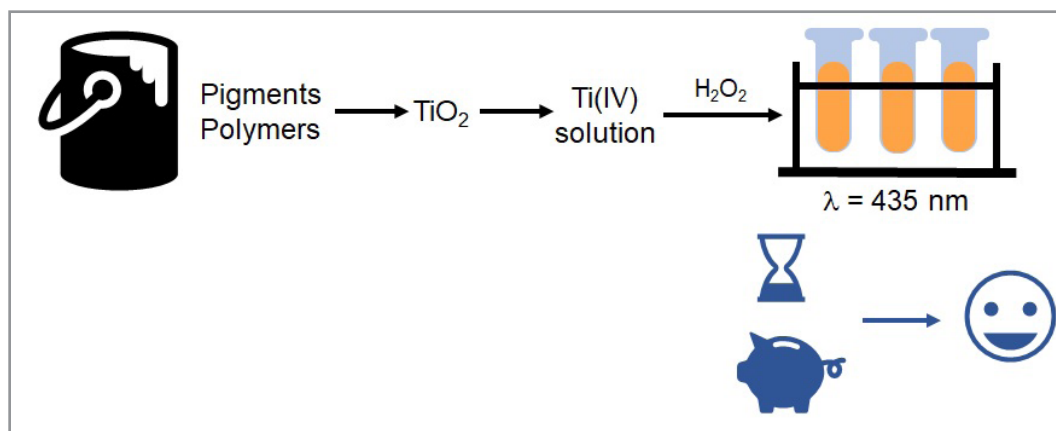# Fast and Simple Spectrophotometric Procedure for Determination of TiO$_2$ in Paint Samples

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Graphical abstract

Titanium dioxide is separated from other components in paint samples, and solubilized. After the addition of hydrogen peroxide, a colored complex with absorption maximum at 435 nm is obtained. Thus, spectrophotometric analytical response can be registered, yielding a simpler, inexpensive, and faster analysis than the titrimetric reference procedure.

Paints are commonly used to protect solid surfaces and to cover imperfections. The composition alters the characteristics of the paint such as brightness, and resistance to abrasion. An important component of paints is TiO$_2$, which yields a strong white color and opacity. Due to the cost of this raw material, its employment is limited. The determination of TiO$_2$ is important for quality control and for developing formulations with lower content of TiO$_2$. Additionally, deformulation studies are generally carried out aiming at aiding market assessment. The reference procedure for determination of TiO$_2$ is based on a volumetric method using highly unstable species such as Ti(III) and Fe(II), making it extremely susceptible to systematic errors. Alternative procedures with atomic absorption or emission techniques are expensive for research laboratories in the industry, especially when the determination of a few metals is required. In this sense, a simple spectrophotometric procedure for TiO$_2$ determination in paint samples is herein proposed, based on the reaction between Ti(IV) and H$_2$O$_2$ that yield a soluble complex with absorption maximum at 435 nm. The univariate optimization of the parameters was carried out aiming at best sensitivity and analytical frequency, and minimum reagent consumption and waste generation. Linear response was observed between 6.0 and 60 mg L^{-1} Ti. Detection limit (n = 20, 99.7% confidence level) and coefficient of variation (n = 20) were estimated at 2.8 mg L^{-1} and 1.2 %, respectively. Sample preparation was based on ashing, and dissolution in hot mixture of sulfuric and hydrochloric acids. The analysis of the digests by the proposed and the titrimetric reference procedures agreed at the 95% confidence level. The developed procedure is a faster, low-cost, reliable and cleaner alternative for determination of TiO$_2$ in paint samples.

Keywords: titanium, pigments, spectrophotometry, paints, deformulation.

INTRODUCTION

Paints are defined as a dispersion of pigments in the presence of polymers [1]. On principle, they were conceived to enhance esthetics, but in actual days they are also used for other ends such as protection. The heterogenous mixture produces a dried thin coat that covers the substrate and yields different characteristics depending on the composition.

The formulations show some common components, such as additives, resins, pigments, and fillers that are varied depending on the specific purpose of the final product, such as resistance to abrasion, higher yield after drying, and brightness [2]. The formation of the coating over the substrate depends on physical and chemical phenomena that occur after the application. The solvent, which is the volatile fraction of the paint, assures adequate homogenization of the mixture, dissolving some components and allowing the equal distribution of particles. Additionally, the viscosity of the paint depends on the solvent, influencing its stability and performance.

