

# SPECTROPHOTOMETRIC DETERMINATION OF TITANIUM (IV) IN STEEL, PAINT AND A COSMETIC CREAM USING TANNIC ACID IN MICELLAR MEDIUM

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## ABSTRACT

A highly simple, rapid and sensitive spectrophotometric procedure is described for micro-amounts determination of titanium (IV) using tannic acid (tannin) as a new reagent in presence of Triton X-100 (micellar medium). Titanium (IV) reacted with tannic acid in slightly acidic medium at pH=6 using citrate buffer solution to form a 1:2 red coloured stable complex with maximum absorption at 436 nm. The complex is instantaneously formed and remain stable over 2 hr. Beer's law is obeyed in the range of 2-26  $\mu\text{g Ti ml}^{-1}$  with molar absorptivity to be  $3.66 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ . The proposed method is successfully applied for titanium determination in steel, paint and pharmaceutical samples.

**Keywords:** Spectrophotometry, Titanium (IV), Tannic acid, Triton X-100  
Beer's law, Steel, Paint and Pharmaceutical samples.

## 1. INTRODUCTION

Tannic acid is a low molecular weight polymer of gallic acid and 3-galloyl gallic acid esterified with glucose of variable composition. It is generally obtained by extraction with water or organic solvents from a number of well-known botanical sources, **Aquilina, et al. (2014)**. It can chelate with more than one metal at a time so, it can be used as a complexing agent for determination of several metal ions such as Fe (III) by forming highly stable coloured complexes at pH range 3-10, **Iffat, et al. (2005)**. It also used for the micro determination of Vanadate ( $\text{VO}_3^-$ ) by forming a 1:1 blue coloured complex, **Pooja, (2012)**.

Titanium exists in the nature in its most and common oxidation state as titanium (IV). Titanium compounds are highly corrosion resistant of chloride solution including sea water, nitric acid and other bleaching agents. Titanium dioxide is also used as white pigment in paints. The paint, pigment, paper and pulp industries discharge a very high amount of titanium, **Reddy, et al. (2015)**, thus the determination of trace amounts of titanium is becoming increasingly importance.

Various analytical techniques used for the determination of titanium (IV) including high performance liquid chromatography using 5, 5'-methylenedisalicylohydroxamic acid, **Bagur, et al. (1997)**, voltammetry using a carbon paste electrode modified with cetyltrimethylammonium bromide, **Stadiober, et al. (1996)**, inductively coupled plasma atomic emission spectrometry, **De Andrade, et al. (1997)** and spectrophotometry.

Spectrophotometric methods occupy special position in titanium determination due to their simplicity, less expensive instrumentation and high sensitivity. A number of chromogenic reagents are reported for the determination of titanium (IV) such as, 2, 4-Dihydroxyacetophenone-isonicotinoylhydrazone by forming a red coloured complex, **Reddy, et al. (2015)**, 5-Bromo-2-hydroxy-3-methoxy benzaldehyde-p-hydroxybenzoic-hydrazone by forming an orange coloured



soluble complex at  $\lambda_{\max} = 390$  nm, **Devireddy, et al. (2014)**, [o-carboxyphenylfluorone] in the presence of hexadecyltrimethyl ammonium chloride, **Hoshino, et al. (2011)** and resacetophenone p-hydroxybenzoylhydrazone in presence of Triton X-100, **Varghese, et al. (2006)**. Titanium (IV) also, determined by the formation of a yellowish-orange ternary complex with thiocyanate ( $\text{SCN}^-$ ) and cetyltrimethyl ammonium bromide, **Tarafder and Thakur, (2008)**, and by using N'-(2-hydroxybenzylidene)-3-oxobutanhydrazide as a reagent forming a reddish orange colored complex at 500 nm, **Srilalitha, et al (2010)**.

## 2. EXPERIMENTAL

### 2.1 Apparatus:

T80 UV/Vis double beam spectrophotometer, PG instruments Ltd. company, United Kingdom. Adwa pH-meter, Model AD 1030, Romania.

### 2.2 Reagents and solutions:

All chemicals are of analytical grade purchased from Sigma company.

