

DETERMINATION OF MOLYBDENUM (VI) BY ITS CATALYTIC EFFECT ON THE OXIDATION OF CHROMOTROPIC ACID BY HYDROGEN PERXIDE

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Abstract

A catalytic Spectrophotometric method is described for the determination of traces of molybdenum (VI) based on its catalytic effect on the oxidation of chromotropic acid by hydrogen peroxide. The reaction was followed Spectrophotometrically measuring the rate of change in absorbance at pH 10.6. Using optimum conditions the proposed method allows the determination of molybdenum (VI) in the range concentration 0.2 to 1 ppm. The coefficient of variation is 2.1%. The effect of different ions on the determination of molybdenum (VI) was studied.

Introduction

Molybdenum is an essential element to plants [1] [2] with action related to important biochemical functions, such as in nitrate reduction and the fixation of molecular nitrogen by micro organisms and bacteria [3]. It is present in low amounts in plants, fertilizers, vitamin and tap waters (4).

A number of sensitive analytical methods have been developed for determination of molybdenum (VI) at trace levels, some of these are based on differential pulse polarography [4] atomic absorption Spectrometry [5], spectrophotometry and titrimetry [6].

The kinetic methods are found to compete with above technique and are interesting as they involve less expensive equipment and have good sensitivity using appropriate conditions. Ensafi *et al.*, [7] have reported catalytic spectrophotometric method for the determination of traces of molybdenum (VI), using a mixture of hydrazine hydrochloride and Nile blue. The decrease in absorbance at 595 nm was measured three minutes after initiation of the reaction. The calibration graph was linear from 0.04 to 3mg/ml of Mo (VI) The method was applied in the analysis of steel alloys.

This paper reports the investigation of the use of chromotropic acid in kinetic determination of molybdenum (VI).

Experimental

Solutions

Chromotropic acid $1 \times 10^{-3} \text{M}$.

Stock solution of $1 \times 10^{-3} \text{M}$ was prepared by dissolving the required amount (0.04g) of chromotropic acid (E. Merck) in Water.

Hydrogen peroxide $1 \times 10^{-1} \text{M}$.

Working solution of the required concentration were prepared daily from the stock solution which was prepared from (30% W/V) Hydrogen peroxide (E. Merck).

Molybdenum (VI) solution. 1000 ppm.

Stock solution was prepared by dissolving the required amount of Ammonium molybdate (1.287 g/100 ml) (Fluka) in water.

Buffer Solution.

Buffer solution was prepared by dissolving required amount (0.71 g) of Potassium hydrogen phosphate and Sodium hydroxide (0.4 g) and ionic strength was adjusted with potassium chloride to 0.1M.

Instruments

Perkin Elmer Lambda model 3BI spectrophotometer was used for measuring changes in absorbance.

Procedure

A volume of 0.5 ml of ($1 \times 10^{-3} \text{M}$) chromotropic acid and Ammonium molybdate (0.5-2.5ml) of 10 ppm solution were transferred to 25 ml of volumetric flask. In a separate flask 5 ml of buffer solution (pH 10.6) and hydrogen peroxide 2.5 ml of $1 \times 10^{-1} \text{M}$ hydrogen peroxide were mixed together. The reagents were mixed and at the same time a stop watch was started. The total volume was kept at 25 ml. The mixture was transferred to a cell of 10 mm light path. Absorbance of mixture was recorded at 360 nm against water, 15 minutes after initiation of the reaction.

Results and discussion:

The catalytic spectrophotometric study of the catalysed oxidation of chromotropic acid with hydrogen peroxide in presence of molybdenum (VI) was made in alkaline solution in the pH range 8-11.5. It was observed that catalytic oxidation occurred in alkaline solution. The spectra of chromotropic acid and hydrogen peroxide and molybdenum showed maximum absorption at 360 nm.

This wave length was selected for determination of molybdenum (VI). In order to choose the optimum conditions for the reaction, effect of different variables on the rate of reaction was studied.

1. Effect of Concentration of Chromotropic acid.

The effect of chromotropic acid concentration on the rate of reaction was studied in the range 2×10^{-5} to 10×10^{-5} M. A plot of $-\log A$ versus concentration of Mo (VI) was plotted for each concentration of the dye. The relationship was found to be linear and slope in each case was identical. The rate reaction shows a first order dependence with Chromotropic acid (fig. 2). The reagent concentration of 4×10^{-5} M was selected for further studies.

