

Kinetics Spectrophotometric Determination of Silver(I) by the Catalytic Effect on the oxidation of Chromotropic Acid by Bromate

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Summary: A kinetic spectrophotometric method for the determination of silver has been described, based on its catalytic effect on the oxidation of chromotropic acid with bromate. The rate of change in absorbance with respect to blank is measured spectrophotometrically at pH 1.7. The effect of pH and concentration of bromate, chromotropic acid and silver on the rate of reaction were investigated. At the optimized conditions the proposed method allows the determination of silver in the range of 2-10 µg/ml. The effect of different ions on determination of silver was examined and the method was applied for the determination of silver in a photographic film.

Introduction

Determination of silver is interesting because of its presence in anodic mud in electroplating processes [1] and it is widely used in photographic industry [2]. A number of methods have been proposed for the determination of silver at ppm to ppb levels using spectrophotometry [3,4], spectrofluorimetry [5], atomic absorption spectrometry [6,7], cyclic voltametry [8], inductively coupled plasma atomic emission spectroscopy [9] and flow injection technique [10]. Kinetic spectrophotometric and spectrofluorimetric methods for the determination of silver reported are based on (1) silver catalysed oxidation of organic reagents [11] (2) use of activators to enhance the oxidation of the reagent [12] (3) by the catalytic effect on the rate of a ligand substitution reaction [13] and (4) on its inhibitory effect of the oxidation [14]. A number of organic reagents have been used including bromopyrogallol red, pyrogallol red sulphanilic acid, fluorescein, luminol, o-diaminisidine, catechol violet, 2-hydroxybenzaldehyde thiosemicarbazone, phloxin, disodium 3-(1H-1,2,4-triazol-3-ylazo) chromotropate, pyrocatechol-1-aldehyde-2-pyridinehydrazone and o-phenylenediamine, [2,11,12,15-22]. Chromotropic acid (disodium salt of 4,5-dihydroxynaphthalene-2,7-disulphonic acid has been used for kinetic determination of copper(II) and iron[23] using spectrophotometer, and vanadium (IV) using fluorimeter [24]. Chromotropic acid has also been reported as a metallofluorescence reagent for the determination of beryllium (II) and aluminum (III),

[25]. Aluminum has been determined in biological samples [26]. In the present work silver catalysed oxidation of chromotropic acid with bromate has been examined for the quantitative determination of silver.

Results and Discussion

Silver catalysed oxidation of chromotropic acid with bromate was examined using spectrophotometer. The absorbance of the solution was measured after 15 min, following the principle of fixed time method. Absorption spectra of catalysed and uncatalysed reaction were recorded (Fig. 1), which shows maximum absorbance at 415 nm. Some enhancement in the absorbance in catalysed reaction at 415 min was observed as compared to uncatalysed reaction. It was therefore catalysed and uncatalysed reactions were further examined for the quantitative determination of silver.

Effect of pH

In order to optimize the conditions of catalysed reaction for the quantitative determination of silver, the absorbances of catalysed reaction (A) and uncatalysed reaction (B) were measured within pH range 1-10. The catalysed reaction was measured at final concentration of silver 10 ppm. The change in A-B was plotted against pH (Fig. 2). It was observed that optimum rate of catalysed reaction

