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A rapid and simple microwave-assisted digestion procedure for spectrophotometric determination of titanium dioxide photocatalyst on activated carbon

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Abstract

Deposition of titanium dioxide (TiO_2) on activated carbon (AC) surface has been widely utilized for the production of TiO_2/AC photocatalyst, which can be used in photo-degradation of pollutants. In this work, a fast and simple digestion procedure has been developed for the spectrophotometric quantitative analysis of TiO_2 in TiO_2/AC photocatalyst. Microwave-assisted digestion was used in the procedure. The microwave-digestion procedure was optimized using the single-variable method. Variables optimized included time of ashing, effective digestion time, volume and concentration of sulfuric acid, effect of adding a digestion catalyst, effect of sample pulverizing and on–off time cycle of the microwave. The analysis was completed spectrophotometrically after addition of hydrogen peroxide to the digested solution. Procedure precision and accuracy was tested by application to photocatalyst samples containing known amounts of TiO_2, and compared with previously published spectrophotometric procedures. The proposed microwave procedure was capable of recovering 98.4–101.1% of TiO_2 in the catalyst in less than 10 min, without the need for sample ashing. Analytical precision is 1.42–2.39% relative standard deviation (R.S.D.). In terms of accuracy and precision, the proposed microwave procedure was comparable with other procedures, but the proposed microwave procedure was superior in terms of shorter procedure duration.

Keywords: Microwave-assisted digestion; Analytical procedure; Titanium dioxide; Activated carbon; Photocatalyst

1. Introduction

Several published papers and review articles have cited the theory and environmental applications of heterogeneous photocatalysis by the use of titanium dioxide (TiO_2) [1–3]. Improving the photocatalyst efficiency may be achieved by deposition of the photocatalyst on a high surface area material (support) that will selectively adsorb the pollutant molecules and concentrate them around the photocatalyst [4–7]. The use of activated carbon (AC) as a support for TiO_2 was proposed by many authors [8–14]. Activated carbon appears to give great advantages over other supports, such as its ability to rapidly adsorb pollutants, as well as its high adsorption capacity due to its high surface area and porosity.

The use of titanium dioxide deposited on activated carbon (TiO_2/AC) as photocatalyst necessitates rapid and accurate analytical procedure for quantitative analysis of titanium dioxide. A common method for titanium dioxide analysis is X-ray fluorescence spectrometry [15] which is relatively an expensive technique to use and the instrument is not always available especially in developing countries. Additionally, establishing a calibration graph by XRF suffers from linearity problem (curvature) at high titanium content, which necessitates difficult dilution with solid matrix. The use of X-ray diffraction is possible for comparative purposes but this technique is limited to the crystalline forms of TiO_2 (anatase, rutile and brokite). Some authors [8,14], who conducted studies on TiO_2/AC photocatalyst for pollutants degradation, have used a colorimetric analytical method for TiO_2 deposited on carbon surface by the use of "Tiron" reagent (sodium 1,2-dihydroxybenzene-3,5-disulfate) as a complexing-agent, but they did not give any validation information regarding the suitability of this procedure in carbon matrix. The procedure was originally pro-

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posed for analysis of titanium dioxide by Yoe and Armstrong [16].

Titanium dioxide is widely used as a digestibility marker, and thus many authors reported preparation procedures for its analysis in feed and fecal samples from animals [17,18–21]. Procedures were generally based on sample digestion followed by addition of hydrogen peroxide (H_2O_2) to produce an intense orange color [22]. This reaction is extremely sensitive; it is known for a long time and can be used for colorimetric detection of titanium and hydrogen peroxide [23–25]. Njaa [18] analyzed titanium dioxide in rat feces using wet-ash digestion of sample in concentrated sulfuric acid in the presence of copper catalyst followed by addition of hydrogen peroxide. Leone [19] reported a procedure for the determination of TiO_2 in cheese, which involved ashing then addition of anhydrous sodium sulfate and sulfuric acid followed by boiling then addition of H_2O_2. This procedure was modified by Short et al. [20] and used for analyzing TiO_2 in chicken excreta, in which samples were ashed then digested in sulfuric acid. Titgemeyer et al. [21] have then modified Short et al.'s procedure for analysis of TiO_2 in bovine fecal samples. Myers et al. [17] have then reported the use of copper (II) sulfate and potassium sulfate as digestion catalyst. These sequential modifications suggest that the matrix, where TiO_2 present, is of significant effect in determining the validity of the TiO_2 sample preparation procedure. For example, Levine et al. [26] reported the analysis of TiO_2 in lung and lymph node tissues by inductively coupled plasma optical emission spectrometry (ICP-OES) after digestion using nitric and hydrofluoric acids. Levine et al. [26] also reviewed in his paper the major instrumental methods for quantitative and semi-quantitative TiO_2 analysis in biological samples, such as ICP-OES, ICP-MS, AAS, SEM-energy dispersive X-ray analysis. The digestion method also plays a role the process. So that authors, such as Korn et al. [27], have reported and compared the use of different decomposition procedures of TiO_2. None of these simple procedures, or any one analogous to any of them, was applied for the determination of TiO_2 photocatalyst deposited on the surface of activated carbon. It is well known that activated carbon has unique surface area and porosity, which may affect the digestion/analysis process. Additionally no procedure has used microwave-assisted digestion of an activated carbon sample containing TiO_2. Therefore, our objective here is to develop and test a simple-sample preparation microwave-digestion procedure for spectrophotometric analysis of TiO_2 in carbon matrix and compare it with previously published spectrophotometric procedures. The primary application of this method is to determine the concentration of unknown TiO_2 in TiO_2/AC photocatalyst samples.