2. Effect of Hydrogen Peroxide.

The dependence of reaction rate on the hydrogen peroxide is shown in fig. 3. The rate of reaction increases with increase of hydrogen peroxide concentration. For the present method a concentration of 1×10^{-2} M was selected keeping in view reaction time of 15 minutes.

3. Effect of temperature.

The influence of temperature on the rate of reaction was studied in the range of 25 to 50°C. Rate of reaction is temperature dependent and increases with rise in temperature (fig. 4). The reaction were however carried out at room temperature (25°C), because of ease of operational conditions.

4. Effect of pH.

The effect of pH on the catalytic reaction was studied within pH range of 8-11.5. The change in absorbance with respect to the water was noted, using fixed time measurement. It was observed that the maximum change in absorbance in catalysed reaction occurred at pH 10.6.

The following optimum conditions were selected.

Chromotropic acid 2×10^{-5} M, Hydrogen peroxide 1×10^{-2} M, temperature 25°C and pH 10.5. The change in absorbance versus the concentration of molybdenum (VI) was examined. A linear calibration graph was obtained by plotting $-\log A$ versus molybdenum (VI) concentration (in the range of 0.2-1 ppm) (fig. 5).

The validity of the calibration curve was checked by analysing test solutions. The relative % error for the analysis of molybdenum (VI) solutions were found within $\pm 6-10\%$. The standard deviation and coefficient of variation for the replicate analysis of 1 ppm. Molybdenum (VI) were found to be 0.0035 and 2.1% respectively ($n=10$).

Finally the effect of foreign ions on the catalytic determination of molybdenum (VI) (1ppm) was determined.

It was observed that V, Fe, Ni, Hg, NO_3 , SO_4 , Mg, Ca, Na, Cl did not interfere.

Chromium (III), Cadmium (II) could be tolerated up to ten times the concentration of molybdenum (VI).

Chromium (VI), Copper (II), Cobalt (II) enhances the rate of catalytic oxidation of chromotropic acid with molybdenum (VI).

Conclusion.

The catalytic method for the determination of molybdenum (VI) in the range of 0.2-1ppm has been developed. The reaction is carried out in alkaline solution (pH 10.6). The relative % error observed is within 6-10% cobalt (II), chromium (VI), copper (II) show interference.

References .

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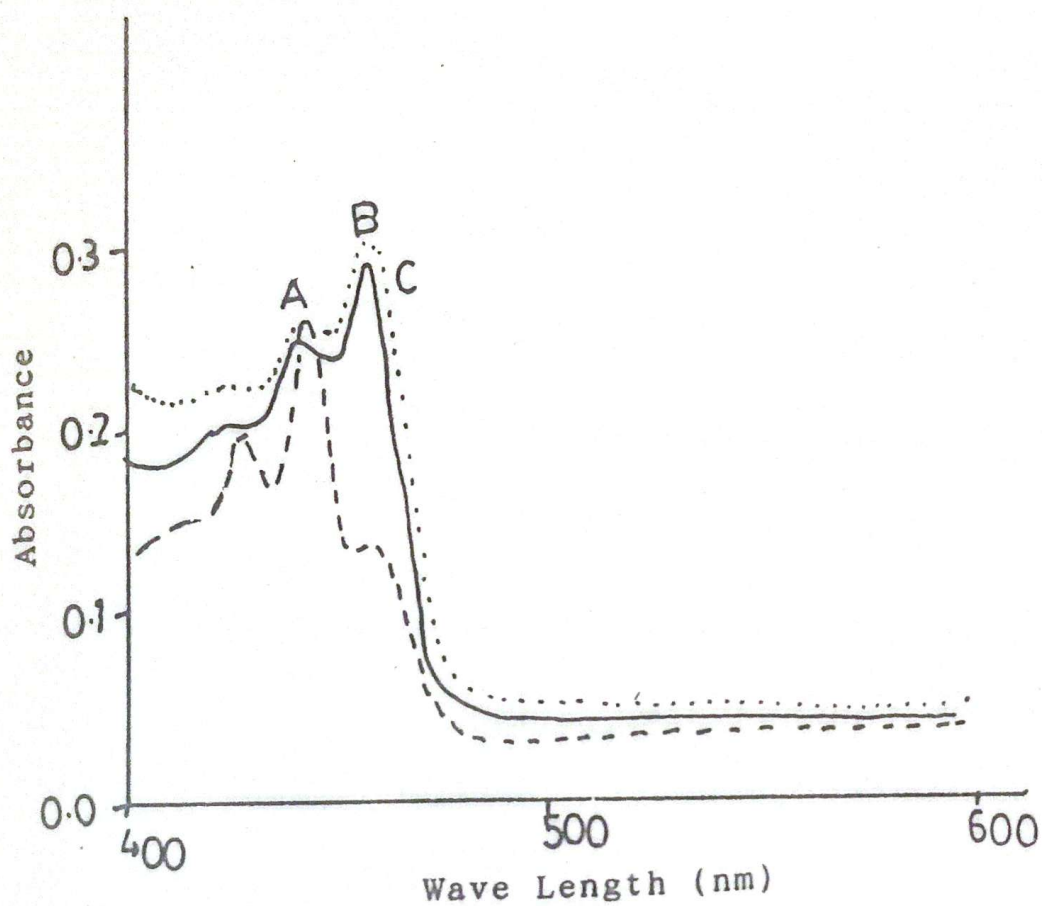