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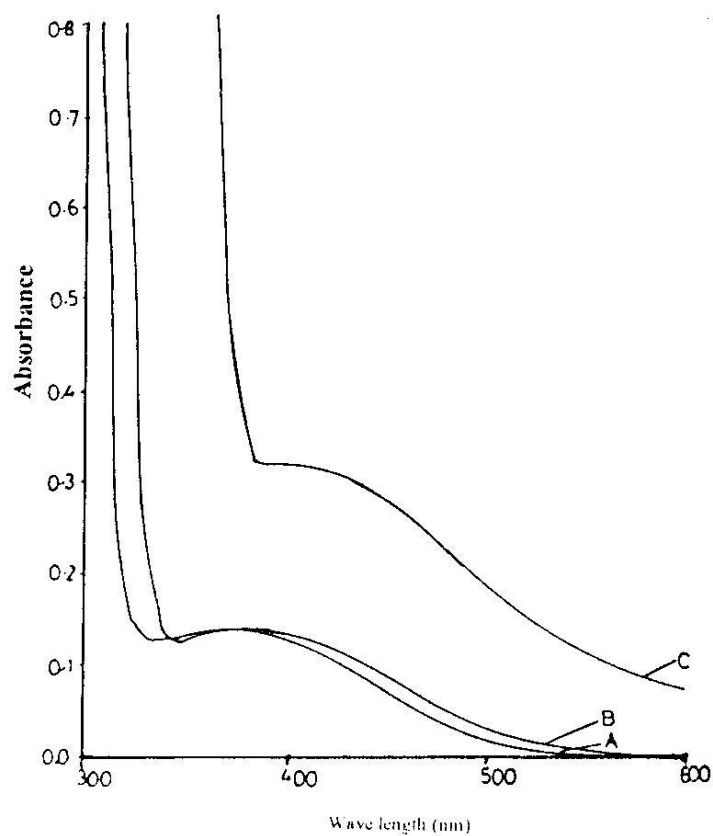


Fig. 1: Absorption spectra of (A) Chromotropic acid (B) Chromotropic acid and bromate (C) Chromotropic acid, bromate and silver(I). Concentrations chromotropic acid 1.2×10^{-3} , bromate 8×10^{-3} , silver 10 ppm and pH 1.7.

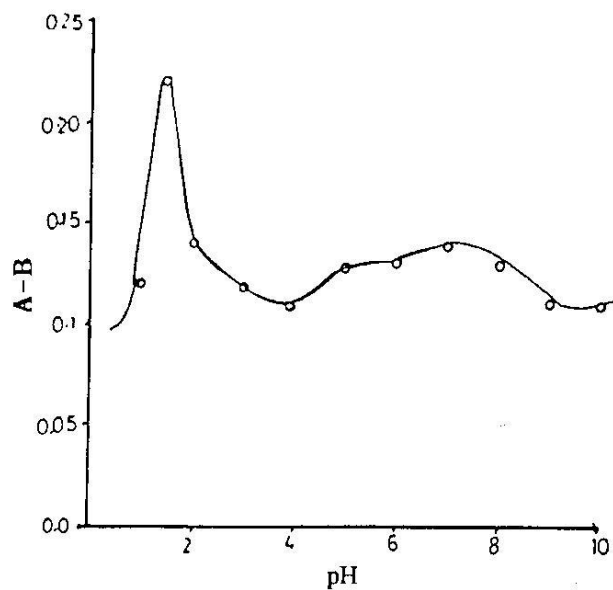


Fig. 2: Effect of pH on A-B of catalysed reaction, conditions chromotropic acid 1.2×10^{-3} M, bromate 8×10^{-3} M and silver 12 ppm.

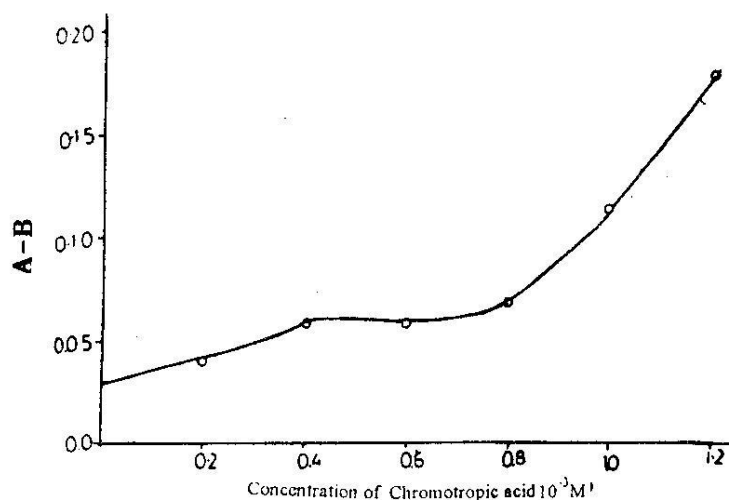


Fig. 3: Effect of chromotropic acid on catalysed reaction. Conditions: bromate $8 \times 10^{-3} M$ silver 10 ppm and pH 1.7.

with maximum difference in A-B was at pH 1.7 and was selected.

