

Simple and Rapid Spectrophotometric Determination of Titanium on Etched Aluminum Foils

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ABSTRACT

Introduction of titanium oxides with high permittivity on etched aluminum foils' surface has been successfully utilized to increase specific capacitance of anode foils for aluminum electrolytic capacitors. In order to quantify the concentration of titanium (IV) on the etched aluminum foil precisely, a simple and rapid spectrophotometric procedure has been developed. After optimizing a series of variables including absorbance wavelength, concentration of nitric acid, concentration of hydrogen peroxide, nitration time and developing time, analytical precision and accuracy were tested by using standard working solution containing known amount of titanium (IV). The results showed that Lambert-Beer's law was obeyed in the range of 0.01 to 3.00 mmol·L⁻¹. The relative standard deviation (RSD) ranged from 0.67% to 1.09% (n = 6), and the recovery was between 99.17% - 100.03%. Investigation on effect of Al³⁺ ion indicated that there was no interference in the absorbance of titanium (IV) at 410 nm. The proposed procedure was applied to real samples for the determination of titanium (IV), and the results were in a good agreement with the values certified by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

KEYWORDS

Titanium Oxide; Spectrophotometry; Hydrogen Peroxide; Etched Aluminum Foil

1. Introduction

The rapid development in electronic science and technology has been resulting in the trend of electronic devices towards miniaturization, multi-functionalization and portability. As an essential component extensively used in electric circuit for filter, smoother and power supply, aluminum electrolytic capacitor is strongly required to scale down its size and light its weight. The key to meeting these requirements is to increase specific capacitance of the aluminum anode foils. The routine process adopted widely is to increase specific surface area of aluminum foil by etching. Recent researches show that it is another promising approach to boosting the specific capacitance further via introducing titanium oxides into dielectric layer of aluminum electrolytic ca-

pacitor after etching the foil [1-11]. It is proposed that the increase in specific capacitance directly depends on the concentration of titanium (Ti) (IV) in dielectric layer because titanium oxides have much higher permittivity than alumina. A more or less amount of Ti (IV) will result in the decline of specific capacitance. In order to determine the concentration of titanium (IV) on the etched aluminum foil precisely, therefore, it is essential to develop a simple and practical analysis of trace amounts of Ti to evaluate its dielectric role.

Various analytical techniques, including neutron activation analysis (NAA) [12], graphite furnace atomic absorption spectrometry (GFAAS) [13], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [14], inductively coupled plasma-mass spectrometry (ICP-MS) [15], X-ray fluorescence (XRF) [16], catalytic adsorptive stripping voltammetry (CASV) [17] and

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spectrophotometry [18-23], were used for the determination of Ti (IV) in different types of matrices. Although NAA, GFAAS, ICP-AES, ICP-MS and XRF can determine simultaneously major & trace elements and the combination is considered to have several advantages over the separate technique, spectrophotometry continues to offer the best alternative for routine analysis of Ti (IV) in the absence of these expensive instruments, due to its common availability, simple procedure, high accuracy and low cost effectiveness.

During the spectrophotometric determination of Ti (IV), a number of organic chromogenic reagents, such as *o*-carboxyphenylfluorone [19], ponceau S [18], diantipyrylmethane [20], resacetophenone *p*-hydroxybenzoylhydrazone [24], thiocyanate [25], 2,3-dihydroxynaphthalene [26], 3,5,7,2',4'-penta hydroxy flavone [27], 5-(2',4'-dimethylphenylazo)-6-hydroxypyrimidine-2,4-dione [28], bromopyrogallol red [29] and *o*-chlorophenylfluorone [30], have been used to produce an intense color for absorbance measurement. Most of these reagents are expensive, harder-to-obtain and environmental-unfriendly. Compared with these organic reagents, hydrogen peroxide (H₂O₂) is a good alternative and widely applied in spectrophotometric determination of Ti (IV), owing to its nontoxicity, low-cost and extremely sensitivity [31-35]. Despite the already abundant literatures describing H₂O₂ procedure, there are relatively few reports, to the best of my knowledge, on determination of Ti (IV) on the surface of etched aluminum foils.

