

Determination of Titanium (IV) in Tap water and Ore Samples with Kinetic - Spectrophotometric Method

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Abstract

A simple, selective and sensitive method for the determination of trace amount of titanium (IV) based on its catalytic effect on methylene blue- ascorbic acid redox reaction has been reported. The reaction was followed spectrophotometrically by measuring the change in absorbance of methylene blue at 665 nm, 5 minutes after the initiation of the reaction. In this study experimental parameters were optimized and the effect of other cations and anions on the determination of titanium (IV) was examined. The calibration graph was linear in the range of 3–25 ng ml⁻¹ of titanium (IV). The relative standard deviation for the determination of 10 and 20 ng ml⁻¹ of titanium (IV) were 2.64% and 1.51% respectively (n=8). The detection limit calculated from three times of standard deviation of blank 3S_b was 0.6 ng ml⁻¹. The method was successfully applied to the determination of titanium (IV) in tap water and ore samples.

Keywords: Titanium (IV), catalytic, Spectrophotometric, Methylene blue

1. Introduction

Titanium is often used in the chemical processing industry because of its resistance to corrosion. This resistance is probably due to a thin coating of titanium dioxide, which protects the metal from further corrosion. The metal has unusually good resistance to corrosion by salt water, and so it is used in propeller shafts and other parts exposed to the sea. The high cost of titanium metal often limits its use to military purposes. Because of its lightness and strength, titanium is used as a structural material in racing bicycles, high-speed aircrafts, rockets, guided missiles, and recoil mechanisms for artillery.

Titanium is added to other metals, such as copper, steel, and aluminum, to affect certain properties. For example, in the manufacture of stainless steel, metallic titanium is used to stabilize the carbon and nitrogen content. Ferrotitanium is added to steel as a deoxidizer. Pure titanium is easily fabricated, but it becomes brittle when contaminated with other elements, such as carbon and nitrogen. The paint, pigment, paper and pulp

industries discharge a very high amount of titanium. The flame spectrometric determination of titanium is limited because of its high oxide dissociation energy and even under careful conditions in a nitrous oxide-acetylene flame the detection limit is high, about 0.1 μg per milliliter.¹

In the flame emission spectrophotometry several elements interfere in the determination of titanium.² The 8-hydroxyquinoline is reported for extraction and flame emission spectrometric determination of titanium.³ Most of the reagents used for extraction, separation and determination of titanium (IV) show serious interference.⁴

The combination of liquid-liquid extraction and ICP-AES is a rather effective and versatile hybrid technique for trace analysis. The analysis of titanium at nM level in various samples has been achieved by adsorptive stripping voltammetric (ADSV) methods which are based on the formation and interfacial accumulation of the surface-active complexes onto a hanging drop electrode (HMDE) or a mercury film electrode.⁵

Only few kinetic methods have been reported for the determination of titanium.^{6,7} Lazaro and co-workers in 1985 reported a catalytic fluorimetric method for the determination of titanium (IV) by flow injection.⁸ In 1992 Wang et al reported a stopped flow kinetic spectrophotometric method for the simultaneous determination of iron, titanium and vanadium. The proposed method is based on their effects on the chromium (VI)-iodide-starch reaction in weakly acidic medium. The reaction was monitored with stopped flow spectrophotometric technique. The method was applied to the determination of titanium in an aluminum alloy and synthetic sample.⁹

Kinetic methods can be implemented on very simple, inexpensive equipment and provide low level determination comparable to those typically offered by much more expensive techniques such as inductively coupled plasma, atomic emission spectrometry (ICP-AES)¹⁰ or electrothermal atomic absorption spectrometry (ETAAS).^{11,12} In this paper we described a simple, sensitive, and highly selective catalytic method for the determination of titanium (IV) based on its catalytic effect on the redox reaction of methylene blue- ascorbic acid.

2. Experimental

2.1 Reagents

All reagents were analytical-reagent grade and double distilled water was used throughout. Formic acid, tri-sodium citrate 5.5-hydrate, sodium hydroxide, potassium dihydrogen phosphate, and di-potassium hydrogen phosphate, titanium dioxide and sodium acetate were purchased from Merck and used without further purification. Methylene blue (Merck) and ascorbic acid (Fluka) and sulfuric acid (Merck) were used without further purification.

Stock solution of titanium (IV) was prepared by weighing 0.8340 g of pure TiO_2 and dissolving in 150 ml of hot H_2SO_4 (1+2). This solution was then diluted to 500 in a volumetric flask. Further dilutions were made using this stock solution when needed. Ascorbic acid 0.02 mol l^{-1} solution was prepared by dissolving 0.880 g of ascorbic acid in water and diluting to 250 ml with water. This solution was prepared daily. Methylene blue solution (1.011×10^{-4} mol l^{-1}) was prepared by dissolving 0.0360 g of methylene blue in water and diluting to 1000 ml. Stock 1000 $\mu\text{g ml}^{-1}$ interfering ion solutions were prepared by dissolving the appropriate amounts of their suitable salts in water.