Stock solutions (100 ml) of tannic acid at a concentration of [ $1 \times 10^{-3}$ ,  $1 \times 10^{-4}$  M] are prepared by dissolving the appropriate amounts of tannic acid (Mwt = 1701.28) in suitable volumes of deionized water and complete to 100 ml. A ( $1 \times 10^{-2}$  M) stock solution (100 ml) of Ti (IV) is prepared by dissolving an accurately weighed amount of titanium dioxide ( $\text{TiO}_2$ ) (Mwt = 79.86) in a minimum volume of conc. sulphuric acid with heating and diluting to 100 ml with distilled water. The solution is standardized by the known procedure, **Vogel, (2002)**.

The surfactant, Triton X-100 is prepared at concentration ( $1 \times 10^{-2}$ ) by drawing the suitable volume from the surfactant and diluting in deionized water and used without further purification.

### 2.3 Buffers:

For the preparation of buffer solutions, a series of different types of buffer including universal buffer in the range of (1.81-11.98) according to **Britton**, borate buffer (7.6-10), acetate, citrate buffer (3-6) and phosphate buffer (7-11) according to **Lurie, (1978)** is prepared.

### 2.4 Procedures

#### 2.4.1 Absorption curve:

A sample solution containing 0.5 ml of Ti (IV) ( $1 \times 10^{-3}$  M), 1.5 ml of tannic acid solution ( $1 \times 10^{-3}$  M) and 8 ml of the citrate buffer pH=6 is prepared, and mix thoroughly. After 5 minutes, the absorbance is measured by scanning wavelength from 200 to 800 nm against the blank.

#### 2.4.2 In presence of surfactant:

A sample containing 0.5 ml of Ti (IV) ( $1 \times 10^{-3}$  M), 1.5 ml of tannic acid solution ( $1 \times 10^{-3}$  M) and 0.3 ml of Triton X-100 is mixed in 10 ml measuring flask, then complete to the mark with citrate buffer pH=6. After 5 minutes and at 25°C, the absorbance is measured by scanning wavelength from 200 to 800 nm against the reagent blank.

#### 2.4.3 Beer's law:

A series of solutions containing 1.5 ml of tannic acid and different concentration of Ti (IV) ranging from 1-34  $\mu\text{g ml}^{-1}$  is prepared in 10 ml measuring flask with 0.3 ml of Triton X-100 as the perfect surfactant and complete to the mark with citrate buffer pH=6. After 5 minutes and at 25°C, the absorbance is measured at 436 nm against the blank solution.

#### 2.4.4 Applications:

##### 2.4.4.1 Determination of Ti (IV) in Steel:

A weighed sample (0.9 gm) of steel is dissolved in 10 ml conc. sulphuric acid with heating at 70°C for few minutes. The solution is cooled to room temperature and diluted to 25 ml with deionized water. Iron, molybdenum and vanadium are masked by using sodium fluoride, acetyl acetone and EDTA, respectively according to [**Shigemats, et al. (1972)**, **Pribil, (1982)**, **Hu and Coetzee (2007)**]. (1ml) from the above solution is mixed with tannic acid according to the above procedures and the absorbance is measured at 436 nm against the blank.

##### 2.4.4.2 Determination of Ti (IV) in paint:

A weighed sample (2.90 gm) of the paint is dissolved in ether, then in a 5 ml of conc. HCl with heating for few minutes and separation of the aqueous layer. The solution is diluted to 25 ml with deionized water. (1 ml) from the above solution is drew, mixed with tannic acid and the absorbance was measured at 436 nm against the blank.

#### 2.4.4.3 Determination of Ti (IV) in a cosmetic (sun screen) cream:

A weighed sample (1.088 gm) of the cream is dissolved in ether, then in a little amount of dil. HCl with heating for few minutes and separation of the aqueous layer. The solution is diluted to 25 ml. (1ml) from the above solution is taken, mixed with tannic acid according to the above method and the absorbance is measured at 436 nm against blank.

### 3. RESULTS AND DISCUSSION

#### 3.1 Absorption curve:

Tannic acid is used as a new spectrophotometric reagent for the determination of titanium (IV), forming a red coloured stable complex at 412 nm as shown in Fig. (1).