Fig. (1)

Absorbance Spectra of (A) Chromotropic acid (B) Chromotropic acid-Buffer-Hydrogen peroxide (C) Chromotropic acid-Buffer-Hydrogen peroxide-Molybdenum (VI).

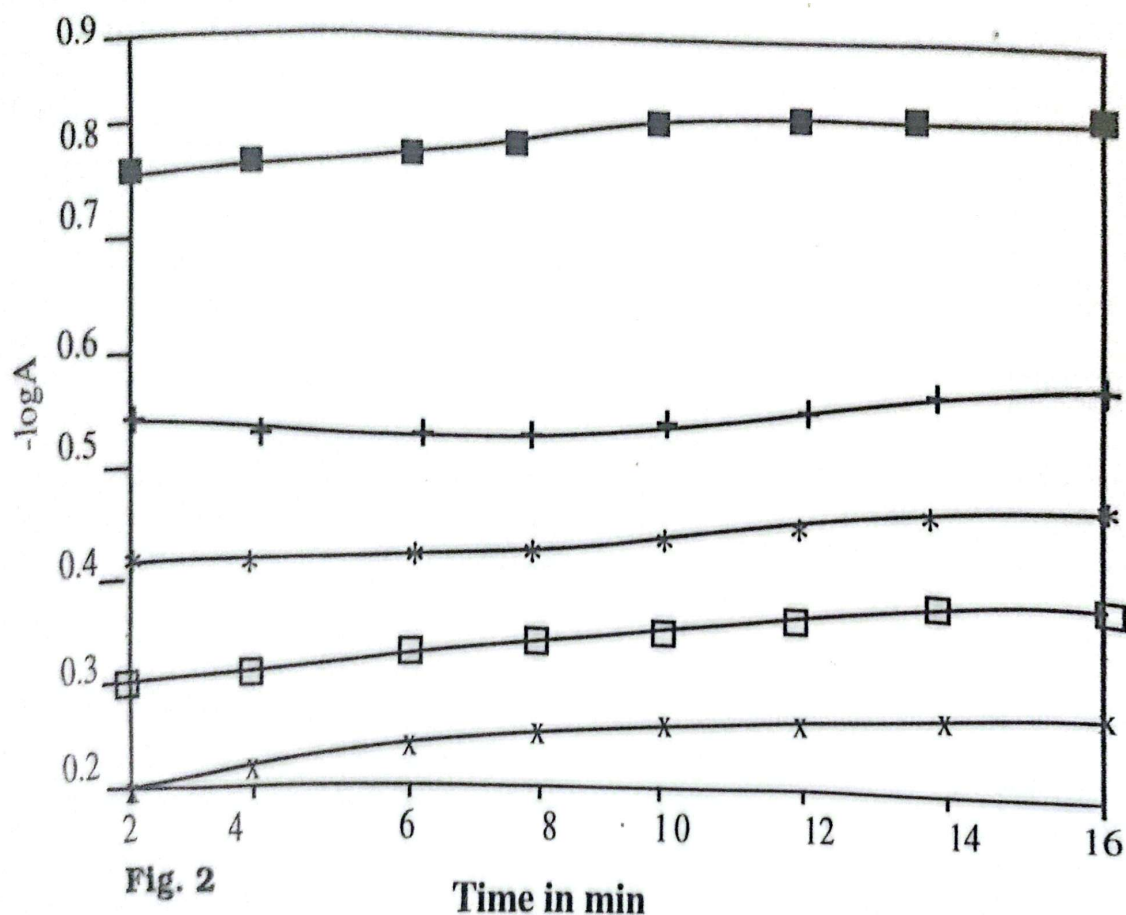


Fig. 2

Time in min

■ 1x10⁻⁵ M + 2x10⁻⁵ M * 3x10⁻⁵ M
 □ 4x10⁻⁵ M x 5x10⁻⁵ M