2. Experimental

2.1. Materials and instruments

Activated carbon "AC" (devoid of TiO_2) was purchased from Sigma (77.5% C, 1.2% H, 0.5% N, 8.3% O and 12.5% ash). Other activated carbons (of different ash contents) were used for studying the effect of changing the carbon source. These carbons were either purchased from Norit (83.5% C, 0.8% H, 0.1% N, 7.3% O and 8.3% ash) or Darco (76.0% C, 1.1% H, 0.2% N, 6.5% O and 16.2% ash); or home-made carbon (84.0% C, 1.3% H, 1.7% N, 6.8%O and 6.2%ash). Titanium (IV) isopropoxide and all other chemicals were supplied by Aldrich. A microwave oven (Frigidaire RCMV5118W, 900 W, percent microwave power 100%, 2450 MHz) was used in sample digestion. Thermolyne furnace 47900 was used in dry-ashing of the solid samples. Absorbance measurements were recorded using Cary 100Bio UV–vis spectrophotometer.

2.2. Preparation of the photocatalyst samples

Six photocatalyst samples (TiO_2/AC) were prepared by deposition of titanium dioxide on activated carbon surface as follows: 1-g samples of activated carbon were placed in 100 ml beakers. Various accurately weighed (±0.1 mg) amounts of titanium (IV) iso-propoxide were added to the beakers and sonicated for few minutes. Samples were then subjected to water vapor for 1 h to hydrolyze the titanium salt, and then placed inside an oven maintained at 150 °C overnight and then calcined for 2 h at 500 °C at inert atmosphere to complete the formation of TiO_2 [15]. Photocatalyst samples (TiO_2/AC) were then weighed accurately (±0.1 mg). Concentration of TiO_2 in the photocatalyst samples was calculated by dividing mass (mg) of TiO_2 (stoichiometrically calculated) by the final mass of the photocatalyst sample obtained. Concentration of TiO_2 in the photocatalyst samples were: 18.0, 33.0, 54.2, 75.9, 97.4 and 112.5 mg TiO_2/g photocatalyst sample. Each sample was then thoroughly homogenized and pulverized. The 18.0 mg/g sample was used in the optimization experiments. Photocatalyst samples are usually prepared to have nominal concentrations in this range. However, if higher concentrations are used, the sample size should be reduced so that TiO_2 mass in the analyzed sample should not exceed 4 mg TiO_2. On the other hand, lower concentrations necessitate the use of larger sample size, and thus possible interferences from activated carbon matrix may occur.

2.3. The microwave-digestion procedure

The general procedure for sample preparation and quantitative analysis of TiO_2 is as follows: photocatalyst sample was accurately weighed (±0.1 mg) in a Pyrex tube, so that mass of TiO_2 in the analyzed photocatalyst sample should not exceed 4 mg. Three milliliters of 18.0 M sulfuric acid was added to the tube. A digestion catalyst (0.04 g copper (II) sulfate ($CuSO_4$) + 0.35 g potassium sulfate (K_2SO_4)) was added to the tube and the sample was then digested in a microwave oven (percent microwave power 100%) for 4 min (on–off time cycle of the microwave was 30–30 (second–second)). The digested solution was then diluted with 7.00 ml distilled water and centrifuged at 3000 rpm to separate residual carbon. All the supernatant was transferred into another test tube, to which 1.00 ml of 30% hydrogen peroxide was added. The final volume was completed to 10.00 ml and the absorbance of the solution was measured at 410 nm. Blank sample was prepared by repeating the above procedure using an activated carbon sample devoid of TiO_2.