2.2 Apparatus

A UV-visible spectrophotometer (JASCO 7850) was used for recording the spectra and a Perkin-Elmer UV-VIS spectrophotometer model 550S was used for absorbance

measurements. A Colora C-1668 thermostat in which temperature could be fixed within $\pm 0.10^\circ \text{C}$ was used for maintaining the temperature.

2.3 Recommended procedure

The catalytic reaction was monitored spectrophotometrically by measuring the change in absorbance of the reaction at 665nm. In a 10 ml volumetric flask were added 2 ml of methylene blue ($1.011 \times 10^{-4} \text{ mol l}^{-1}$), 1 ml of acetate buffer solution pH 4, 1 ml of standard titanium (IV) solution so that its final concentration would be in the range 3-25 ng ml^{-1} in the final solution and enough water to bring the solution to about 9 ml. Then 1 ml of ascorbic acid 0.02 mol l^{-1} was added and diluted to the mark with water. The absorbance was measured at 665 nm after a fixed time (5min). The time was measured immediately after the addition of last drop of ascorbic acid solution. A blank solution was also prepared in the some way using water instead of titanium (IV).

3. Results and Discussion

3.1 Absorption spectra of methylene blue

Methylene blue is a dye (C.I No. 52015) and its absorption spectra in acidic medium shows that the maximum absorbance occurs at 665 nm. Methylene blue that could be reduced by ascorbic acid to a colorless product. The reaction between Methylene blue and ascorbic acid is very slow but when traces of titanium (IV) are present, the rate of reaction is increased. In this study the change in absorbance of the reaction was monitored with a fixed time of 5 minute, because highest ΔA was obtained.

3.2 Effect of variables

The effect of pH on the reaction rate in the presence of 10 ng ml^{-1} of titanium (IV) was studied. Results are shown in Fig. 1. As it is seen from the figure 1 the change in absorbance was increased with increasing pH from 1 to 4, whereas it was decreased at pH values greater than. Therefore acetate buffer with pH = 4 was used as optimum pH because higher sensitivity was achieved for determination of titanium (IV).

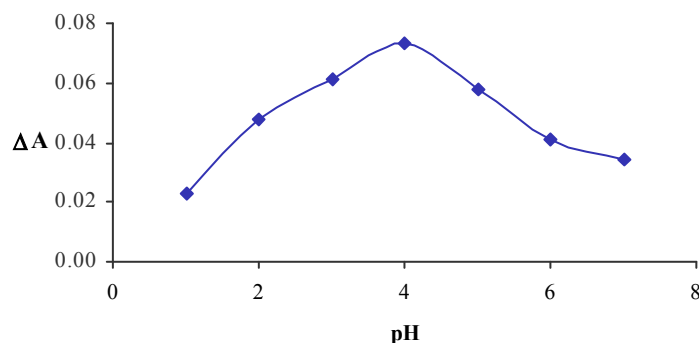


Figure 1. The effect of pH on the ΔA , Conditions: 10 ng ml^{-1} of titanium (IV); $1.01 \times 10^{-5} \text{ mol l}^{-1}$ of methylene blue; $1 \times 10^{-3} \text{ mol l}^{-1}$ of ascorbic acid; time interval, 5min.

The effect of methylene blue concentration on the reaction rate is shown in Fig. 2. When methylene blue concentration increasing from $5.05 \times 10^{-6} \text{ mol l}^{-1}$ to $3.03 \times 10^{-5} \text{ mol l}^{-1}$ the change of absorbance (ΔA) was increased. The concentration of 2.02×10^{-5}

mol l⁻¹ of methylene blue in the final solution was selected. At higher concentration of methylene blue the absorbance of the solution became too high.

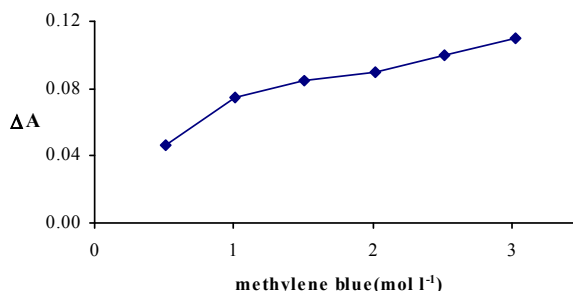


Figure 1. Effect of methylene blue concentration on the ΔA , Conditions: 10 ng ml⁻¹ of titanium (IV); 1 × 10⁻³ mol l⁻¹ of ascorbic acid; temperature 25°C; 1 ml of acetate buffer solution at pH=4; time interval, 5 min

The influence of ascorbic acid concentration on the reaction rate was also studied by adding different concentration of the ascorbic acid concentration and applying the recommended procedure. A concentration of 0.002 mol l⁻¹ of ascorbic acid in final solution gave highest ΔA and was selected for further work.