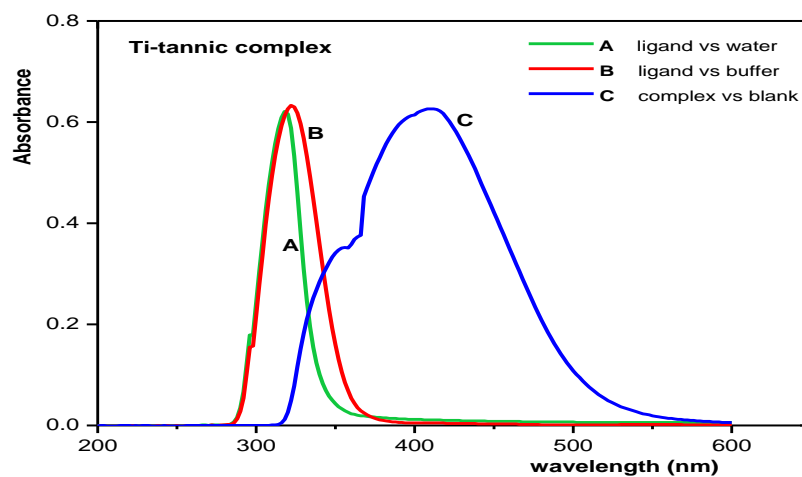


Fig. (1): Absorption spectra of Ti (IV)-Tannic complex.

#### 3.2 Effect of pH and buffer:

The study of the effect of pH on the colour intensity of the complex showed that the appropriate pH range for the complex is from 5 to 8 with optimum value at pH = 6 as shown in Fig. (2). Studying the effect of different buffer types in the range of (5-8) indicated that, the maximum absorbance value is obtained using citrate buffer at pH=6 as shown in Fig. (3).

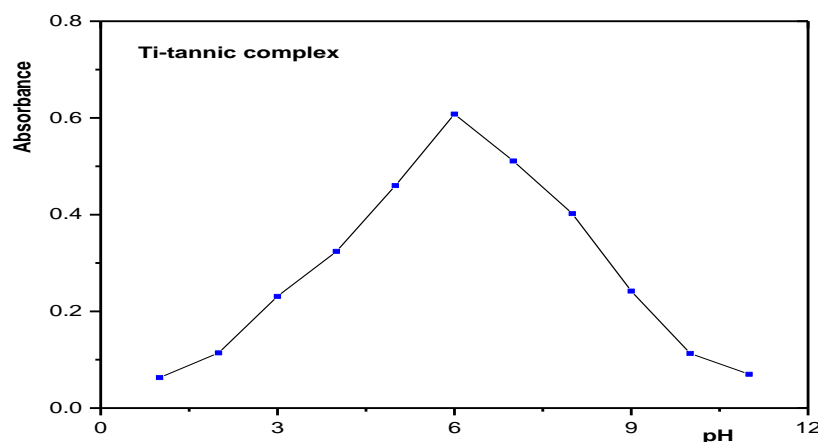


Fig. (2): Effect of pH on the formation of Ti (IV)-Tannic complex.

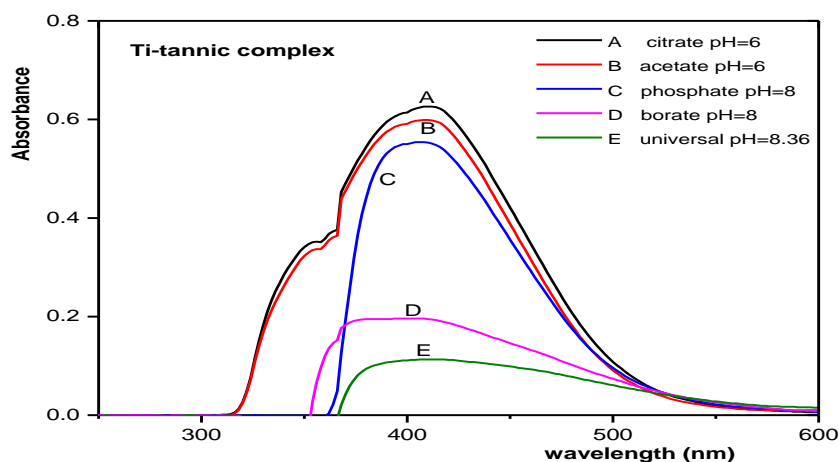


Fig. (3): Effect of different buffer types on the formation of Ti (IV)-Tannic complex

### 3.3 Effect of the sequence of addition:

The effect of the sequence of addition on the formation of Ti (IV) – tannic acid complex showed that, the order (ligand-buffer-metal) gave the highest value of absorbance.