The above procedure is the optimized proposed microwave procedure which was developed by using the single-variable optimization method. Variables studied included time of ashing, effective digestion time, on–off time cycle of the microwave oven, sulfuric acid concentration, volume of sulfuric acid and presence or absence of digestion catalyst and sample particle size. The effect of carbon source was also studied.

2.4. Previously published procedures

Two previously published procedures, which have been previously used by other authors for analysis of TiO_2 in feed and fecal samples, were used in this work for comparison with the proposed microwave procedure.

2.4.1. Short et al.'s procedure

This procedure was described by Short et al. [20] for analysis of TiO_2 in feed or excreta samples. It involved sample dry-ashing then digestion in H_2SO_4 and then spectrophotometric analysis. Summary of the procedure is as follows: sample size, 0.1000 g; time of ashing, 13 h; ashing temperature, 580 °C; H_2SO_4 concentration, 7.4 M; H_2SO_4 volume, 10.0 ml and digestion time, 60 min. Total time of the procedure is approximately 18 h.

2.4.2. Myers et al.'s procedure

This procedure was described by Myers et al. [17] for analysis of TiO_2 in feed and fecal samples. It involved direct sample digestion in H_2SO_4 then spectrophotometric analysis. Summary of the procedure is the following: sample size, 0.5000 g; H_2SO_4 concentration, 18 M; H_2SO_4 volume, 13.00 ml; digestion time, 2 h; catalyst, 3.5 g K_2SO_4 + 0.40 g $CuSO_4$. Total time of the procedure is approximately 4 h.

3. Results and discussion

3.1. Effect of various variables on the microwave-digestion procedure

Sample preparation by the proposed procedure for quantitative analysis of titanium dioxide is generally based on microwave assisted-digestion of the sample with sulfuric acid prior to colorimetric analysis by addition of hydrogen peroxide (H_2O_2). It was thought that sample dry-ashing may be useful to eliminate matrix effects of activated carbon during the digestion step. Other factors that may enhance procedure recovery or reduce the time of the procedure were also considered. Thus, our objective here is to test the effect of various variables on the recovery obtained with the microwave-digestion procedure.

3.1.1. Effect of digestion time and ashing time

Using 0.1000 g sample and 1.00 ml of 18 M H_2SO_4 solution, the effective digestion time was varied between 0.5 and 10 min. The obtained results are plotted in Fig. 1. From Fig. 1, it is clear that the best recovery (68%) was obtained when 4 min of effective digestion time was used. Shorter time gave lower recovery while longer time did not improve the recovery. Varying time of ashing was then studied (Fig. 2), while effective digestion time was maintained at 4 min and other procedure conditions were maintained as well. It is seen from Fig. 2 that best recovery of TiO_2 could be obtained (90%) with 240 min of ashing.

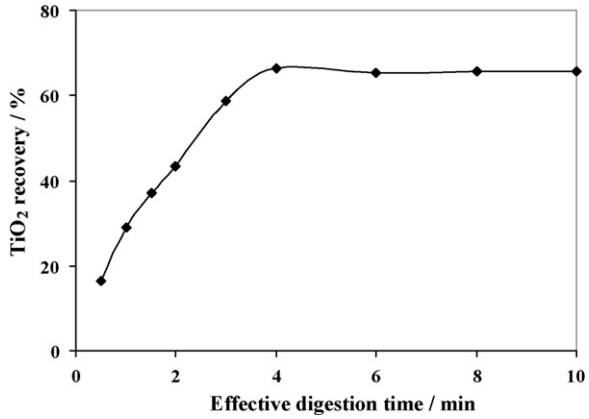

Fig. 1. Effect of effective digestion time on the percentage recovery of TiO_2 (sample not pulverized, no ashing, no digestion catalyst added, 1 ml of 18.0 M H_2SO_4).