Effect of chromotropic acid

Effect of concentration of chromotropic acid on the catalysed (A) and uncatalysed (B) reactions were investigated at final concentration within 0.2×10^{-3} to $1.2 \times 10^{-3} M$. Graph A-B plotted versus concentration of chromotropic acid (Fig. 3) shows that value of A-B increases with increase in concentration of chromotropic acid, but value of B also increases with the increase of chromotropic acid. Thus to keep the absorbance and photometric error within the limits the final concentration of chromotropic acid was selected at $(1.2 \times 10^{-3} M)$.

Effect of bromate

The effect of bromate concentration on A and B were examined in the range of 2×10^{-3} to $10 \times 10^{-3} M$ and plot of A-B versus concentration of bromate (Fig. 4) shows that there is some increase in the value of A-B with the concentration of bromate, but to keep the absorbances of A within limits bromate concentration of $8 \times 10^{-3} M$ was selected.

Effect of temperature

The effect of temperature on A and B was examined in the temperature range 25-50°C at the

interval of 5°C. It was observed that absorbance of A and B increases with increase in temperature with a little increase in A-B, therefore because of the ease of operational conditions at room temperature, 30°C was selected.

At the optimized conditions, pH 1.7 temperature 30°C and final concentrations of chromotropic acid $1.2 \times 10^{-3} M$ and bromate $8 \times 10^{-3} M$, the effect of concentration of silver(I) on catalysed reaction was examined. A linear relation was observed by plotting A-B versus concentration of silver(I) in the range of 2-10 µg/ml, with coefficient of correlation ($r = 0.955$) (Fig. 5). The test solutions of silver were analysed and relative % error was found within ± 0.05 to 3.7. Coefficient of variation of replicate analyses ($n=10$) of 4 µg/ml of silver was observed 2.5%.

The effect of diverse ions on the determination of silver 2 µg/ml was also examined. It was observed that Hg(II), Ni(II), Zn(II), Mn(II), Co(II) could be tolerated upto ten times, the concentration of silver. However Cu(II), Fe(II), V(IV), Cr(VI) enhanced the catalytic reaction at the concentration similar to silver and interfered the determination.

Finally a photographic film was analysed for the silver contents and amount found was 110 µg/g

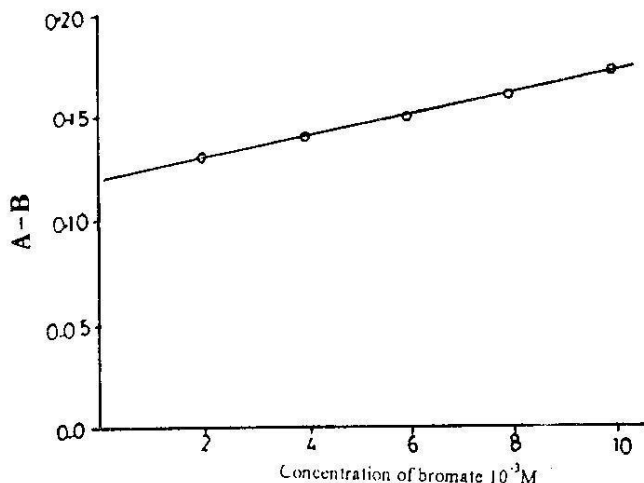


Fig. 4: Effect of bromate on catalysed reaction conditions: chromotropic acid $1.2 \times 10^{-3} M$, silver 10 ppm and pH 1.7.