### 3.4 Effect of time and temperature:

Studying the effect of time and temperature on stability and colour intensity of the complex formed between Ti (IV) and tannic acid illustrated that, the complex is formed instantaneously and the absorbance reached to its maximum value after 5 minutes and at room temperature ( $25 \pm 2$  °C).

### 3.5 Effect of surfactant:

The results showed that, the presence of 0.3 ml of Triton X-100 as a surfactant shifted the absorption peak to hyper and bathochromic shifts and this may be due to the formation of micelles or formation of a double or triple complex with surfactant itself.

### 3.6 Determination of stoichiometric ratio:

#### 3.6.1 Molar ratio method:

A series of solutions is prepared in which the metal ion concentration was kept constant at 0.5 ml ( $1 \times 10^{-3}$  M), while that of the ligand is regularly varied from 0.1 to 1.5 ml of  $1 \times 10^{-3}$  M. The absorbance of these solutions is measured at 436 nm with all optimum conditions. Fig. (4) gave the absorbance – molar ratio curve which showed that Ti (IV) formed a 1: 2 complex with tannic acid, **Yoe and Jones (1944)**.

#### 3.6.2 Continuous variation method:

A series of solutions was prepared by mixing equimolar solutions of Ti (IV) and ligand in different proportions from 0.1 ml to 0.9 ml ( $1 \times 10^{-3}$  M) of the same concentration while keeping the total molar concentration constant. A plot of absorbance measured at the recommend wavelength versus mole fraction is used to determine the Ti (IV)-reagent ratio. Fig. (5) showed that the maximum absorbance obtained at a molar ratio of 1:2 for the complex, **Job, (1928)**.