Therefore, the objectives of this work are to develop a simple and rapid ultrasonic-assisted digestion procedure suitable for Ti (IV) with analysis by spectrophotometry and to validate the applicability of this method as an alternative for the measurement of Ti (IV) on etched aluminum foil. The results showed that this method had been successfully applied in determination of Ti (IV) in real samples.

2. Experimental

2.1. Apparatus

A UV-3300S UV-Vis spectrophotometer (Shanghai Mapada Co. China) connected to a computer was used for all spectral measurements in the wavelength range of 350 - 550 nm using 1 cm matched stoppered quartz cells. The instrument was optimized daily before measurement and operated as recommended by the manufacturers. The optimized parameters included scan speed of 5 nm·s⁻¹, slit width of 2 nm, and $\Delta\lambda = 1$ nm for first-order derivative mode. A model JY-ULTIMA inductively coupled plasma-atomic emission spectrometry (ICP-AES) (JY-HORIBA Co. France) was employed to determine concentration of Ti (IV) in real samples for the comparison with the result from our approach. The ultrasonic-as-

sisted digestion was carried out in a KQ-300B ultrasonic cleaner (Kunshan Ultrasonic Instruments Co., Ltd., China). The water used in this work was prepared by Milli-Q-Reference water system (Millipore Co. Bedford, MA).

2.2. Reagents and Solutions

All chemicals used were of analytical grade and purchased from Sinopharm chemical reagents Co. Ltd., China. All the solutions were made up by Milli-Q-Reference-purified water ($\rho > 15$ M Ω ·m). Stock solution of nitric acid (HNO₃) with the concentration of 7.5 mol·L⁻¹ was prepared daily by dilution of 70% nitric acid with water. Stock solution of H₂O₂ containing 1.0 mol·L⁻¹ was made freshly right before use by dilution of 30% hydrogen peroxide with water. The standard stock solution of titanium with 20 mmol·L⁻¹ was prepared daily by dissolving 0.6903 g titanium (IV) *n*-butoxide in 5 mL of 7.5 mol·L⁻¹ HNO₃ and diluting to 100 ml with water in a volumetric flask.

2.3. Procedure

The standard working titanium (IV) solutions with different concentration (0.01, 0.02, 0.10, 0.20, 1.00, 2.00, 2.50, 3.00, 3.60 mmol·L⁻¹) were prepared daily as follows: First, the required amount of standard stock titanium (IV) solution was mixed with a certain volume of stock HNO₃ solution and nitrified at 60°C for some time. The resulting solution was then cooled down to room temperature followed by adding a given volume of stock H₂O₂ solution. After that, the above solution was diluted to 100 mL with water in a volumetric flask and developed at room temperature for some time. The samples containing Al³⁺ were made by adding aluminum nitrate (Al(NO₃)₃) into standard working titanium (IV) solution. Blank sample was prepared by repeating the above procedure without standard stock titanium (IV) solution. The absorbance between 350 - 550 nm was measured against the blank sample.

2.4. Preparation of Real Samples

Aluminum foils coated with titanium oxides were prepared as reference [2]. The only difference was titanium dioxide instead of barium titanate. The obtained aluminum foil with the geometric area of 4 cm² was cut into pieces and then digested in stock HNO₃ solution at 60°C in ultrasonic cleaner until all aluminum was dissolved. The digested solution was cooled down to room temperature and added with stock solution of H₂O₂. Afterwards, the obtained solution was diluted to 25 mL with water in a volumetric flask and developed for some time. Then the spectrophotometric measurement given above was applied.