Effect of different concentration of Chromotropic acid on the rate of reaction

Final concentration.

Hydrogen peroxide: 1x10⁻² M

Molybdenum (VI): 1ppm

pH 10.6

Temperature: 25°C

λ_{max} : 360

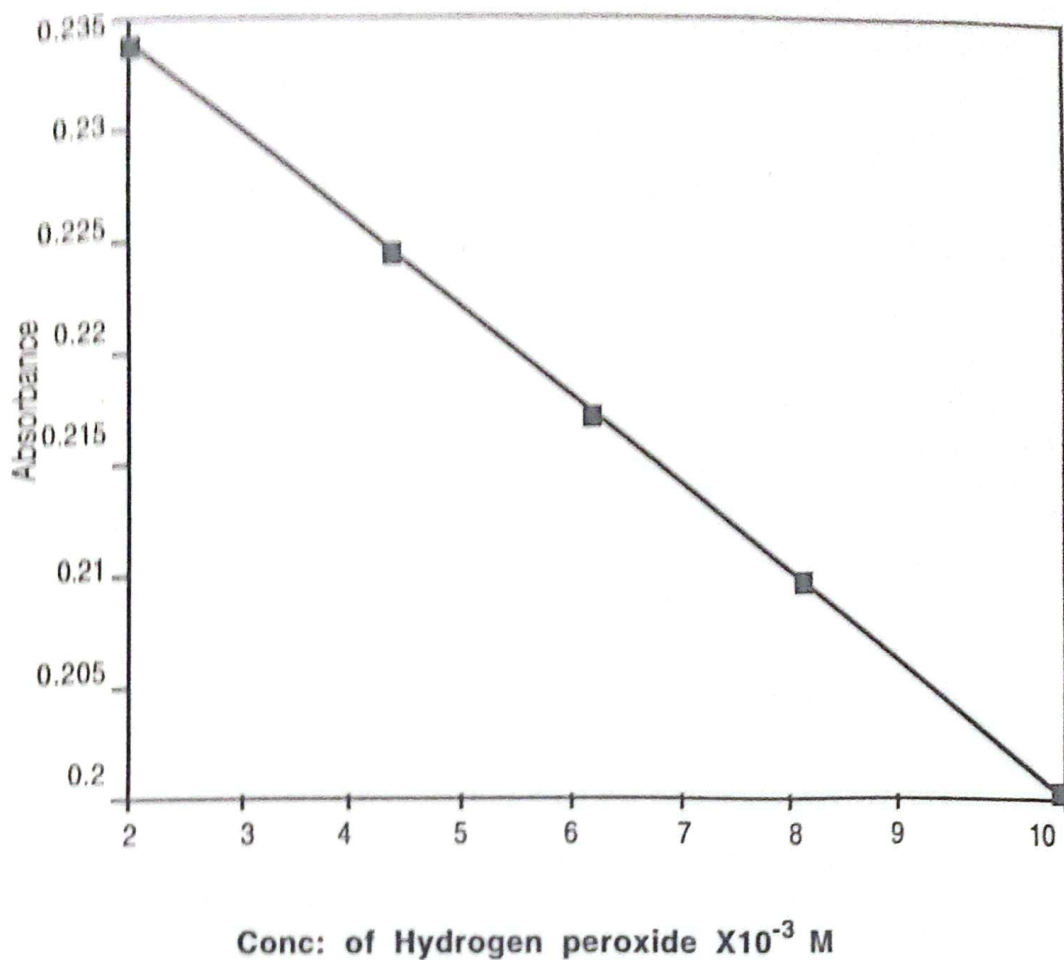


Fig. (3)

Effect of hydrogen peroxide on the rate of reaction.