3.1.2. Effect of volume and concentration of sulfuric acid and presence of digestion catalyst

It was thought that addition of a digestion catalyst, to this stage of optimized conditions, can improve the recovery, but this did not happen. When the same experiment was repeated by adding a digestion catalyst and without ashing, the TiO_2 recovery decreased probably due to the large amount of solid relative to the amount of liquid. But when 2.00 ml H_2SO_4 was added, instead of 1.00 ml, with the same conditions (no ashing step, digestion catalyst was added, 4 min digestion, 18.0 M H_2SO_4), the recovery increased to 95.5% without the need to an ashing step. Doubling the catalyst amount reduced the recovery due to inappropriate ratio of solid to liquid. Thus, it is important here to use an appropriate volume (of sulfuric acid) to digestion catalyst ratio. Varying the volume of sulfuric acid (with constant amount of digestion catalyst of 0.4 g and without ashing) gave the results shown in Fig. 3, in which best recovery was obtained when 3.00 ml of 18 M H_2SO_4 was used.

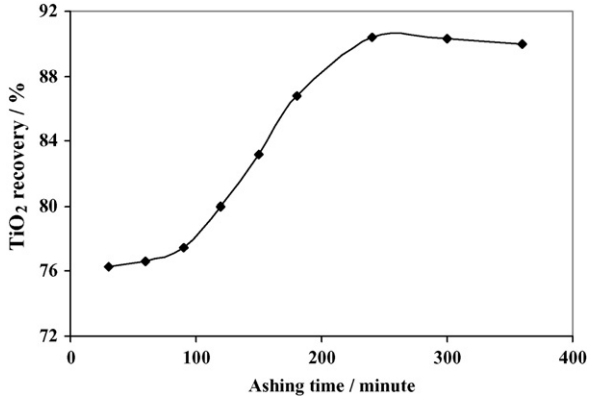

Fig. 2. Effect of ashing time on the percentage recovery of TiO_2 (sample not pulverized, no digestion catalyst added, 4 min digestion, 1 ml of 18.0 M H_2SO_4).

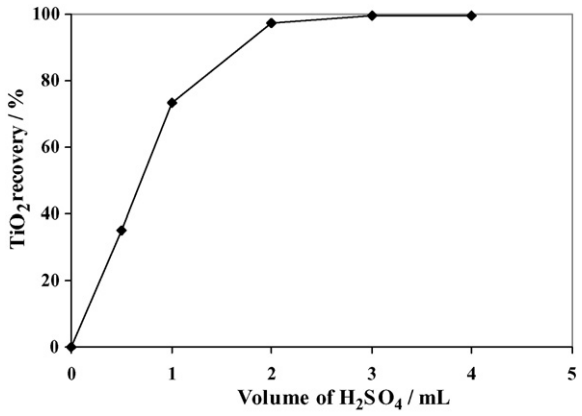

Fig. 3. Effect of sulfuric acid volume (18.0 M) on percentage recovery of TiO_2 (sample pulverized, no ashing, 0.4 g digestion catalyst added, 4 min digestion).

Varying sulfuric acid concentration was also studied (Fig. 4), in which it is clear that decreasing the sulfuric acid concentration significantly reduced the recovery. As it is seen, the best recovery was obtained with 18.0 M H_2SO_4. When the experiment was repeated without the catalyst but under the same other optimized conditions, the recovery decreased to 86.6%, which indicates the positive catalyst role in the digestion process.

3.1.3. Effect of sample pulverization

Further recovery increase was obtained with sample pulverization. With all the optimized conditions (no ashing, 3.00 ml of 18.0 M H_2SO_4, digestion catalyst added, 4 min digestion, sample pulverized to pass 100 mesh screen), the recovery could be improved up to 99.7%.

3.1.4. Effect of on–off time cycle of the microwave

On–off time cycle of the microwave oven was varied. It was found that when using 60–30, 45–30 and 30–15 (second–second) on–off time cycles, overheating occurred in the early stages of the digestion process and some acid was lost. When 15/15-time cycle was used, digestion was slow and recovery was low probably because energy supplied was not sufficient to cause complete sample digestion within the specified digestion time. When 30–30 on–off time cycle was used, digestion was finished without gas evolution and with almost full recovery (99.7%).