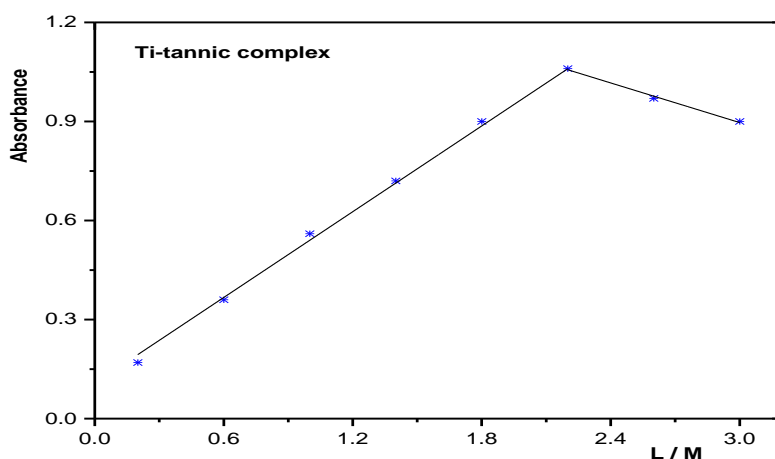


Fig. (4): Molar ratio method of Ti (IV)-Tannic complex

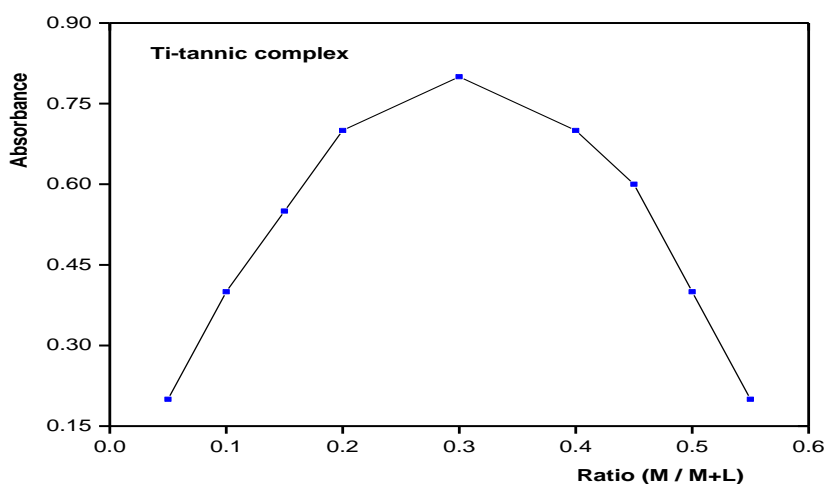
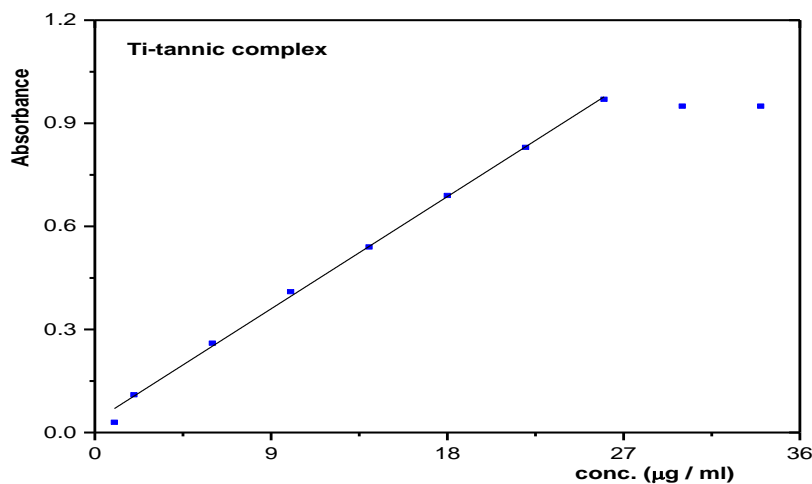


Fig. (5): Job's method of Continuous variation of Ti (IV)- Tannic complex

### 3.7 Calibration curve:

Several complexes are prepared where the concentration of the ligand is kept constant at  $1 \times 10^{-2}$  M while the concentration of the metal ion is varied from  $1 \times 10^{-6}$  to  $1 \times 10^{-3}$  M and their absorbance values are measured versus the concentration of titanium (IV) at 436 nm in presence of Triton X-100 and other optimum conditions. Beer's law is obeyed from 2 to  $26 \mu\text{g ml}^{-1}$  as shown in Fig. (6).

Fig. (6): Calibration curve ( $2\text{-}26 \mu\text{g ml}^{-1}$ ) of Ti (IV)-Tannic complex.

### 3.8 Effect of foreign ions (Interferences):

The effect of 50 fold molar excess of many species of different cations and anions added relative to ( $17 \mu\text{g ml}^{-1}$ ) of Ti (IV) showed that  $\text{Se}^{4+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Te}^{4+}$ ,  $\text{Cr}^{3+}$ ,  $\text{W}^{6+}$ ,  $\text{As}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Ce}^{3+}$ ,  $\text{La}^{3+}$  and  $\text{U}^{6+}$  do not interfere, while  $\text{Fe}^{3+}$ ,  $\text{V}^{5+}$ ,  $\text{Mo}^{6+}$  and  $\text{Hg}^{2+}$  do.

### 3.9 Statistical treatment of [Ti (IV)-Tannic acid] complex data:

The molar absorptivity, detection limit, quantification limit, standard deviation etc., are shown in the Table-1. The value of molar absorptivity and low values of relative standard deviation and standard error of the mean indicated that the method is highly sensitive with high precision and good accuracy.

Table-1: Statistical analysis of [Ti (IV)-Tannic acid] complex data.

| Parameter   | Direct method (436 nm) |
|---|------------------------|
| Molar absorptivity $\text{L mol}^{-1} \text{cm}^{-1}$ | $3.66 \times 10^4$     |
| Standard deviation (SD)                               | 0.01825                |
| Relative standard deviation (RSD %)                   | 0.1300                 |
| Standard error of the mean (SEM)                      | 0.00689                |
| Student t-test  | 4.3491                 |
| Slope   | 0.03571                |
| Limit of detection ( $\mu\text{g/ml}$ )               | 1.6595                 |
| Limit of quantification ( $\mu\text{g/ml}$ )          | 5.0289                 |

### 3.10 Applications:

The present method is applied for the determination of titanium (IV) in steel, white paint and a cosmetic cream (Sun screen, Spectra BAN 55, Stiefel Mexicana, S.A. de C.V. Company) samples as the above. The results are given in Tables-2, 3 and 4.