The additives, such as defoamers, humectants and dispersers, and resins are important for enhancing the fabrication process, the stability, and the application of the paint. Fillers and pigments generally form a suspension, and they are responsible for color, opacity and resistance of the paint. Additionally, the content and refraction index of these components affect efficiency of the coating and brightness. The most used pigment in paint samples is TiO$_2$ that yields high efficient coating and whiteness [3].

Titanium dioxide shows adequate stability, reflectance and opacity, and low toxicity, making it suitable for producing paints. The crystalline forms of TiO$_2$ are anatase, rutile, and brookite, but important physical properties of the pigment are not significantly altered with the crystalline form. The best coating conditions using TiO$_2$ is evidenced by comparing refraction indexes (RIs). The forms anatase and rutile show 2.55 and 2.73, respectively, indicating the wider use of the rutile form [3]. The RI of TiO$_2$ is 1.7-fold and 1.4-fold higher than of calcium carbonate and zinc oxide, respectively. However, the use of TiO$_2$ is limited by its cost. Generally, low-cost fillers substitutes, such as CaCO$_3$ and SiO$_2$, are generally used to reduce the price, and to yield different properties to paints. Therefore, investigating the formulation of paints of different brands through deformulation enhances the competition in the market and aids research and development to optimize the performance of the product. Additionally, quality control also requires monitoring of TiO$_2$.

Deformulation comprises decomposition of the sample aiming at identifying and characterizing its contents [4]. The reverse engineering is used as a tool for marketing and for studies in the technical area. For paint samples, a common strategy for deformulation is thermal decomposition, in which groups of chemicals are eliminated by increasing temperature. By reaching 900 ºC, the digests basically comprise silicates, and metal oxides, including TiO$_2$, which is submitted to chemical analysis.

The determination of Ti in paints can be carried out according to recommended protocols based on titrimetric analysis after the dissolution of ashes in hot concentrated sulfuric acid [5]. After cooling down, the digest is mixed with aluminum foils under heating for Ti(IV) reduction to Ti(III). The reaction must be carried out under an oxygen-free atmosphere (saturation with CO$_2$ is generally exploited) due to instability of Ti(III). The derivatized analyte is then titrated with a Fe(III) solution using NH$_4$SCN as indicator. Therefore, the end point occurs when an excess Fe(III) yields the red [Fe(SCN)]$^{2+}$. The detection of the end point is difficult because of the grayish color that the mixture assumes due to excess of aluminum foil in the solution. Additionally, analytical frequency is not suitable for laboratories with high demand for analysis.

In general, inductive coupled plasma optical emission spectrometry (ICP OES) and mass spectrometry (ICP-MS) are alternatives for Ti determination [6-8]. Despite the possible multielementary determinations of ICP OES and ICP-MS, such variety of elemental analysis is not required, as well as high sensitivity procedures for analysis of paint samples. Therefore, the cost of acquisition and maintenance of the equipment are too high for implementation in those analytical laboratories.

Spectrophotometric procedures require lower-cost instrumentation, but Ti determination is carried out with selective reagents, such as ponceau S [9], and 4´-dimethylphenylazo-6-hydroxypyrimidine-

2,4-dione [10]. These chemicals make the procedures expensive and might show higher toxicity. Therefore, selective and low-cost reagents for Ti determination is sought. An alternative has been used for determination of Ti in digests of aluminum foils [11]. Hydrogen peroxide was used for generating a colored complex with Ti, and a hot concentrated nitric acid was employed prior to the addition of the reagent for a nitration step that took 10 min, hindering analytical frequency.

In this work, a simple spectrophotometric procedure is proposed based on the reaction between Ti(IV) and H_2O_2, generating a coordination compound with absorption maximum at 435 nm. The colorimetric reagent is cheap, and easy to find and to discard in comparison to organic reagents used for spectrophotometric determination of TiO_2.

MATERIALS AND METHODS
Reagents and solutions
All solutions were prepared with analytical grade reagents, and deionized water. The stock solution of Ti(IV) was prepared by addition of 100 mg of titanium dioxide (99.8% w/w, Synth), in 10 mL of concentrated H_2SO_4 and of HCl (both Merck). The mixture was heated until rising of white fumes, and kept under heating for 30 min. The dissolution of TiO_2 was observed during the process. After cooling down, 70 mL of deionized water was carefully added to the solution, transferred to a 100 mL volumetric flask, and diluted up to the mark with water, and kept in a dark flask. Reference solutions were prepared by adequate dilution of the stock. H_2O_2 0.3% (v/v) solution was daily prepared by dilution of the concentrated reagent (30%, Merck) in water. White paint samples were furnished by BASF S.A.