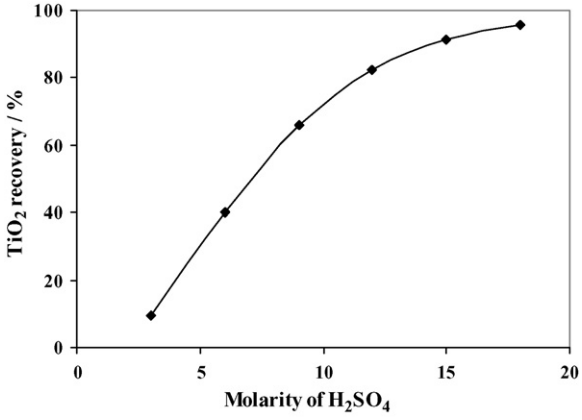

Fig. 4. Effect of sulfuric acid concentration on percentage recovery of TiO_2 (sample not pulverized, no ashing, 0.4 g digestion catalyst added, 4 min digestion, 2 ml of 18.0 M H_2SO_4).

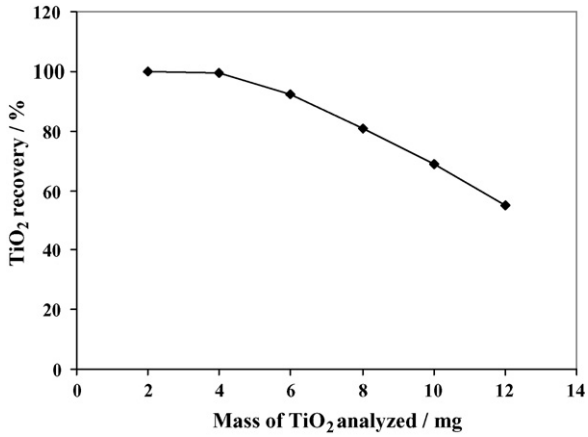

Fig. 5. Effect of mass of TiO_2 analyzed (sample mass) on percentage recovery of TiO_2 (sample pulverized, no ashing, 0.4 g digestion catalyst added, 3.00 ml of 18 M H_2SO_4, 4 min digestion).

3.1.5. Effect of TiO_2 mass contained in the photocatalyst sample (sample mass)

The effect of sample mass was studied by applying the optimized microwave-digestion procedure on various masses of samples containing various amounts of TiO_2. Fig. 5 shows recovery change with mass of digested TiO_2 in the tube. It is clear that to obtain the full recovery; the mass of TiO_2 in the sample should not exceed 4 mg TiO_2.

3.1.6. Effect of carbon source

Effect of carbon source was also studied by applying the proposed microwave procedure on various photocatalyst samples prepared using various activated carbons (from Norit, Darco, Sigma and home-made activated carbons) and containing similar amounts of TiO_2. The analysis showed a small variation (less than 3% R.S.D.) for different carbon sources.

3.2. Analytical precision

Six photocatalyst (TiO_2/AC) samples were analyzed for TiO_2 (in four replicates) by the proposed microwave procedure and by

Table 1
Precision of TiO_2 determination after digestion with the microwave procedure, Myers et al.'s procedure and Short et al.'s procedure

Sample identification (mg added TiO_2/g photocatalyst)	R.S.D. (%) of the found TiO_2 ($n = 4$)		
	Microwave procedure	Myers et al.'s procedure	Short et al.'s procedure
18.0	2.39	2.56	4.85
33.0	2.02	2.20	3.70
54.2	1.75	1.86	2.71
75.9	1.70	1.76	2.38
97.4	1.52	1.48	2.06
112.5	1.42	1.46	1.63

Table 2
Comparative determination of TiO_2 in TiO_2/AC photocatalyst samples after digestion with the proposed microwave procedure, Myers et al.'s procedure and Short et al.'s procedure ($n = 4$)

Sample identification (mg added TiO_2/g photocatalyst)	Found TiO_2/g sample (±95% confidence limits)		
	Microwave procedure	Myers et al.'s procedure	Short et al.'s procedure
18.0	18.2 (±0.4)	17.9 (±0.4)	11.5 (±0.5)
33.0	33.1 (±0.7)	32.5 (±0.7)	22.1 (±0.8)
54.2	54.0 (±0.8)	53.0 (±0.8)	35.3 (±0.9)
75.9	74.7 (±0.9)	74.7 (±0.9)	50.2 (±0.8)
97.4	96.4 (±0.9)	94.7 (±0.9)	65.5 (±0.9)
112.5	111 (±2)	110 (±2)	73.9 (±0.9)
Recovery range (%)	98.4–101.1	97.3–99.2	63.8–67.2
Relative error range (%)	0.384–1.61	0.800–2.74	32.8–36.2

the previously published procedures (Myers et al.'s and Short et al.'s procedure). The results are shown in Table 1, in which it can be concluded that the analytical precision is nearly equal for the proposed microwave procedure and the Myers et al.'s procedure, while the scatter of the results obtained using the Short et al.'s procedure was higher (1.30–4.85% R.S.D.). However the three procedures gave less than 5% R.S.D.

