

## Kinetic-Spectrophotometric Determination of Tungsten(VI) Based on Azure I-Ti(III) Reaction in the Presence of Thiocyanate as an Activator

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The catalytic effect of tungsten(VI) and activating effect of thiocyanate on the reduction reaction of Azure I by Ti(III) was used to develop a sensitive and rapid kinetic spectrophotometric method for the determination of tungsten(VI). The reaction was monitored spectrophotometrically by measuring the change in absorbance ( $\Delta A$ ) at 646 nm using a fixed time method (2.5 min). The effect of different variables on the reaction was investigated and optimized in order to achieve the highest sensitivity. The calibration graph was linear in the range 5-90 ng mL<sup>-1</sup> and the detection limit was 2.9 ng mL<sup>-1</sup>. The relative standard deviation for ten replicate measurements of 10 and 50 ng mL<sup>-1</sup> of tungsten was 4.7 and 3.5, respectively. The method was successfully applied to the determination of tungsten in spring water samples.

**Key Words:** Tungsten(VI), Azure I, Kinetic-Spectrophotometric, Thiocyanate, Ti(III).

### INTRODUCTION

Tungsten usually exists as WO<sub>4</sub><sup>2-</sup> in environmental water and soil samples and due to its biological and toxic effects monitoring of tungsten concentration in environmental samples is of great importance. Various methods such as spectrophotometric<sup>1-3</sup>, flame atomic absorption (AAS)<sup>4</sup>, inductively coupled plasma atomic emission (ICP-AES)<sup>5</sup>, inductively coupled plasma mass spectrometry (ICP-MS)<sup>6</sup>, neutron activation analysis (NAA)<sup>7</sup>, X-ray fluorescence (XRF)<sup>8</sup> and kinetic-spectrophotometric<sup>9-12</sup> have been used for the determination of tungsten. The sensitivity of tungsten determination by AAS is poor even when nitrous oxide acetylene flame is used. Separation and pre-concentration procedures are often required prior to trace determination by AAS. Although NAA and ICP-MS are more sensitive they have the disadvantage of high cost of instrument. The kinetic-spectrophotometric methods offer sensitivity and simplicity compared to other techniques.

In this work, a sensitive and simple kinetic-spectrophotometric method for the determination of tungsten based on the reduction reaction of Azure I by Ti(III) is described.

## EXPERIMENTAL

Absorption spectra were recorded on a Jasco model 7850 UV-Visible spectrophotometer and the absorbance measurements were made using a Perkin Elmer 550S spectrophotometer with 1cm glass cell. A Colora C-1668 thermostat in which temperature could be fixed within  $\pm 0.10^\circ\text{C}$  was used for maintaining the temperature.

Double distilled water and analytical grade chemicals were used throughout. A stock solution of tungsten ( $1000 \text{ mg mL}^{-1}$ ) was prepared by dissolving 0.1794 g of  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  in water and diluting to 100 mL in a volumetric flask. More dilute solutions were prepared from this stock solution whenever needed. A  $2.24 \times 10^{-4} \text{ mol L}^{-1}$  solution of Azure I was prepared by dissolving 0.04 g of the solid in water and diluting to 500 mL in a volumetric flask. More dilute solutions of Azure I, were prepared from this solution. A Ti(III) solution ( $4.4 \times 10^{-3} \text{ mol L}^{-1}$ ) was prepared by dissolving 0.0105 g of titanium powder (Merck) in hydrochloric acid and diluting to 50 mL with water. A few zinc granules were added to this solution in order to prevent oxidation of titanium(III). A hydrochloric acid ( $1 \text{ mol L}^{-1}$ ) was prepared by diluting 16.6 mL of concentrated acid (Merck) to 200 mL with water.  $0.1 \text{ mol L}^{-1}$  of potassium thiocyanate solution was prepared by dissolving 2.4295 g of KSCN (Merck) in water and diluting to 250 in a volumetric flask.

**Recommended procedure:** 3 mL of Azure I ( $5.6 \times 10^{-5} \text{ mol L}^{-1}$ ), 2.5 mL potassium thiocyanate ( $1 \times 10^{-3} \text{ mol L}^{-1}$ ), 1 mL of HCl solution ( $1 \text{ mol L}^{-1}$ ) and appropriate amounts of tungsten stock solution were added to a 20 mL volumetric flask and made up to the mark with water. Then 0.2 mL of titanium solution ( $4.4 \times 10^{-3} \text{ mol L}^{-1}$ ) was added, diluted exactly to the mark and mixed. The absorbance was measured at 646 nm after a fixed time (2.5 min). The time was measured immediately after the addition of the last drop of titanium solution. A blank solution was also prepared in the same way using distilled water instead of tungsten solution.