Apparatus
Spectrophotometric responses were obtained with a modular spectrophotometer comprising a tungsten-halogen light source (Ocean Optics), a support with a 10 mm optical path quartz cuvette, and a multichannel spectrometer based on charge-coupled devices (Ocean Optics), allowing acquisition of spectra between 200 and 800 nm. Optical fiber cables were used to transport the radiation from the light source to the cuvette and to the spectrometer. For data acquisition, a microcomputer Intel Pentium IV (Hewlett-Packard), and the software SpectraSuite (Ocean Optics) were used. For sample preparation, a multiprocessing oven (Quimis, model Q318M35T) was employed.

Proposed procedure
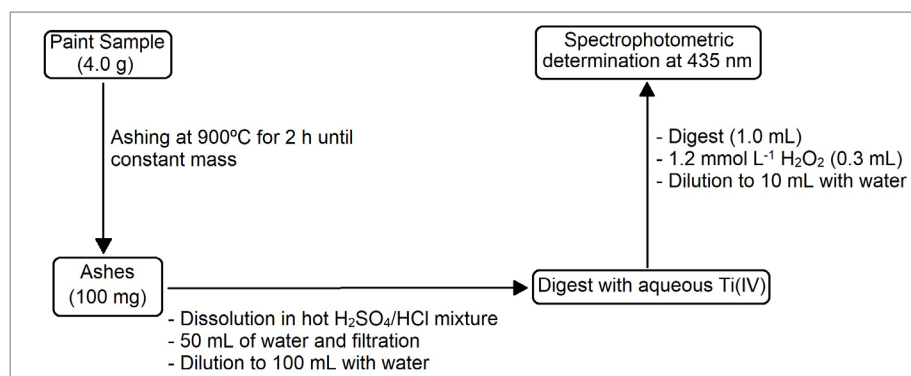The proposed procedure for TiO_2 determination in paint samples is schematically described in Figure 1.

Figure 1. Schematic representation of the proposed procedure for TiO_2 determination in paint samples.

For sample preparation, *ca.* 4.0 g of paint sample was weighted in a porcelain crucible and heated at 900 ºC for 2 h. After cooling down, the ashes were macerated, and 100 mg of the fine powder was

weighted and transferred to an Erlenmeyer. Afterwards, 10 mL of concentrated sulfuric acid and of hydrochloric acid were added to the ashes. The mixture was heated until white fumes were observed and kept under heating for 30 min. After cooling down, *ca.* 50 mL of water was added. The solution was quantitatively filtered, transferred to a 100 mL volumetric flask, and diluted with deionized water. For spectrophotometric determination, 1.0 mL of the diluted digest and 300 µL of 1.2 mmol L^{-1} (0.3% v/v) H$_2$O$_2$ were transferred to a 10 mL volumetric flask and diluted with water. Afterwards, the spectrophotometric detection was assessed at 435 nm.

Reference procedure

For determination of TiO$_2$ with the reference procedure, sample preparation was also based on ashing as described in the above mentioned section. The ashes were weighted (200 mg) and transferred to a 500 mL Erlenmeyer followed by the addition of 20 mL of concentrated H$_2$SO$_4$, and 8.0 g of ammonium sulfate. The mixture was heated until white fumes were observed, and kept under heating for 20 min. Afterwards, 120 mL of water and 20 mL of concentrated HCl were carefully added. The mixture was boiled again for another 20 min. After cooling down, 1.0 g of aluminum foil was added to the digest. The flask was closed with a stopper coupled to the end of a U-shaped tube. The other end of the tube was used to close an Erlenmeyer containing boiling NaHCO$_3$ solution. In this way, the CO$_2$ generated was transferred to the reaction flask. After dissolution of the aluminum foil, the mixture was boiled for 5 min and cooled down to 60 ºC. The indicator NH$_4$SCN was added to the digest, which was titrated with a standardized FeNH$_4$(SO$_4$)$_2$.12H$_2$O solution. The end-point was observed by the rising of a reddish color of the titrate.