3. Results and Discussion

3.1. Optimization of Absorbance Wavelength

In order to study the optimal absorbance wavelength, a series of standard working solutions of titanium (IV) containing 0.02, 0.10, 0.20, 1.00, 2.00, 3.00 $\text{mmol}\cdot\text{L}^{-1}$ Ti (IV), prepared in section 2.3, were measured for the absorbance spectra in the wavelength range of 350 - 550 nm, respectively. The obtained results were plotted in **Figure 1**. The maximum absorbance wavelength of each spectrum was also shown in **Figure 2**. From **Figure 2**, it was clear that the maximum absorbance of most samples occurred at 410 nm which was consistent with the reports of El-Sheikh [23] and Bassan [36]. The linear regression coefficients (r^2) of the calibration graphs gained at 410 nm was 0.9999. Furthermore, there was hardly any absorbance at 410 nm in spectra of nitric acid or hydrogen peroxide (see **Figure 3**). Therefore, 410 nm could be used as optimal absorbance wavelength.

3.2. Effect of Concentration of Nitric Acid

The concentration of nitric acid is a very important factor for digestion of real samples containing titanium (IV) on the surface of etched aluminum foils in the present work. Therefore, the effect of concentration of nitric acid on the absorbance of standard working solution of titanium (IV) was investigated in the range of 0.047 - 3.75 $\text{mol}\cdot\text{L}^{-1}$. Varying the concentration of nitric acid gave the results depicted in **Figure 4**. The absorbance at 410 nm was observed to be maximum and almost constant in the range of 1.125 to 3.75 $\text{mol}\cdot\text{L}^{-1}$. Consider that aluminum would consume nitric acid during digestion via chemical reaction with HNO_3 , the concentration of 3.75 $\text{mol}\cdot\text{L}^{-1}$ was recommended for the determination of Ti (IV).

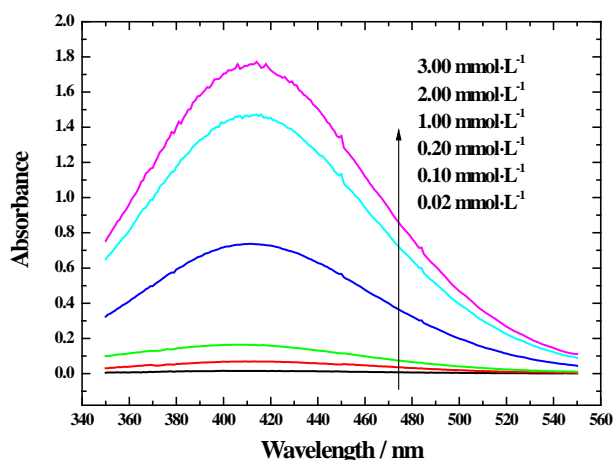


Figure 1. Effect of concentration of Ti (IV) on absorbance spectra: concentration increased from bottom (0.02 $\text{mmol}\cdot\text{L}^{-1}$) to top (3.00 $\text{mmol}\cdot\text{L}^{-1}$) (each solution containing 3.75 $\text{mol}\cdot\text{L}^{-1}$ HNO_3 , 200 $\text{mmol}\cdot\text{L}^{-1}$ H_2O_2 , nitrified for 20 min, developed for 10 min).

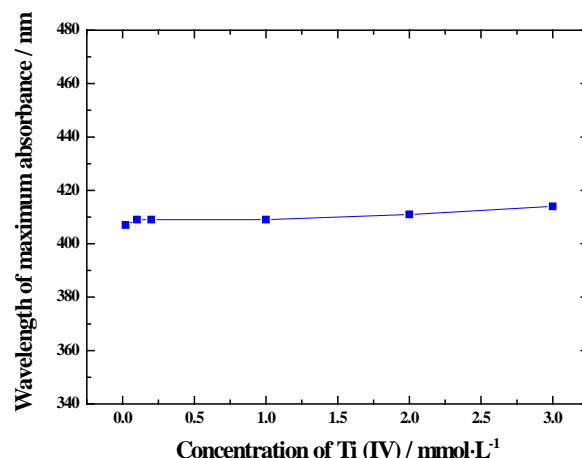


Figure 2. Effect of concentration of Ti (IV) on the wavelength of maximum absorbance (each solution containing 3.75 $\text{mol}\cdot\text{L}^{-1}$ HNO_3 , 200 $\text{mmol}\cdot\text{L}^{-1}$ H_2O_2 , nitrified for 20 min, developed for 10 min).