Final concentration.

Chromotropic acid : $2 \times 10^{-5} M$

Molybdenum (VI): 1 ppm

pH: 10.6

Temperature: $25^{\circ}C$

λ_{max} : 360 nm.

Absorbance

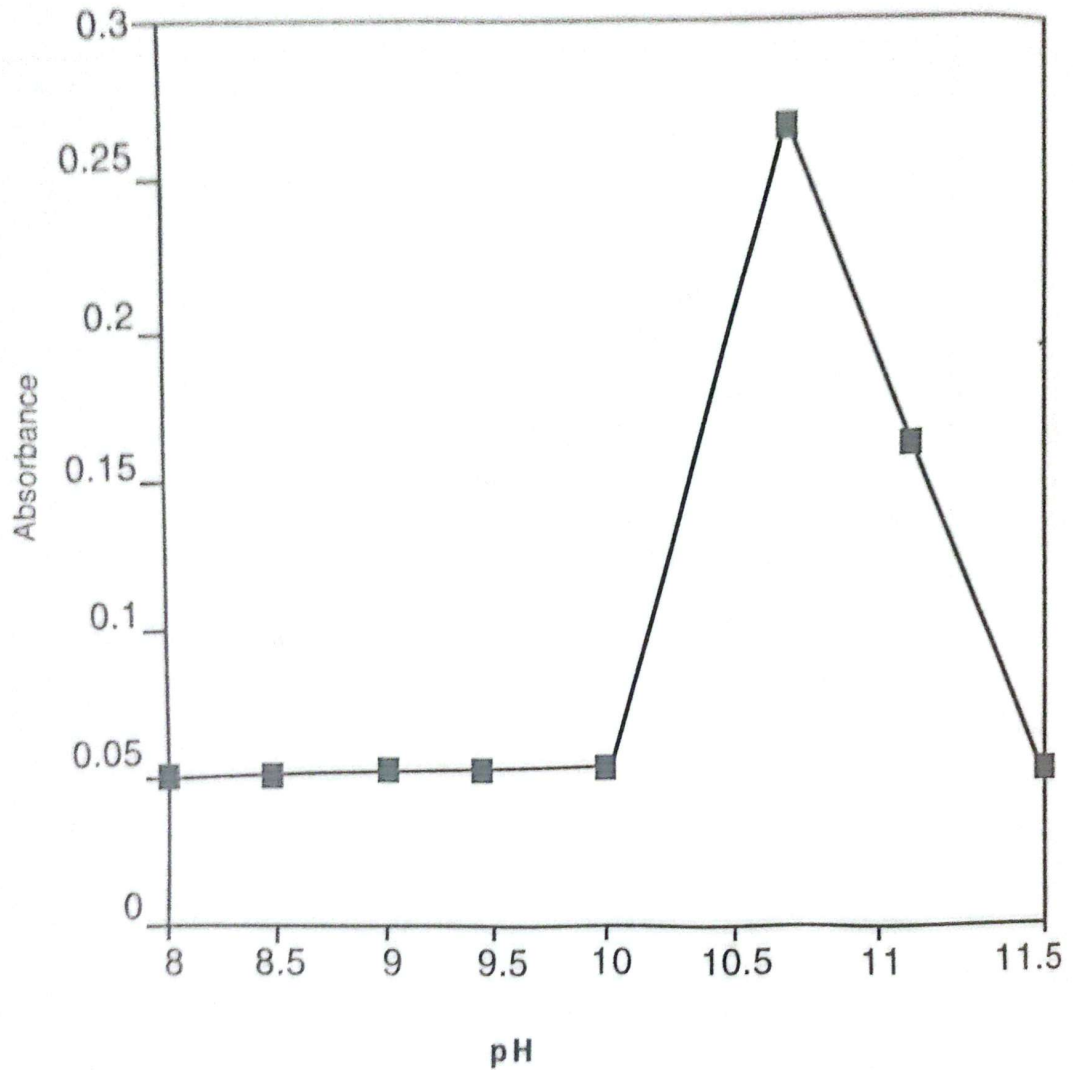


Fig. (4)

Effect of pH on the rate of reaction.