## RESULTS AND DISCUSSION

The dye, Azure I reacts with Ti(III) solution in acidic media slowly. The rate of this reaction is increased when a trace amount of tungsten is present. The reaction will proceed much faster in the presence of thiocyanate as an activator. The catalytic effect of tungsten and activating effect of thiocyanate was used to develop a kinetic method for sensitive determination of tungsten. Thus change in absorbance ( $\Delta A$ ) of Azure I with time at

646 nm was taken as an indication of the amount of tungsten present in the sample using a fixed time method (2.5 min).

### Effect of variables

In order to achieve highest sensitivity, the effect of different variables on the reaction was investigated and optimum conditions were established.

As the reaction proceeds in acid media, hydrochloric was chosen to perform the reaction. The effect of hydrochloric acid concentration on the reaction is shown in Fig. 1. Highest change in absorbance ( $\Delta A$ ) was obtained when HCl concentration was  $0.05 \text{ mol L}^{-1}$  in the final solution, therefore it was chosen as the optimum and 1 mL of HCl solution ( $1 \text{ mol L}^{-1}$ ) was added to the solutions to achieve this acidity.

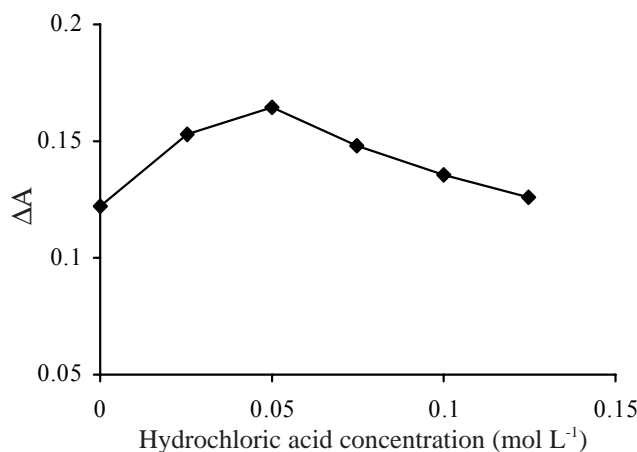


Fig. 1. Effect of HCl concentration on change in absorbance ( $\Delta A$ )

As thiocyanate showed an activating effect on the reaction, the influence of its concentration on the catalyzed reaction was studied. The results shown in Fig. 2 indicate that  $\Delta A$  is increased by increasing thiocyanate concentration up to  $1.25 \times 10^{-4} \text{ mol L}^{-1}$  and is constant above this. Therefore all the measurements were made using thiocyanate concentration of  $1.25 \times 10^{-4} \text{ mol L}^{-1}$ .

The influence of Azure I concentration on the change in absorbance was studied. The highest  $\Delta A$  is obtained when Azure I concentration is  $8.4 \times 10^{-6} \text{ mol L}^{-1}$  in the final solution. As a result  $8.4 \times 10^{-6} \text{ mol L}^{-1}$  was selected as optimum concentration and 3 mL of Azure I solution ( $5.6 \times 10^{-5} \text{ mol L}^{-1}$ ) was added to achieve this concentration.

Increasing Ti(III) concentration increased the reaction rate (Fig. 3). However the rate of both catalyzed and uncatalyzed reactions is increased