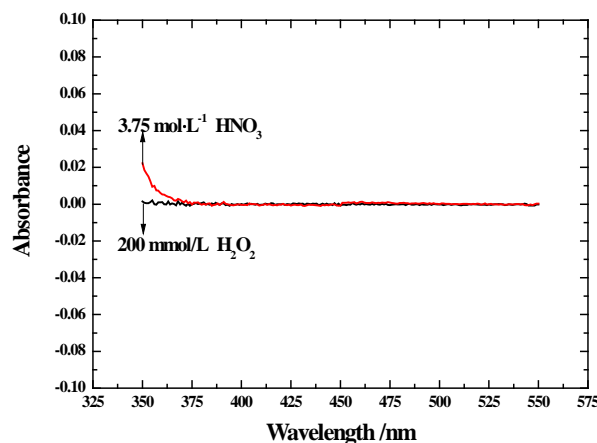


Figure 3. Absorbance spectra of 3.75 $\text{mol}\cdot\text{L}^{-1}$ HNO_3 and 200 $\text{mmol}\cdot\text{L}^{-1}$ H_2O_2 .

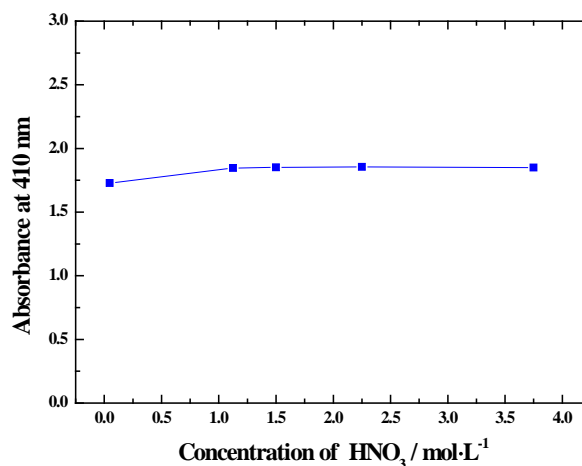


Figure 4. Effect of concentration of nitric acid on the absorbance at 410 nm (each solution containing 2.5 $\text{mmol}\cdot\text{L}^{-1}$ Ti (IV), 200 $\text{mmol}\cdot\text{L}^{-1}$ H_2O_2 , nitrified for 20 min, developed for 10 min).

3.3. Effect of Concentration of Hydrogen Peroxide

Chromogenic reagent of hydrogen peroxide was used to produce an intense color for absorbance measurement here. Hence, it was necessary to study the effect of concentration of H_2O_2 on the absorbance of each standard working solution. Varying amount of stock solution of hydrogen peroxide was added to standard working solution with a fixed Ti (IV) concentration of $2.5 \text{ mmol}\cdot\text{L}^{-1}$ and the absorbance was measured according to the standard procedure. The results were given in **Figure 5**.

The effect of concentration of H_2O_2 was found to be ignorable when the concentration of H_2O_2 exceeded $25 \text{ mmol}\cdot\text{L}^{-1}$. It was noticed that these colored species were stable and their absorbance remained constant at least 24 h at room temperature. Thus, in the light of these results, for all subsequent works, H_2O_2 concentration $200 \text{ mmol}\cdot\text{L}^{-1}$ was adopted as optimum for the determination of Ti (IV).