The influence of temperature was also studied in the range 15 –40°C and it was observed that the change in absorbance (A) was increased up to 30°C but decreased at higher temperature. In this study laboratory temperature (25± 0.1 °C) was used for further studies.

The effect of ionic strength on the reaction rate was investigated. The ionic strength was varied from 0.01 to 0.1 mol l⁻¹, using sodium nitrate solution. The results showed that this parameter had no effect on the reaction rate up to 5 × 10⁻² mol l⁻¹.

3.3 Interference study

To study the selectivity of the proposed method the effect of various cations and anions on the determination of 10 ng ml⁻¹ of titanium were examined. The results are presented in Table 1. The tolerance limit was defined as the concentration of added ion causing a relative error less than 4%. The results indicate that most of common anions and cations did not interfere in determination of titanium (IV).

Table 1. Effect of Foreign ions on the determination of 10 ng ml⁻¹ titanium (IV) under optimum conditions

Foreign ions	Tolerance ratio
K ⁺ , Ca ²⁺ , Na ⁺ , Cl ⁻ , Cd ²⁺ , IO ₃ ⁻ , NO ₃ ⁻ , PO ₄ ³⁻ , ClO ₄ ⁻ , NO ₃ ⁻	1000
Co ²⁺ , Mg ²⁺ , Li ⁺ , Sn ²⁺ , CH ₃ COO ⁻ , Pb ²⁺ , S ₂ O ₅ ²⁻ , Cu ²⁺ , SO ₄ ²⁻ , HCOO ⁻ , F ⁻ , PO ₄ ³⁻ , SO ₃ ²⁻ , Br ⁻ , Cu ²⁺ , Hg ²⁺	500
I ⁻ , Mn ²⁺ , Fe ²⁺ , Sr ²⁺ , Fe ³⁺ , Li ⁺ , SCN ⁻ , Cr ³⁺	150
Mo(VI), Ag ⁺ , I ⁻ , Mn ²⁺ , Al ³⁺ , Hg ²⁺ , W(VI), ClO ₃ ⁻ , C ₂ O ₄ ⁼	50

3.4 Calibration graph and precision

The calibration graph was obtained using the recommended procedure for different amounts of titanium (IV). Calibration graph was linear in the range of 3- 25 ng ml⁻¹ of titanium (IV). The data were analyzed by least square method and the best straight line was drawn. The equation of the line was $\Delta A = 0.006 + 0.011C$ where, ΔA and C are change in absorbance and concentration of titanium (IV) in ng ml⁻¹ respectively. The correlation coefficient is $r = 0.9993$. The relative standard deviation for the determination of 10 and 20 ng ml⁻¹ of titanium (IV) were 2.64% and 1.51% respectively (n=8). The detection limit calculated from three times of standard deviation of blank $3S_b$ was 0.6 ng ml⁻¹.

3.5 Application

A standard addition method was applied to titanium (IV) determination in real samples. The results of titanium (IV) determination in ores and tap water samples are compared with standard method¹⁵. Matrix interference was verified by comparison of the slopes of calibration graph with that using standard addition method. The results indicate that the proposed method is useful for determination of titanium (IV) in the presence of other ions (Table 2, 3).

3.6 Preparation of ore samples

0.5 g of locogranite (containing titanium) was powdered and dissolved in 20 ml of nitric acid and 10 ml hydrochloric acid by heating in a hot plate. Then 30 ml of H₂SO₄ 1:1 was added, the solution was cooled, filtered and its pH adjusted to 4-5 with sodium hydroxide solution. Then this solution was diluted to 250 ml with water in volumetric flask.

Table 2. Determination of titanium (IV) in ore samples

Sample No.	Standard method % found	Proposed catalytic % found*	Relative error %
1	0.320	0.330	3.12
2	0.354	0.368	3.95
3	0.421	0.445	5.70

* Mean of three determinations

Table 3. Determination of titanium (IV) in tap water

Sample No.	Titanium added ng ml ⁻¹	Titanium found* ng ml ⁻¹	Recovery %
1	10	10.4	104.0
2	15	16.0	106.6
3	20	21.5	107.5

* Mean of three determinations

4. Conclusions

The catalytic spectrophotometric method described in this work was convenient for the determination of trace amount of titanium (IV). In practically, the system showed high tolerance to interferences from matrix elements. The linear range is wider than

some of previously reported methods and has a lower detection limit¹¹. The proposed method is sensitive, simple, and selective and it can also be conveniently applied to the analysis of different samples.

5. Acknowledgments

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