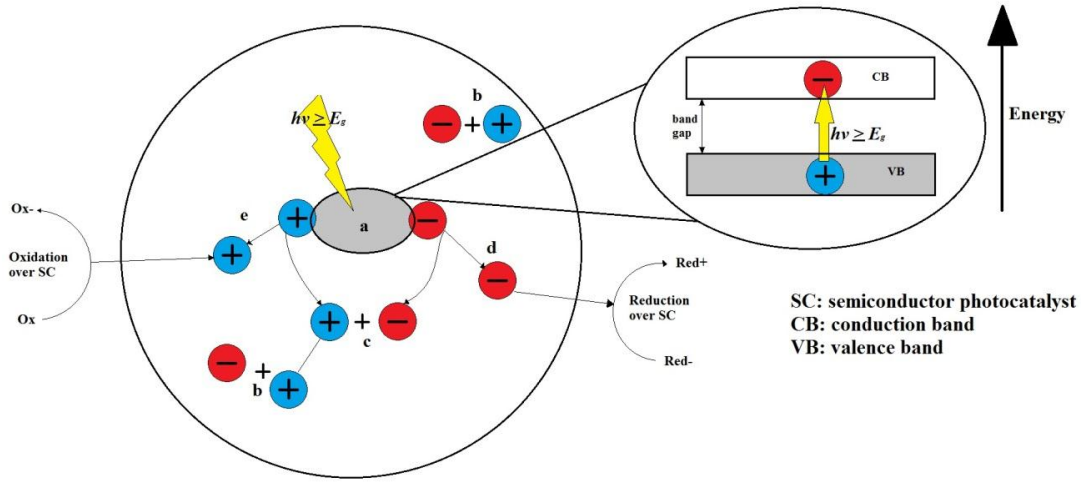

Figure 1. Schematic photophysical and photochemical processes over photon activated semiconductor cluster (a) photogeneration of electron/hole pair, (b) surface recombination, (c) recombination in the bulk, (d) diffusion of acceptor and reduction on the surface of SC, and (e) oxidation of donor on the surface of SC particle.

Due to its high catalytic activity, the anatase phase of titanium dioxide is usually the most used in the processes of photocatalysis. However, due to its band gap, around 3.2 eV, only the ultraviolet light (i.e., light with wavelength < 387 nm) sensitize the semiconductor (CHATZISYMEON et al., 2011).

It is estimated that only 3 to 5% of the sunlight energy incident on the planet is in the ultraviolet range, whereas the visible light corresponds to approximately 45%. Therefore, studies indicate that the photocatalytic efficiency of the process is improved when using a mixture of anatase and rutile, since the second has a "band gap" of 3.0 eV. Although rutile

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presents a lower catalytic activity, it uses part of the visible spectrum for activation (~413 nm). Studies also indicate that the catalytic activity of TiO_2 exposed to sunlight in a proportion of 70% anatase and 30% rutile samples is greater than single-phase anatase under natural sunlight (BACSA; KIWI, 1998).

Rietveld refinement

The Rietveld refinement (or Rietvield method) was proposed in the late 1960s by Hugo M. Rietveld (RIETVELD, 1969). However, it became popular on the '80s and '90s when computers availability and ease of use increased.

The method consists in adjusting the theoretical diffraction pattern of a crystal structure obtained from a crystallographic information (CIF), to its diffraction pattern obtained experimentally from data collected using a diffractometer. The curve fitting between the theoretical and experimental diffraction patterns, minimized by the difference of the squares sums, results in a scale factor, which, with other parameters of refinement, provides a detailed analysis of the analyzed sample. If several crystalline structures are present within the sample, the amount of each structure can be determined.

In an X-ray diffractogram a graph of intensity (y) versus diffraction angle (2θ) is presented. Rietveld refinement of the calculated intensity of the i-th point is given by Equation 1,

$$y_{ci} = s\varphi_{rsi} \sum_K J_K Lp_K |F_K|^2 G_{Ki} a_{Ki} P_K + y_{bi} \quad (1)$$

where s is the scale factor, φ_{rsi} is the correction roughness factor at the point i; k is the Miller indices hkl for Bragg reflection (the direction of the crystallographic plane); J_K is the multiplicity of reflection; $L\rho_K$ is the Lorentz factor and polarization; F_K is structure factor; G_{Ki} is the profile function; α_{Ki} is the function of asymmetry; P_K is the correction function preferred structure, y_{bi} is the background radiation of the i-th point.

Each of the functions given in Equation (1) contains a number of parameters widely discussed in the literature (YOUNG, 1993) that, taken together, may characterize a crystalline arrangement.