Table-2: determination of Ti (IV) in steel

| No. | Procedure   | Ti (IV)   |           |              |
|-----|-------------|-----------|-----------|--------------|
|     |             | Taken (%) | Found (%) | Recovery (%) |
| a   | Proposed    | 5         | 4.97      | 99.40        |
| b   | Recommended | 5         | 4.99      | 99.80        |

Table-3: determination of Ti (IV) in paint (10%).

| No. | Procedure   | Ti (IV)   |           |              |
|-----|-------------|-----------|-----------|--------------|
|     |             | Taken (%) | Found (%) | Recovery (%) |
| a   | Proposed    | 10        | 9.91      | 99.10        |
| b   | Recommended | 10        | 9.98      | 99.80        |

Table-4: determination of Ti (IV) in a cosmetic cream (Sun screen, 1.5 %  $\text{TiO}_2$ )

| No. | Procedure   | Ti (IV)   |           |              |
|-----|-------------|-----------|-----------|--------------|
|     |             | Taken (%) | Found (%) | Recovery (%) |
| a   | Proposed    | 0.898     | 0.886     | 98.66        |
| b   | Recommended | 0.898     | 0.890     | 99.10        |

Where, a: Proposed method for Ti (IV) with tannic acid.

b: Recommended method following to Lassner, et al. (1961).

#### 4. CONCLUSION

This article suggested a new simple spectrophotometric method for the determination of titanium (IV) with tannic acid as a chromogenic reagent using citrate buffer at pH=6. The presence of Triton X-100, which is a non ionic surfactant improve the method by increasing the value of absorbance for the formed complex. The proposed method has advantages in terms of save time, no need to heat or using any organic solvent, sensitivity, selectivity, accuracy, precision and simplicity. In the determination of titanium (IV) by this method, validity of Beer's law is achieved in a low range of Ti (IV) concentration 2–26  $\mu\text{g ml}^{-1}$  which is sensitive for trace amount of analysis and with an effective molar absorption coefficient (at 436 nm) of  $3.66 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ . The method is free from interfering with most elements. This method finds a successful application for the determination of titanium (IV) in steel, white paint and cosmetic cream samples.

#### 5. REFERENCES

- Aquilina, G., Bampidis, V., Bastos, M. D. L. and Costa, L.G. (2014)** Tannic acid for all animal species, *EFSA J.*, 12, 1-18.
- Bagur, G., Sanchez-Vinas, M. and Gazquez, D. (1997)** Determination of Titanium (IV) as an Additive in Organic Matrices by Reversed-Phase High-Performance Liquid Chromatography with 5, 5' Methylenebis(salicylohydroxamic Acid), *J. Chromatogr. Sci.*, 35, 131-134.
- Britton, H. T. S. (1952)** "Hydrogen ions", 4 th edition, Chapman and Hall, 28, 359- 364.
- De Andrade J. B., Nunes, G. S., Veiga, M. P., Costa, A. C., Ferreira, S.L., Amorim, A. M. and Reis, S. T. (1997)** Spectrophotometric and inductively coupled plasma atomic emission spectrometric determination of titanium in ilmenites after rapid dissolution with phosphoric acid, *Talanta*, 44, 165-168.
- Devireddy, M., Saritha, B., Giri, A. and Reddy, T. S. (2014)** Direct spectrophotometric determination of titanium(IV) with 5-bromo-2-hydroxy-3-methoxybenzaldehyde-p-hydroxybenzoic hydrazine, *J. Chem. Pharm. Res.*, 6, 1145-1150.
- Hoshino, M., Kamino, S., Mitani, S., Asano, M., Yamaguchi, T. and Fujita, Y. (2011)** Spectrophotometric determination of titanium with o-carboxyphenylfluorone in cationic micellar media, and its equilibrium and kinetic studies, *Talanta*, 85, 2339-2343.
- Hu, M. and Coetzee, p. p. (2007)** Vanadium speciation by chromatographic separation of V(IV) and V(V) in acidic solution followed by ICP-OES determination, *Water SA*, 33, 291-296.
- Iffat, A. T., Maqsood, Z. T. and Fatima, N. (2005)** Study of complex formation of Fe (III) with tannic acid, *J. Chem. Soc. Pak.*, 27, 174-177.
- Job, P. (1928)** Formation and stability of inorganic complexes in solution, *Anal. Chim.*, Paris, 9, 113-119.
- Lassner, E., Puschel, R. and Scharf, R. (1961)** Analytical Applications of EDTA and Related Compounds, *Z. Anal. Chem.*, 179, 345.