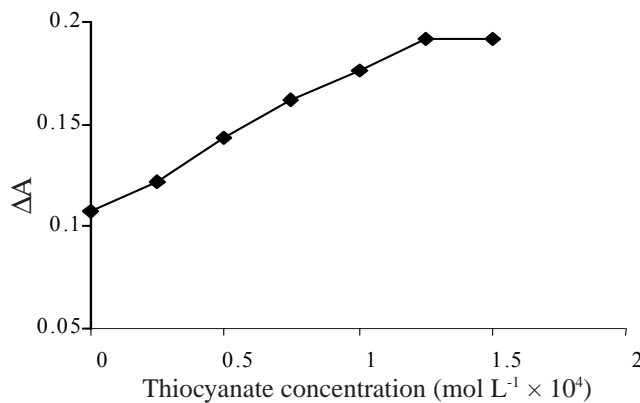


Fig. 2. Effect of thiocyanate concentration on the reaction

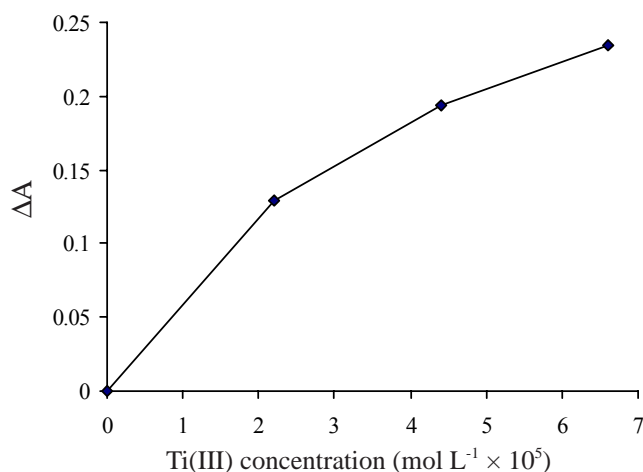


Fig. 3. Effect of Ti(III) concentration on the rate of reaction

faster at high concentrations of Ti(III). Since it was also difficult to read absorbances at 2.5 min time using high concentrations of Ti(III), therefore a concentration of  $6.6 \times 10^{-5} \text{ mol L}^{-1}$  in the final solution was chosen for convenience.

The effect of temperature was also studied in the range 18-45°C under the conditions given in the recommended procedure. It was observed that the change in absorbance was increased at higher temperatures up to 30°C and above that decreased again. Although the rate of both catalyzed and uncatalyzed reaction was increased at higher temperatures, the rate of catalyzed reaction became considerably lower at higher temperatures and therefore  $\Delta A$  was decreased. This is because most of the reaction occurs at

the first minute of the reaction at high temperatures. Therefore a temperature of 25°C was selected as the working temperature.

**Analytical figures of merit:** The calibration graph of change in absorbance ( $\Delta A$ ) vs. tungsten concentration was linear in the range of 5-90 ng mL<sup>-1</sup> of tungsten by applying the fixed time method (2.5 min) under the recommended procedure. The equation of the line was  $\Delta A = 5.45 \times 10^{-3} + 3.22 \times 10^{-3} C_M$  where  $C_M$  is tungsten concentration in ng mL<sup>-1</sup> and the correlation coefficient was 0.9996. The detection limit based on 3S<sub>b</sub> criterion was 2.9 ng mL<sup>-1</sup> and the relative standard deviation (RSD) for ten replicate measurements of 10 and 50 ng mL<sup>-1</sup> of tungsten was 4.7 and 3.5, respectively.

**Interference studies:** In order to assess the selectivity of the method, the interference effects of various cations and anions on the determination of 50 ng mL<sup>-1</sup> of tungsten was examined. The tolerance ratio of each foreign ion was taken as the largest amount yielding an error of less than 5 % in the absorbance. The results are presented in Table-1.

TABLE-1  
EFFECT OF INTERFERING IONS ON THE DETERMINATION  
OF 50 ng mL<sup>-1</sup> OF TUNGSTEN

Interfering ion	Tolerance ratio
Na <sup>+</sup> , NH <sub>4</sub> <sup>+</sup> , Zn <sup>2+</sup> , Ba <sup>2+</sup> , Ni <sup>2+</sup> , Pb <sup>2+</sup> , Al <sup>3+</sup> , H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	1000
Hg <sup>2+</sup> , Mg <sup>2+</sup> , NO <sub>3</sub> <sup>-</sup> ,	750
Ca <sup>2+</sup> , Cd <sup>2+</sup> ,	100
I <sup>-</sup> , Br <sup>-</sup> , Mn <sup>2+</sup>	50
Sr <sup>2+</sup> , NO <sub>2</sub> <sup>-</sup> , SO <sub>3</sub> <sup>2-</sup> , F <sup>-</sup>	10
Fe <sup>2+</sup> , Fe <sup>3+</sup>	5
Mo (VI), IO <sub>3</sub> <sup>-</sup> , Cu <sup>2+</sup>	1

**Application:** In order to check the applicability of the method, it was applied to the determination of tungsten in spring water. The results in Table-2 show that good recoveries are obtained using standard addition method.

TABLE-2  
DETERMINATION OF TUNGSTEN IN SPRING WATER

Volume of the sample (mL)	Tungsten added (ng mL <sup>-1</sup> )	Tungsten found (ng mL <sup>-1</sup> )	Tungsten in spring water (ng mL <sup>-1</sup> )	Recovery (%)
2.5	–	9.57	76.56	
2.5	15	25.35		103.1
5.0	–	19.82	79.28	
5.0	25	46.93		102.4

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