The theoretical curve calculated from the observed values is given by the least squares method in which the quantity to be minimized is given by the minimization function

$$M = \sum_i w_i \, (y_i - y_{ci})^2 \quad (2)$$

where y_i is the i-th observed value of intensity. Deriving each adjusted parameter and equating to zero, it is obtained the minimum.

$$\frac{\partial M}{\partial p_j} = 0 \quad (3)$$

When a sample with j crystalline phases is analyzed, equation (1) can be rewritten as follows:

$$y_{ci} = \sum_j s_j \varphi_{rsij} \sum_{K,j} J_{Kj} Lp_{Kj} \left|F_{Kj}\right|^2 G_{Kij} a_{Kij} P_{Kj} + y_{bi} \quad (4)$$

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Thus, the adjustment of the scale factor becomes important to calculate the mass fraction of the phases present in a crystalline sample, according to the equation below

$$f_n = \frac{s_n \rho_n V_n^2 / \tau_n}{\sum_{n=1}^{j} s_n \rho_n V_n^2 / \tau_n} \quad (5)$$

where ρ_n is the density of the n-th phase, V_n is the unit cell volume, calculated from the lattice parameters refined, τ_n τ_n is Brindley factor for correcting effects of X-ray absorption.

The evaluation of the refinement is done by analyzing R_{WP} (weighted R factor) and R_{exp} (expected R factor) (equations 6 and 7), calculated according to the following equations, where N is the number of points used in the refinement and P the number of refined parameters. If the ratio between them [S = R_{wp} / R_{exp}] (goodness of fit) is close to 1.0, it means that a good fitting was made.

$$R_{wp} = 100 \cdot \left[\frac{\sum_i w_i (y_i - y_{ci})^2}{\sum_i w_i (y_i)^2} \right]^{1/2} \quad (6)$$

$$R_{exp} = 100 \cdot \left[\frac{(N - P)}{\sum_i w_i (y_i)^2} \right]^{1/2} \quad (7)$$

Materials and Methods

For this paper, TiO_2 nanoparticles synthesized by the flame aerosol method with the Vapor-phase Axial Deposition equipment of Laboratory of Photonic Devices, FEM/UNICAMP (SANTOS et al., 2011) were studied. This method consists on the synthesis of nanoparticles from the precursor gas titanium tetrachloride ($TiCl_4$) in an oxygen-hydrogen flame. This leads to a reaction of hydrolysis and oxidation, according to the equation (8) (DHUMAL et al., 2009). Dhumal et al. indicate that the characteristics of the nanoparticles vary according to the concentration of the gases in the flame, the precursor gas and the exposure time of the precursor in the flames.

$$TiCl_4(g) + 2O_2(g) + 4H_2(g) \rightarrow TiO_2(s) + 4HCl(g) + 2H_2O(g) \quad (8)$$

For synthesizing the particles studied in this work, it was used a 5-way burner made of silica glass, in which the precursor gas ($TiCl_4$), hydrogen, oxygen and a high purity inert gas (nitrogen, in order to protect the system) were injected and ignited. The flame from this burner was pointed at a target made of silica glass with constant rotation (25 rpm). The samples were synthesized following the parameters listed in the Table 1, with flow rates given in sccm (standard cm^3/min), by maintaining a distance of 54 mm from the burner exit to the central axis of the target.

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Table 1. Parameters used for TIO_2 synthesis.

Sample	H2/O2 (sccm)	H2 (sccm)	O2 (sccm)	N2 (sccm)	TiCl4 (sccm)
A	0.75	3000	4000	1000	500
B	1.25	5000	4000		
C	2.25	9000	4000		
D	3.00	12000	4000		

Thus, the exposure time of the precursor gas in the flame is constant, and only the amount of hydrogen and oxygen for each sample is varied. The Figure 2 presents a schematic drawing of the experiment.

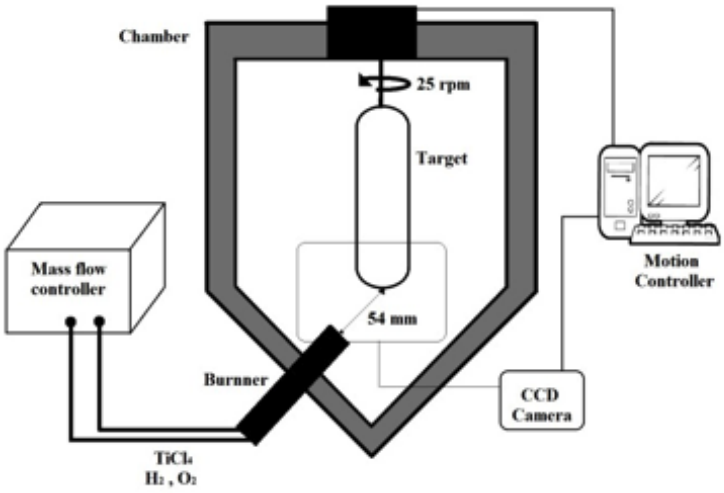

Figure 2. Experimental setup.