3.3. Analytical accuracy

Photocatalyst (TiO_2/AC) samples were digested by the proposed microwave-digestion procedure and analyzed for the TiO_2 as outlined in Section 2.3. The same samples were also analyzed for TiO_2 by the Myers et al. and Short et al. procedures as outlined in Section 2.4. Four replicates of each sample were analyzed and the average found concentration of TiO_2 (±95% confidence limits) was recorded in Table 2.

Compared to Myers et al.'s procedure, which has been originally used for TiO_2 analysis in feed and excreta samples; the recovery of TiO_2 by the proposed microwave procedure ranges between 98.4 and 101.1%. This is slightly higher than the quoted recoveries of the Myers et al.'s procedure for the same TiO_2/AC photocatalyst samples, which ranged from 97.3 to 99.2%. However, Myers et al. [17] reported that 4 h and half are required to analyze one sample. But with the proposed microwave-digestion procedure, we could analyze four photocatalyst samples in less than half an hour.

The recoveries of TiO_2 for the same samples treated with the Short et al.'s procedure were much lower than the proposed microwave procedure, and ranged from 63.8 to 67.2%. Fig. 6 shows relationships between the found TiO_2 using the proposed microwave procedure against the found TiO_2 using Myers et al.'s procedure and Short et al.'s procedure.

3.4. Linearity and limit of detection

The calibration curves for TiO_2 are linear ($R^2 > 0.9996$) within the studied concentration range (18.0–112.5 mg TiO_2/g photocatalyst) for all the three procedures. Calibration curves have slopes of 0.0971(±0.000296), 0.0960(±0.000301) and 0.0655(±0.000578) absorbance unites (AU) per (mg TiO_2/g photocatalyst) and y-intercepts of 0.0330(±0.0201), 0.0250(±0.0204) and −0.0170(±0.0192) (mg TiO_2/g photocatalyst) for the microwave procedure, Myers et al.'s procedure and Short et al.'s procedure, respectively.

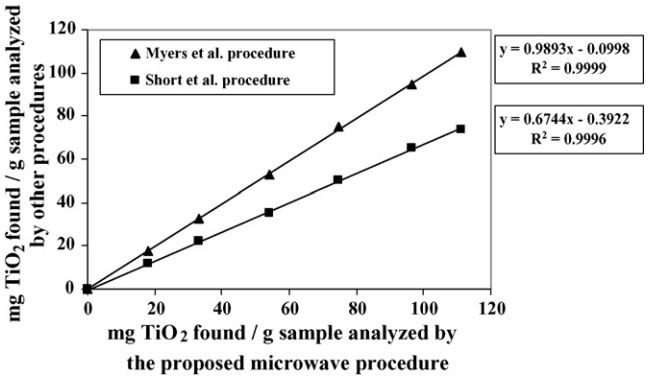

Fig. 6. Relationships between the found TiO_2 using the proposed microwave procedure against the found TiO_2 using Myers et al.'s procedure and Short et al.'s procedure.

The limits of detection were calculated (4 replicate blank runs) and found to be 0.0981, 0.124 and 0.281 (mg TiO_2/g photocatalyst) for the microwave procedure, Myers et al.'s procedure and Short et al.'s procedure, respectively.

4. Conclusion

The proposed microwave digestion of TiO_2/AC photocatalyst is a fast and simple method of sample treatment prior to TiO_2 spectrophotometric analysis. This is superior to other procedures because: (1) it is capable of full recovery of TiO_2 in much shorter digestion time, (2) no ashing step is required, (3) less chemicals and sample size are required and (4) many samples can be treated simultaneously. Ashing is not necessary because complete recovery is obtained without ashing. The use of sulfuric acid is an appropriate digesting reagent in this procedure, which is capable of dissolution of TiO_2 while activated carbon will remain undigested. This is appropriate since this will reduce the complexity of the matrix and thus reduce possible interferences. The % recovery of TiO_2 is affected by sample particle size, the presence of a digestion catalyst and the concentration

and volume of sulfuric acid. Complete analysis of four samples is possible in 30 min by the use of the proposed microwave procedure. Precision, accuracy and other figures of merit of the proposed microwave procedure are comparable to or even better than that of Myers et al.'s procedure.

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