RESULTS AND DISCUSSION

The procedure for the determination of TiO$_2$ was based on the reaction between Ti(IV) and H$_2$O$_2$, yielding a yellow solution with absorption maximum at 435 nm. In the literature, more than one structure has been proposed for the complex, such as [TiO$_2$]$^{2+}$ [12], TiO(H$_2$O$_2$)$^{2+}$ [13], and TiO^{2+} [14], being reaction 1 the most accepted. Nevertheless, the works agreed that reaction stoichiometry Ti(IV):H$_2$O$_2$ is 1:1. Additionally, the reaction is selective, fast, and pH-dependent.

$$Ti^{4+} + H_2O_2 \longleftrightarrow [TiO_2]^{2+} + 2H^+ \qquad \text{(Reaction 1)}$$
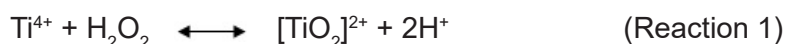
Optimization

The optimization was carried out with the univariate method aiming at maximum sensitivity and precision, and minimum waste generation and reagent consumption. The initial conditions were 1.2 mmol L^{-1} Ti (60 mg L^{-1}), 1.2 mmol L^{-1} H$_2$O$_2$, and pH 1.0 adjusted with sulfuric acid. Readings were carried out at 435 nm.

The first study was a simple kinetic assessment carried out for 20 min to evaluate reaction rate (Figure S1 in Supplementary Material). Spectrophotometric readings were performed right after mixing analyte and reagent solutions (after less than 3 s). It was not observed significant variation of the signal during the study for Ti(IV) and blank solutions. Therefore, readings were carried out right after mixing sample and reagent.

The effect of H$_2$O$_2$ concentration on the analytical response was evaluated between 0.70 and 2.0 mmol L^{-1} (Figure 2A). Best response was observed with 1.1 mmol L^{-1}, indicating quantitative conversion following the stoichiometry 1:1 Ti(IV):H$_2$O$_2$ previously proposed [12,14,15]. Higher amounts of the reagent did not alter the response significantly due to the lack of Ti(IV). Despite this observation, 1.2 mmol L^{-1} H$_2$O$_2$ was used for further experiments to assure enough amount of reagent as H$_2$O$_2$ is susceptible to degradation. The use of higher concentrations of H$_2$O$_2$ is also recommended as analytical signal is not significantly affected.
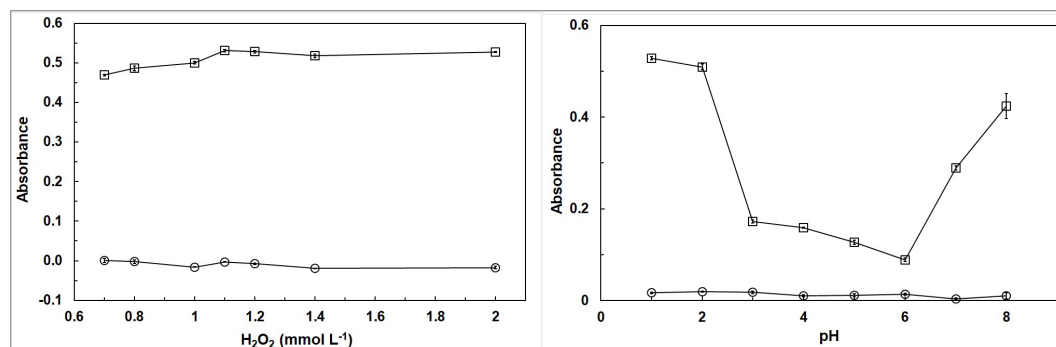
Figure 2. Variation of analytical (-□-) and blank (-○-) signals with H_2O_2 concentration (A), and pH (B). The responses were obtained with 60 mg L^{-1} Ti(IV) solutions.

As pH is a critical chemical parameter, its effect on the analytical signal was also evaluated from 1.0 to 8.0 (Figure 2B). The adjustment was carried out by using proper amounts of 2.0 mol L^{-1} NaOH solution. Lower analytical signals were observed at higher pH because Ti(IV) hydrolysis is favored in alkaline medium. Therefore, soluble molecular species of Ti(IV) associated to hydroxyl or oxygen were formed [13], hindering the formation of Ti/H_2O_2 complex. The evidence of hydrolysis was reinforced at pH higher than 7.0 because it was observed the formation of TiO_2 that caused light scattering and consequently increased absorbance readings [16]. Therefore, pH 1.0 was chosen for further experiments.