After the nanoparticles deposition on the targets, the obtained powder was prepared for characterization in X-ray diffractometer DMax 2200 (Rigaku Corporation) using a fine focus copper tube (λ = 1.54Å) with an exposure time of 4 seconds for a step of 0.05 ° in the range 20° ≤ 2θ ≤ 60°. For comparison purposes, it was also measured a diffractogram of a sample of commercial titania Degussa P-25 with well-known properties (OHNO et al., 2001; CHATZISYMEON et al., 2011). X-ray source was operated at 40 KV and 20 mA.

From the XRD patterns obtained, the mass fraction of anatase and rutile phases was analyzed in two different ways. In the first analisys method, the (SPURR; MYERS, 1957) relation (Equation 9) was used to calculate the rutile fraction compared to the anatase fraction, from the areas A_A and R_A under the most intense diffraction peaks of the respective phases. The software Origin (version 8.1) was used to calculate the normalized intensity of the diffraction pattern and calculate the area under the peaks representing anatase and rutile, in order to apply Equation (9) for calculation.

$$\chi_R = \left(1 + 0.8\,\frac{A_A}{R_A}\right)^{-1} \tag{9}$$

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For the second analisys method, the Rietveld refinement was applied, and the MAUD software (LUTTEROTTI et al., 1999) was used to make the adjustments of the theoretical curve and the experimental one, thereby adjusting the scale factor and leading to the calculation of the mass fraction of each of the crystalline phases. A total of 23 parameters were refined for each of the samples, as described below:

- 1 intensity parameter of the X-ray equipment;
- 3 background parameters (2^{nd} degree polynomial function);
- 1 displacement parameter of the sample;
- 2 scale factors parameters (one for each crystalline phase);
- 4 crystal lattice parameters;
- 4 scattering factor parameters;
- 8 microstructure parameters.

Results and Discussion

In Figure 3, XRD patterns of all samples are presented, as well as the Degussa P-25 sample. The curves calculated by Rietveld refinement are also shown in red color.

The Table 2 shows the result of the quantitative analysis of rutile mass fraction X_R present in each sample. The table also shows the value X_R calculated by the Rietveld refinement, as well as the value of accuracy *S* for the fit and the relative error between the two methods.

Although the optimal *S* value is close to 1.0, it can be seen that the calculated curve fits adequately to the experimental data. In sample C, the *S* value above 1.8 occurs because there was no anatase growth, despite the crystallographic data of both anatase and rutile phases were inserted in the calculation of the fitting curve and due to the experimental conditions. It is noted that in sample D, when there is some fraction of the anatase phase (1.2%), the S value converges to a value close to 1.5.

It can be observed that there is a strong influence of the amount of gas flame in the synthesis of TiO_2. According to Boery (2011), in general, the percentage of rutile increases with the increase of the H_2/O_2 ratio. This tendency was confirmed in this experiment, which shows that the methodology of flame aerosol is effective for controlling the growth of anatase and rutile phases just by controlling the gas flow in the burner.

According Bacsa (1998), samples with 30% rutile and 70% anatese content showed a maximum photocatalytic activity. Several studies (CHATZISYMEON, 2011; FERREIRA 2004) indicate that the use of TiO_2 for water treatment is effective and feasible. For this paper, the value of 0.75 H_2/O_2 was considered as optimal for obtaining a sample with the percentage of rutile desired for the best photocatalytic performance under sunlight.

In general, the analysis carried out by using the Rietveld refinement was faster in comparison to those obtained by equation 9, since neither the process of standardizing the diffractograms nor the process of calculating the peak areas for subsequent determination of the fraction of rutile were needed anymore. The Rietveld method itself includes all of these steps, from the calculation of the theoretical curve and parameter settings, generating

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reliable results automatically, as shown in Table 2. For sample P-25, the result obtained from the Rietveld refinement was close to the one found in the literature (OHNO et al., 2001).