- Lurie, Ju. (1978)** Handbook of Analytical Chemistry, 2<sup>nd</sup> edition, Mir publishers, Moscow.
- Pooja, J. V. (2012)** The spectrophotometric determination of metavanadates ( $\text{VO}_3^-$ ) using tannic acid as a reagent, Asian J. Res. Chem., 5, 1123-1128.
- Pribil R. (1982)** Applied Compleximetry, 5<sup>th</sup> edition, Pergamon Press Ltd., England, 73-74.
- Reddy, B. V. N., Basha, V.S. and Reddy, T. S. (2015)** Rapid, selective direct and derivative spectrophotometric determination of titanium with 2',4-Dihydroxyacetophenone isonicotinoylhydrazone, Int. J. Anal. Bioanal. Chem., 5, 28-33.
- Shigematsu, T., Matsui, M. and Uesugi (1972)** Spectrophotometric determination of Palladium with Eriochrome Cyanine R, Bull. Inst. Chem. Res., 50, 634-644.
- Srilalitha, V., Prasad, A. R. G., Kumar, K. R., Seshagiri, V. and Ravindranath, L. R. (2010)** A new spectrophotometric method for the determination of trace amounts of titanium (IV), Phys. Chem. Technol., 8, 15 – 24.
- Stadiober, M., Kalcher, K., Raber, G. and Neuhold, C. (1996)** Anodic stripping voltammetric determination of titanium(IV) using a carbon paste electrode modified with cetyltrimethylammonium bromide, Talanta, 43, 1915-1924.
- Tarafder, P. K. and Thakur, R. (2008)** Micelle mediated extraction of titanium and its ultra-trace determination in silicate rocks, Talanta, 75, 326–331.
- Varghese, A., Khadar, A. M. A. and Kalluraya, B. (2006)** Simultaneous determination of titanium and molybdenum in steel samples using derivative spectrophotometry in neutral micellar medium, Spectrochim. Acta, Part A, 64, 383–390.
- Vogel, A. I. (2002)** Text book of Quantitative Inorganic analysis, 6<sup>th</sup> edition, Pearson Education, Singapore.
- Yoe J. H. and Jones A. L. (1944)** Colorimetric determination of Fe with disodium 1, 2-dihydroxybenzene-3, 5-disulfonate, Indust. Eng. Chem. Analyst. Ed., 16, 111-118.



## طريقة طيفية لتقدير التيتانيوم الرباعي في الصلب والطلاء ومستحضرات التجميل باستخدام حمض التانيك في أوساط نشطة سطحيا

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استخدمت طريقة طيفية بسيطة ودقيقة لتقدير كميات ضئيلة من عنصر التيتانيوم الرباعي باستخدام مركب من مشتقات البولي فينول وهو حمض التانيك (tannic acid) وذلك في وجود Triton X-100 كمادة نشطة سطحيا. لقد تم التفاعل بين التيتانيوم الرباعي وحمض التانيك في وسط ضعيف الحامضية عند أس هيدروجيني ٦ و باستخدام السترات كمحلول منظم للأس الهيدروجيني (citrate buffer) حيث تم تكوين مترابك بنسبة ١:٢ عند طول موجي ٤٣٦ . ولقد أثبتت النتائج سرعة تكوين المترابك وثباته لفترة زمنية طويلة، وبتطبيق قانون بيير للامتصاص وجد أنه يطبق في مدى تراوح من ٢ الي ٢٦ ميكروجرام / مللي للتيتانيوم وكانت قيمة معامل الامتصاص الجزئي (ε) لهذا المترابك هي  $3,66 \times 10^4$  لتر / مول . سم. وأخيرا قد تم تطبيق الطريقة المقترحة بنجاح لتعيين عنصر التيتانيوم في الحديد الصلب والدهان الأبيض ومستحضر تجميلي للحماية من أشعة الشمس.