3.4. Effect of Nitration Time

A series of $2.5 \text{ mmol}\cdot\text{L}^{-1}$ standard working Ti (IV) solutions containing $3.75 \text{ mol}\cdot\text{L}^{-1}$ HNO_3 were used to test the effect of nitration time varied between 10 and 45 min on the absorbance at 410 nm. The obtained results were graphed in **Figure 6**. It was clear that the maximum absorbance was gained when nitration time reached 20 min. Shorter time gave lower absorbance while longer time did not improve obviously the absorbance. Consequently, 20 min was selected as nitration time for the subsequent experiments.

3.5. Effect of Developing Time

In order to react fully with Ti (IV) and form more colored complexes that were the base of quantitative determination of Ti (IV), the standard working solution usually developed for some time after adding hydrogen peroxide. The effects of developing time on the absorbance at 410 nm were studied. **Figure 7** showed absorbance changes with developing time. It was shown that the absorbance at 410 nm reached maximum after developing 5 min, then it changed little. Therefore, to make sure H_2O_2 thoroughly reacted with Ti (IV), under optimized conditions, 10 min was adopted for all further work.

3.6. Effect of Al^{3+} Ion

The problematic effects from foreign ions at high levels were known as “matrix effect” in the spectrophotometric determination of Ti (IV) [37,38]. Therefore, in consideration of real sample containing abundant Al^{3+} , the effect of Al^{3+} ion on the spectrophotometric determination of Ti

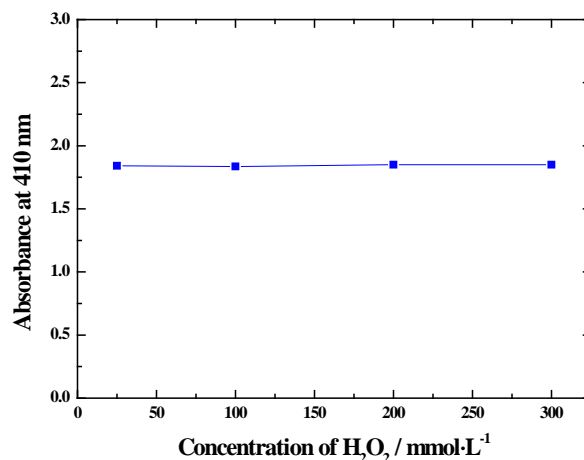


Figure 5. Effect of concentration of hydrogen peroxide on the absorbance at 410 nm (each solution containing $2.5 \text{ mmol}\cdot\text{L}^{-1}$ Ti (IV), $3.75 \text{ mol}\cdot\text{L}^{-1}$ HNO_3 , nitrified for 20 min, developed for 10 min).

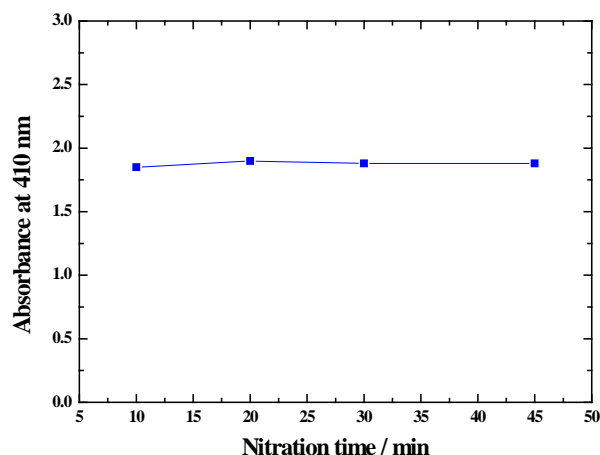


Figure 6. Effect of nitration time on the absorbance at 410 nm (each solution containing $2.5 \text{ mmol}\cdot\text{L}^{-1}$ Ti (IV), $3.75 \text{ mol}\cdot\text{L}^{-1}$ HNO_3 , $200 \text{ mmol}\cdot\text{L}^{-1}$ H_2O_2 , developed for 10 min).