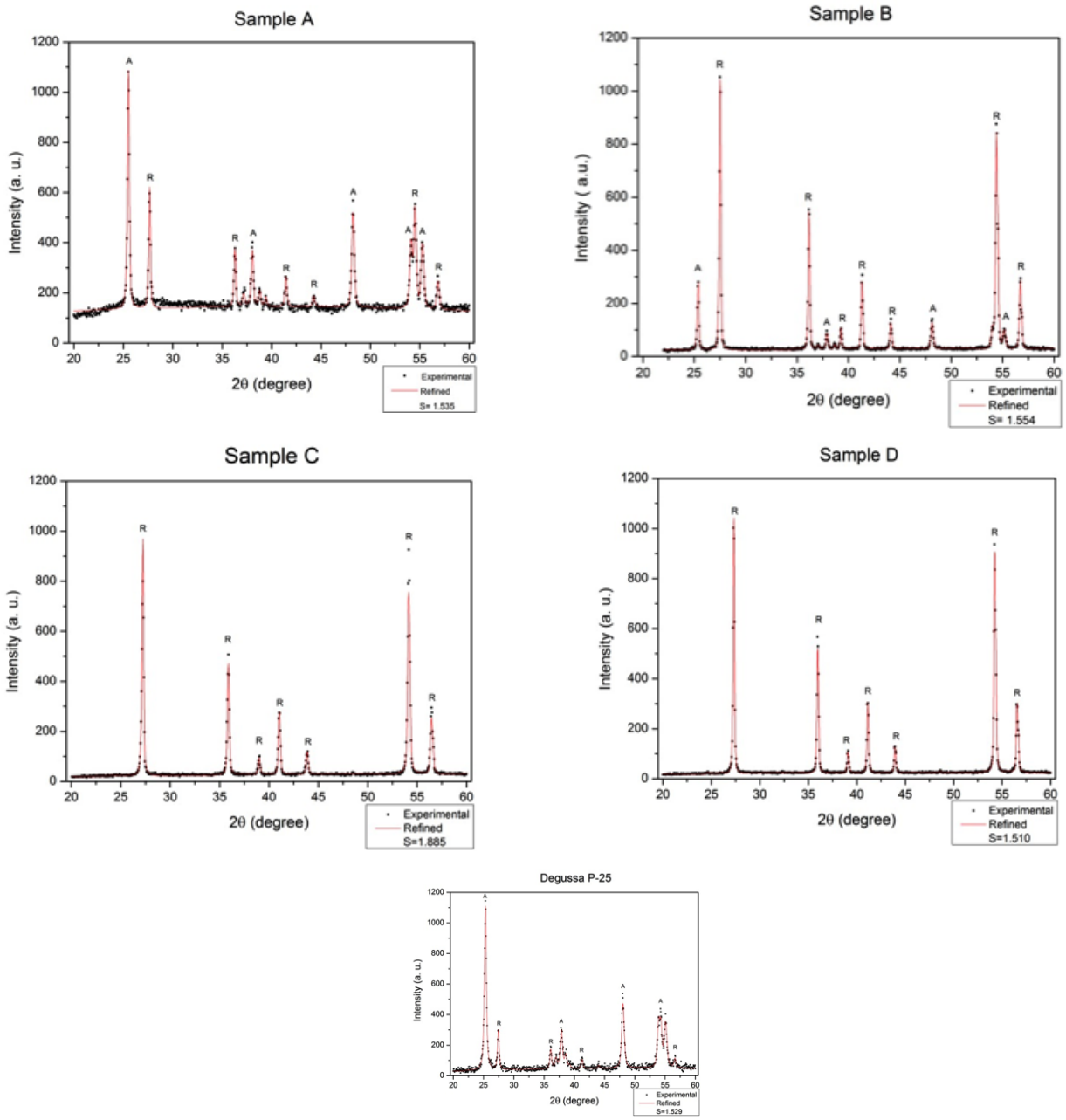

Figure 3. XRD pattern observed and Refined curve by Rietveld method.

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Table 2. Rutile mass fraction obtained by the two different techniques

Sample	Spurr & Myers	Rietveld		Relative Error
	X_R	X_R	S	
A	35%	38.4%	1.535	9.7%
B	83%	83.1%	1.554	0.1%
C	100%	100.0%	1.885	0%
D	99%	98.8%	1.510	0.2%
P-25	25%	23.3%	1.529	6.8%

Conclusions

Several TiO_2 samples were synthesized by the flame aerosol method, and the sample obtained by setting a 0.75 H_2/O_2 ratio showed the best fraction of anatase/rutile when taking into account its use in photocatalyst processes.

Crystalline phases were quantified with two different methods, which showed very similar results. The Rietveld refinement proved to be faster, since the quantitative method almost ends up being a consequence of the adjustments of the fitting curve.

The present result shows that this technique is effective for precise determination of anatase/rutile ratio for the synthesis of titania for photocatalysis applications to eliminate pathogenic microorganisms in water and air.

The Rietveld refinement itself is not a technique recommended for characterizing a fully unknown material. The possible constituents of the sample should be known beforehand. Nevertheless, this methodology proved to be effective for quantitative analysis, and, considering the current hardware processing capabilities and the amount of crystallographic data available, it is possible to perform quantitative analysis quickly and reliably by implementing this method.

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