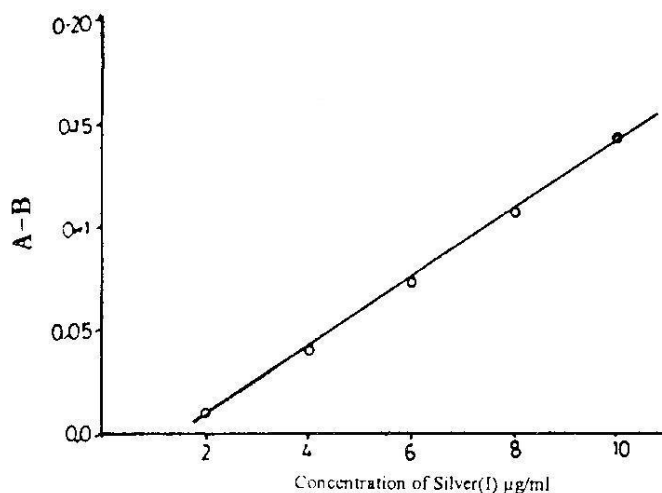


Fig. 5: Calibration graph of silver, conditions: chromotropic acid 1.2×10^{-3} bromate $8 \times 10^{-3} M$ and pH 1.7.

with C.V. 3.2%. The sample was also analysed for silver contents with a spectrophotometric method using dithizone as complexing reagent and amount of silver found was $109 \mu g/g$ with C.V. 4.5%.

Experimental

A. Solution

All the chemicals and chromotropic acid disodium salt were GR Grade (E. Merck). Solution potassium bromate ($1 \times 10^{-1} M$) was prepared by dissolving (1.67 g) in water and volume was made

up to 100 ml. Chromotropic acid solution ($1 \times 10^{-2} M$) was prepared by dissolving 0.4 g in water and volume was adjusted to 50 ml. Silver (I) containing 1 mg/mL was prepared by dissolving (0.15 g) silver nitrate in water and volume was adjusted to 100 ml.

Buffer solutions in pH 1-10 were prepared from the following:

Potassium chloride (1M), hydrochloric acid (0.1M), acetic acid (1M), sodium acetate (1M), ammonium chloride (1M) and ammonia (1M).

B. Analytical procedure

Chromotropic acid solution ($1.2 \times 10^{-3} \text{M}$) (5 ml), silver(I) solution (0.5-2.5 ml) containing 50-250 μg , 3 ml of potassium chloride-hydrochloric acid buffer solution pH 1.7 and 2 ml of bromate ($8 \times 10^{-3} \text{M}$) was transferred to volumetric flask (25 ml) and stop watch was started. The final volume was adjusted with water to 25 ml. The absorbance of the solution against water was measured at 415 nm after 15 min at room temperature (30°C). Uncatalysed reaction was also carried out simultaneously following the same procedure except addition of silver (I) solution was omitted.

C. Analysis of silver in photographic film

From unexposed photographic film for black and white (Kodak Panatomic-X Eastman Kodak Company, USA) a part (5 g) was cut with scissor. The film was transferred to crucible and heated in muffle furnace (Phoenix Furnaces Ltd Sheffield England) at 550°C for 5-6 hrs. White residue was added nitric acid (0.5 ml) and was dissolved in water. The final volume was adjusted to 50 ml.

To volumetric flask (25 ml) was transferred chromotropic acid solution ($1.2 \times 10^{-3} \text{M}$) (5 ml) and sample solution (2.5 ml). The remaining was followed as analytical procedure.

D. Spectrophotometric Determination of Ag(I) in Photographic film

Dithizone (0.01% w/v in Ethanol) (5 ml) were transferred to separating funnel and was added sulphuric acid (4N) (2 ml) and chloroform (5 ml), the contents were mixed well and layers were allowed to separate. The organic layer was separated and aqueous layer was added silver (I) solutions (0.6-2.0 ml) containing (60-200 μg). Chloroform (5 ml) was then added and contents were well mixed. The organic layer was collected in 10 ml flask and volume was adjusted with chloroform and absorbance was measured at 426 nm against reagent blank.

The solution 1 ml and 2 ml from sample were taken and procedure was followed as above. The absorbance was measured at 426 nm. The amount of silver was evaluated from calibration curve.

Equipments

A Hitachi 220 spectrophotometer with 1 cm silica cuvette was used for measurements of absorbances. pH measurements were made on Orion model 420A pH meter with glass electrode and combined reference electrode. A stop watch was used for recording of the time.

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