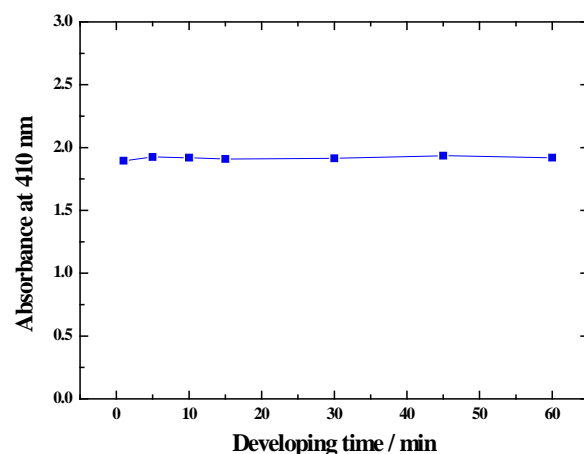


Figure 7. Effect of developing time on the absorbance at 410 nm (each solution containing $2.5 \text{ mmol}\cdot\text{L}^{-1}$ Ti (IV), $3.75 \text{ mol}\cdot\text{L}^{-1}$ HNO_3 , $200 \text{ mmol}\cdot\text{L}^{-1}$ H_2O_2 , nitrified for 20 min).

(IV) was studied and the results were shown in **Figure 8**. It was observed that even $300 \text{ mmol}\cdot\text{L}^{-1} \text{ Al}^{3+}$ did not interfere in the absorbance of Ti (IV) at 410 nm, which was in accord with the results of Varghese [24], Mondal [26], and Aydin [39].

3.7. Linearity and Limit of Detection

Under the optimum conditions described above, Lambert-Beer's law was obeyed in the range of 0.01 to $3.00 \text{ mmol}\cdot\text{L}^{-1}$. The calibration curve was linear within this range as shown in **Figure 9**. The inset showed the results of calculation using least square method. The calibration curve had a slope of $0.74935 (\pm 0.00316)$ and a y-intercept of $-0.00371 (\pm 0.00486)$. The correlation coefficient r^2 was 0.99996.

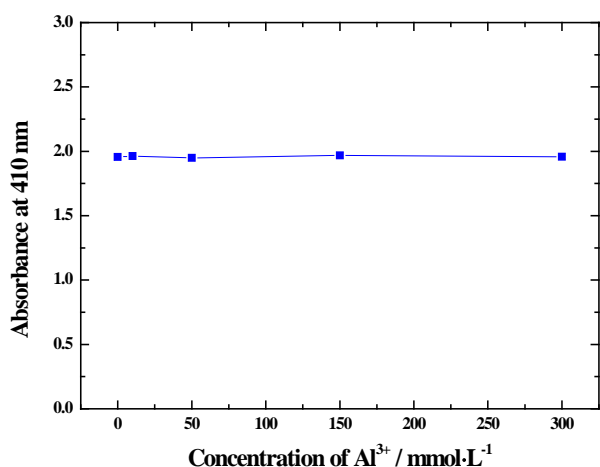


Figure 8. Effect of concentration of Al^{3+} on the absorbance at 410 nm (each solution containing $2.5 \text{ mmol}\cdot\text{L}^{-1} \text{ Ti (IV)}$, $3.75 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$, $200 \text{ mmol}\cdot\text{L}^{-1} \text{ H}_2\text{O}_2$, nitrified for 20 min, and developed for 10 min).