Analytical features and interference studies

After optimization, it was observed linear response between 6.0 and 60 mg L^{-1} Ti (0.12 and 1.2 mmol L^{-1}), described by equation A = 0.0082 C_{Ti} + 0.053 (R^2 = 0.999), where A is absorbance at 435 nm, and C_{Ti} is Ti(IV) concentration in mg L^{-1}. The analytical curve is presented in Figure S2 in Supplementary Material. The coefficient of variation (n = 20, 30 mg L^{-1} Ti), and the detection limit (n = 20, 99.7% confidence level) were estimated at 1.2% and 2.8 mg L^{-1}, respectively. The analysis of the samples 1-3 and 4-6 were performed in different days and changing the analyst and the equipment. The coefficients of variation remained < 7.0% in both cases (standard deviation < 0.2% w/w, except for sample 3). The variation of the signals obtained with reference solutions was < 5.0%. Per determination, 0.40 mg of H_2O_2 was consumed.

Paint samples show some elements that yield oxides during sample preparation, being Fe the main concomitant. Other elements are negligible in view of the mass of sample and dilutions applied in the procedure, especially for white paints. As iron content can reach up to 0.1% (w/w), the influence of this metal ion on the analytical response was evaluated at 1.0 mg L^{-1} in the presence of 30 mg L^{-1} Ti(IV), which represents an excess of fivefold in relation to the expected concentration of Fe. Both Fe(II) and Fe(III) were evaluated and signal variations were < 1.0%, indicating that interference was not significative (< 5.0%).

Application and critical evaluation

For accuracy assessment, six paint samples were analyzed by the proposed and reference procedures [5]. The results obtained by both procedures (Table I) agreed at the 95% confidence level, showing relative errors < 4.7%.

In comparison to the reference procedure [5], the proposed procedure minimized reagent consumption. Waste generation was reduced threefold, and analytical frequency was drastically enhanced, demonstrating that this procedure is more suitable for quality control of paints in the industry. Additionally, tiring and time-consuming steps were eliminated, such as the generation of inert atmosphere and heating for analyte reduction.

Table I. Main values and uncertainties for TiO$_2$ determination in white paint samples by the proposed and reference procedures

	TiO$_2$ (% w/w)		
Sample	Proposed procedure	Reference procedure [5]	Relative Error (%)
1	12.5 ± 0.2	12.6 ± 0.3	0.79
2	12.8 ± 0.2	12.7 ± 0.2	0.78
3	11.0 ± 0.5	11.3 ± 0.2	2.6
4	16.5 ± 0.1	16.6 ± 0.2	0.60
5	17.9 ± 0.2	17.1 ± 0.2	4.7
6	5.6 ± 0.2	5.4 ± 0.4	3.7

The content of TiO$_2$ in % w/w was calculated based on the use of 4.0 g of paint sample, and solubilization of 100 mg of ashes in 100 mL of acidic mixture, as described in the experimental section.

Procedures based on ICP OES, and flame atomic absorption spectrometry (FAAS) techniques for Ti determination in cement [17] required similar sample preparation applied to paint samples in this work, except for the employment of HF for dissolving SiO$_2$. The proposed procedure showed higher detection limits, which is not critical for paint analysis. The employment of special gases for ICP OES and FAAS techniques increased the cost per analysis due to maintenance of the equipment. Additionally, HF was used for sample preparation, increasing the hazards associated to this step.

Acidic digestion with nitric acid has also been exploited for sample preparation prior to determination of Ti in cosmetics by ICP OES [6], but the time for digestion was not significantly reduced compared to ashing of the sample generally used for TiO$_2$ determination. ICP-MS has also been used for Ti determination in ceramic materials [8]. Despite the low detection limit for Ti (0.11 µg L^{-1}), which is not strictly necessary due to the content of TiO$_2$ in paint samples, acquisition and maintenance costs of the equipment hinders its employment.