Final concentrations.

Chromotropic acid: $2 \times 10^{-5} \text{M}$

Hydrogen peroxide: $1 \times 10^{-2} \text{M}$

Temperature: 25°C

Molybdenum (VI): 1ppm

λ max: 360 nm.

Absorbance

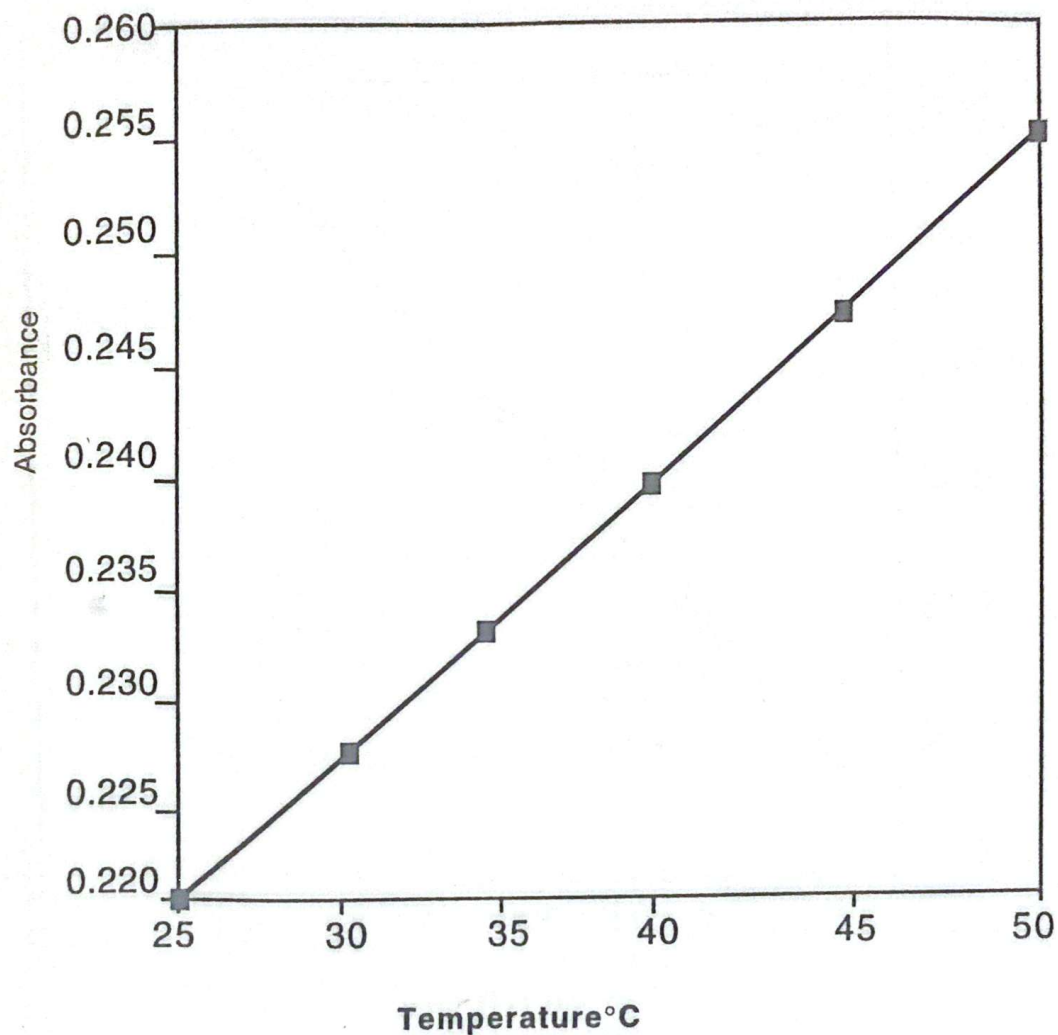


Fig. (5)

Effect of temperature on the rate of reaction.