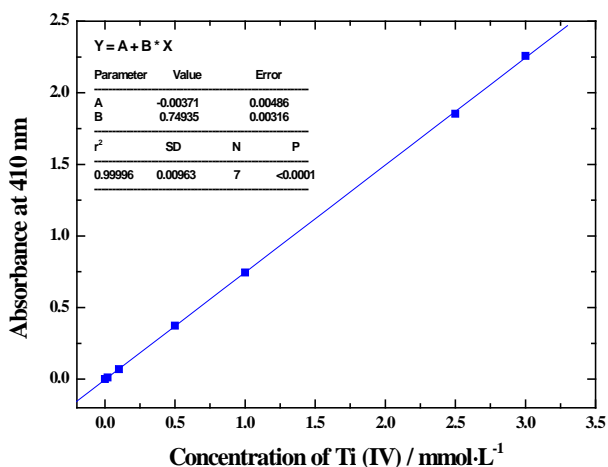


Figure 9. Relationships between concentration of Ti (IV) and the absorbance at 410 nm (each solution containing $3.75 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$, $200 \text{ mmol}\cdot\text{L}^{-1} \text{ H}_2\text{O}_2$, nitrified for 20 min, and developed for 10 min).

The limit of detection, defined as $C_L = 3 S_B/m$ [25,40], where C_L , S_B , and m are the limit of detection, standard deviation of the blank ($n = 15$), and the slope of the calibration curve, respectively, was $0.002814 \text{ mmol}\cdot\text{L}^{-1}$.

3.8. Analytical Precision and Accuracy

The precision and accuracy of the determination of Ti (IV) were verified by analyzing samples containing different concentration of titanium under optimized conditions. Each determination was carried out 6 times. The results were presented in **Table 1**, in which it was evident that the analytical performance was very well. The relative standard deviation ranged from 0.67% to 1.09% ($n = 6$) and the recovery was in the range of 99.17% - 100.03%, which indicated that the proposed method could be effectively used to quantitatively determine titanium.

3.9. Analysis of Real Samples

The validation and applicability of the present procedure was confirmed by determination of titanium (IV) in real samples. Analytical results of these samples were listed in **Table 2**. The results found were in good agreement with the values certified by ICP-AES.

4. Conclusion

A simple, fast and economic procedure for spectropho-

Table 1. Precision and accuracy of Ti (IV) determination using standard working solution ($n = 5$) (each solution containing $3.75 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$, $200 \text{ mmol}\cdot\text{L}^{-1} \text{ H}_2\text{O}_2$, nitrified for 20 min, and developed for 10 min).

Sr No.	Ti (IV) added ($\text{mmol}\cdot\text{L}^{-1}$)	Ti (IV) found ($\text{mmol}\cdot\text{L}^{-1}$)	RSD (%)	Recovery (%)
1	0.20	0.198 ± 0.003	1.09	99.17
2	1.00	0.995 ± 0.009	0.91	99.53
3	2.00	2.001 ± 0.010	0.73	100.03
4	2.50	2.485 ± 0.025	0.67	99.40
5	3.00	2.978 ± 0.028	1.00	99.26

Table 2. Analysis of Ti (IV) in real samples ($n = 4$) (each digested solution containing $3.75 \text{ mol}\cdot\text{L}^{-1} \text{ HNO}_3$, $200 \text{ mmol}\cdot\text{L}^{-1} \text{ H}_2\text{O}_2$, nitrified for 20 min, and developed for 10 min).

Sr No.	Ti (IV) found ($\mu\text{mol}\cdot\text{cm}^{-2}$)	Ti (IV) certified by ICP-AES ($\mu\text{mol}\cdot\text{cm}^{-2}$)
1	1.780 ± 0.051	1.6456
2	1.961 ± 0.063	2.0914
3	0.356 ± 0.011	0.3472
4	0.579 ± 0.024	0.5815

tometric determination of Ti (IV) has been established in the present work. The proposed procedure offers the advantages of high recovery (>99%) and low RSD (<1.1%) in such a short time without extraction by organic solvent, preconcentration, pre-separation or ashing. Aluminum ion coming from matrix does not interfere with the determination of Ti (IV) in real samples, and the observed concentration of Ti (IV) is in keeping with the value certified by ICP-AES. The present method can be used as an alternative method for the determination of Ti (IV) on the surface of etched aluminum foils.

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