Spectrophotometric procedures required lower cost instrumentation, but a step for chemical derivatization is often necessary. Organic ligands have been employed for the determination of Ti in several types of samples, such as 5-(2',4'-dimethylphenylazo)-6-hydroxipyrimidine-2,4-dione [10], and 4-(2-pyridilazo) resorcinol [18]. Despite efficient and with proper quantification limits, the use of those reagents increases the cost of the analysis due to acquisition of chemicals and waste treatment. Alternatively, a flow-based spectrophotometric procedure has been proposed for determination of TiO$_2$ in sunscreens [19]. In this case, sample preparation was based on microwave digestion for approximately 1 h. In spite of the reduction on analytical frequency, HF was employed for dissolving the sample, requiring a step for eliminating the mineral acid. Additionally, chromotropic acid was used as colorimetric reagent. These characteristics show that the herein developed batch procedure is more environment-friendly.

CONCLUSIONS

The proposed procedure for the spectrophotometric determination of TiO$_2$ in paint samples was developed in view of the analysis in quality control and deformulation laboratories. Cost, waste generation, and reagent consumption were minimized in relation to the reference and alternative procedures. Additionally, analytical frequency was drastically increased in comparison to titrimetric determinations.

Procedures based on atomic spectrometry can be used for determination of Ti, but the cost of acquisition and maintenance hinders their applications mainly in deformulation laboratories. The proposed procedure requires a spectrophotometer that shows lower cost, and the detection can also be carried out in lab-made devices.

The use of one low-cost colorimetric reagent is also advantageous, also in view of waste treatment. Additionally, H$_2$O$_2$ can be easily standardized by spectrophotometric methods to evaluate the purity of

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the reagent that eventually is stored for long periods. In summary, the developed procedure is a fast, reliable, and low-cost alternative for determination of TiO_2 in paint samples, attending to the demand of routine laboratories and for deformulation studies.

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SUPPLEMENTARY MATERIAL

In this section, the data related to the kinetic study and analytical curve are presented in Figures S1 and S2, respectively.
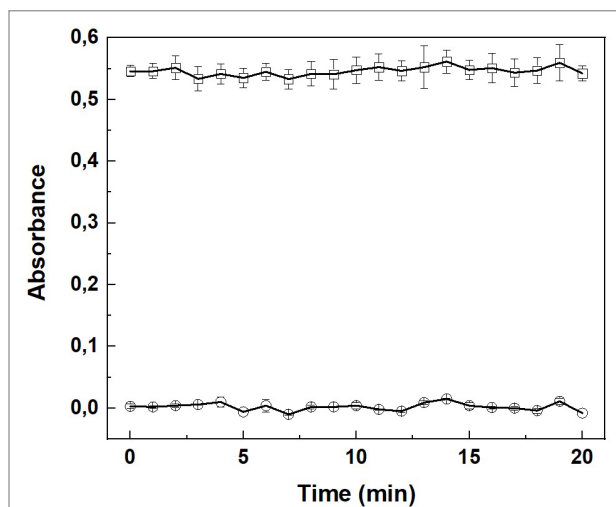
Figure S1. Variation of the response of analyte (-□-) and blank (-○-) solutions with time for the kinetic study on the reaction between Ti(IV) and H$_2$O$_2$. Conditions: 60 mg L^{-1} Ti(IV) in 1.8 mol L^{-1} H$_2$SO$_4$; 1.2 mmol L^{-1} H$_2$O$_2$.
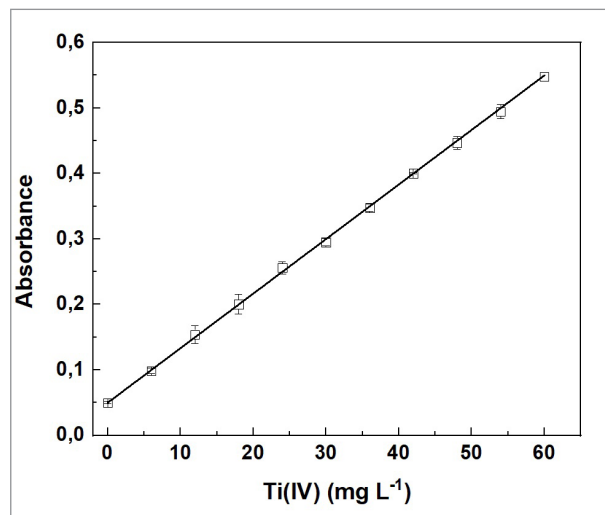
Figure S2. Analytical curve obtained for determination of TiO$_2$ in paint samples. Conditions: Ti(IV) solutions in 1.8 mol L^{-1} H$_2$SO$_4$ and 1.2 mmol L^{-1} H$_2$O$_2$.