Final concentrations.

Chromotropic acid: $2 \times 10^{-5} \text{M}$

Hydrogen peroxide: $1 \times 10^{-2} \text{M}$

pH: 10.6

Molybdenum (VI): 1ppm

λ max: 360 nm.

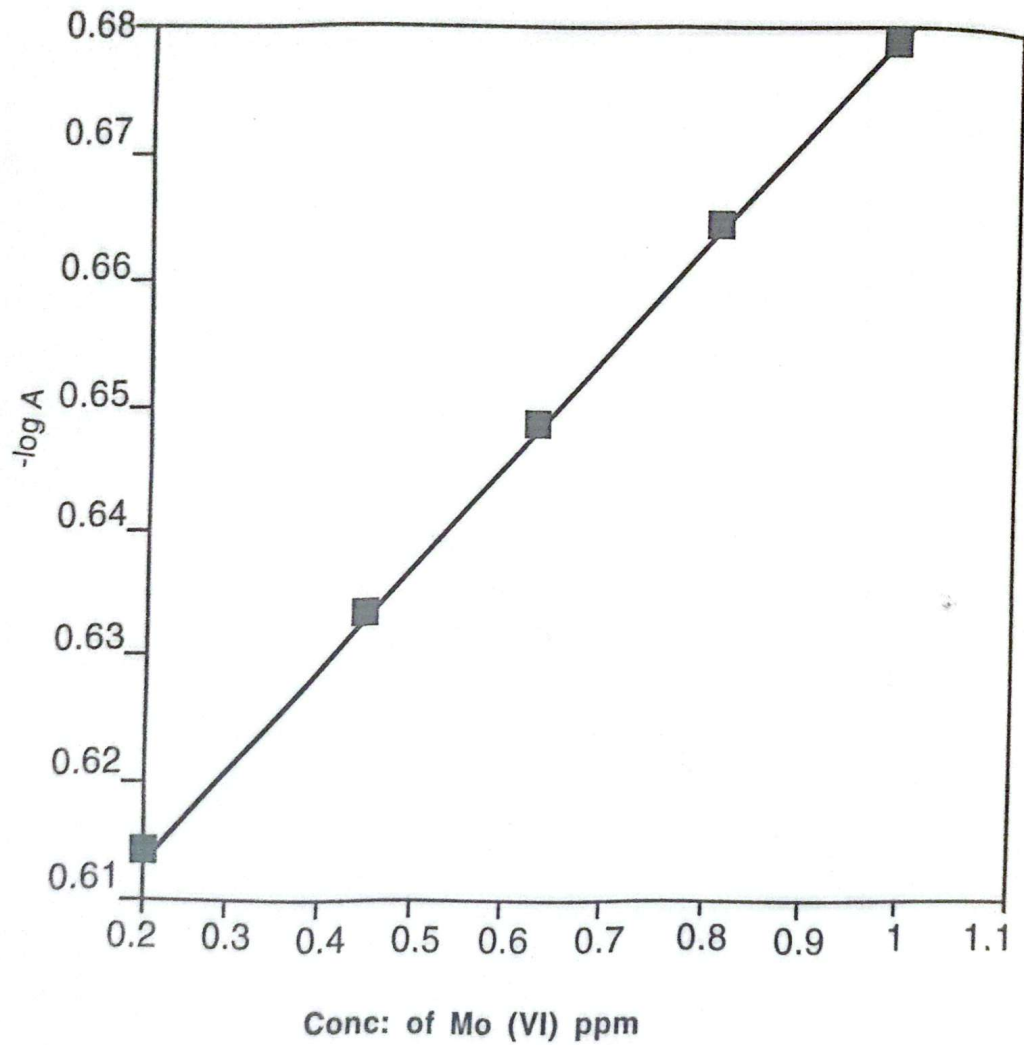


Fig. (6)

Calibration curve for Mo (VI).

Final concentrations.

Chromotropic acid: $2 \times 10^{-5} \text{M}$ Hydrogen peroxide: $1 \times 10^{-2} \text{M}$

Temperature: 25°C λ max: 360 nm.