

DEVELOPMENT OF A NEW ANALYTICAL METHODOLOGY BASED ON THE CATALYTIC EFFECT OF AG(I) IN A NEW FUCHSIN-PEROXODISULFATE-1,10-PHENANTROLINE SYSTEM: APPLICATION TO THE DETERMINATION OF TRACE AMOUNTS OF SILVER

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(Received: March 3, 2011 - Accepted: April 5, 2012)

ABSTRACT

A simple, rapid and sensitive kinetic spectrophotometric method is proposed for the determination of trace amounts of silver ion in the concentration ranges of 2–20 and 20–50 $\mu\text{g L}^{-1}$. The proposed method is based on the catalytic effect of Ag(I) on the oxidation reaction of new fuchsin by potassium peroxodisulfate in the presence of 1,10-phenantroline as an activator at pH:5.0. The reaction is followed spectrophotometrically by measuring the change in absorbance at 547 nm using the initial rate method during the indicator reaction of 5 minute. The reaction rate variables like pH, reagent and activator concentrations and effect of reaction time and temperature were optimized in order to achieve the maximum analytical sensitivity. The experimental and theoretical detection limits of the developed method were found as 0.475 $\mu\text{g L}^{-1}$ and 1.50 $\mu\text{g L}^{-1}$, respectively. The relative standard deviations for five replicate measurements of 15 and 35 $\mu\text{g L}^{-1}$ of Ag(I) were 5.27% and 3.32%, respectively. The effect of different diverse ions on the determination of silver was studied and found to be free from most interference. The method was successfully applied to the determination of silver in photographic solutions and different real water samples such as tap water, pond water and natural spring waters.

Keywords: Kinetic spectrophotometry, new fuchsin, catalytic effect, 1,10-Phenantroline, Ag(I) determination

INTRODUCTION

Silver is an extremely important metal due to its antibacterial properties and high corrosion resistivity. The various compounds of this commercial metal have extensively been used in photography industry and medicine. In spite of the well-known useful properties, silver toxicity is characterized with strongly lung oedema, hemorrhoids and osteomyelitis, hepatitis and nephritis [1,2]. Therefore, the long-term exposure of human being to silver compounds and colloidal silver may cause grey or grayish black staining on skin and stoma [3]. The low concentrations of silver are widely existed in different matrix-structured complex samples such as drinking water, soil, rock, coal-fly ash, air, smoke, plants and seawater [4]. Silver is also discharged into the environment from industrial pollutants and photographic waste-washing waters. Therefore, in view of analytical-viewpoint, an economical method development having high precision, sensitivity and selectivity is extremely important for the quantitative determination of silver when it is available at trace amounts on the complex matrices. Although this determination is generally carried out with cost effective-analytical methods such as ICP-AES [5,6], ICP-MS [7-9] and ET-AAS [10], these methods are suffered from the interferences at different types and several complex analysis and data-processing steps [11,12]. It can partly be avoided from these drawbacks by using the pre-concentration processes like liquid-liquid and solid phase extraction [13,14]. Although they can be very applicable, these methods are suffered from a lot of problems; for example liquid-liquid extraction techniques are generally harmful to the environment and solid phase extraction techniques are often recognized as time-consuming as well as low repeatability.

Analytical methods based on the measurement of time changes in the concentrations of certain components of suitable reaction systems are very varied, differing both methodically and in application. Catalytic determinations are the most widely used of the kinetic methods. The field of catalytic methods includes the methods of determination of trace concentrations of metal ions, anions and many organic substances. Low detectable quantities and high sensitivities are recognized as major advantages of catalytic determinations. Selectivity, on the other hand, can be considered to limit the practical application of these determinations. The kinetic-catalytic methods have shown some very promising features for determination of metal ions in ultra-trace levels [15]. These methods have proved to be a cheaper and more reliable alternative to the instrumental analyses for trace determinations [16]. Ag(I) is a good catalyst for the oxidation of various organic reagents in the presence or absence of an activator [17-21].

For example, piperazine acts as an activator in the oxidation of p-nitrodiazio aminoazobenzene [22], o-phenantroline was used as an activator in the oxidation of bromopyrogallol red [23], and for the oxidation of Brilliant Cresyl Blue. 1,10-Phenantroline was also used as an activator in the oxidation of certain azo dyes [24]. Ethylenediamine and triethylenetetramine have also

been studied as activators [25]. However many of these methods suffer from poor selectivity or sensitivity. Although many kinetic methods have been used in the silver determination up to now, nevertheless there is still a need to the development of more sensitive and selective analytical method due to its increasing importance for plants, animals and human beings.

The present study describes a simple, rapid, precise, relatively selective and sensitive analytical method for the kinetic determination of silver at trace levels using its catalytic effect on the oxidation of new fuchsin by peroxodisulfate at pH 5.0 phosphate buffers in the presence of 1, 10-phenantroline as an activator.

EXPERIMENTAL

Reagents and solutions

All reagents were of analytical reagent grade and were used directly further purification. Triply distilled water was used to prepare buffer and reagent solutions. A silver stock solution (1000 mg L^{-1}) was prepared by dissolving 0.1574 g of AgNO_3 (Merck) in water and diluting to the mark in a 100 mL volumetric flask. All working solutions were prepared by a serial dilution of stock solution at suitable proportions. A stock solution of peroxodisulfate (0.1 M) was prepared by dissolving 13.516 g of its potassium salt in distilled water and diluting to 500 mL. New fuchsin solution (3.2×10^{-4} M) was prepared by dissolving 0.029 g of the indicator dye as chloride salt in distilled water and diluting with water to 250 mL. 0.01 M 1,10 phenantroline solution was prepared by dissolving 0.500 g of 1,10 phenantroline (Merck) in water, adding 2-3 drops of sulfuric acid, and diluting to 250 mL with water. The phosphate buffer pH: 5.0 were prepared by mixing 248 mL of 0.067 M KH_2PO_4 and 2 mL of 0.067 M Na_2HPO_4 . Stock solutions of 1000 $\mu\text{g mL}^{-1}$ of interfering ions were prepared by dissolving appropriate amounts of suitable salts of each ion in distilled water, HNO_3 or NaOH .

Instrumentation

In this study, a Shimadzu Model UV-Visible 1601 PC spectrophotometer equipped with a 1 cm quartz cell was used for absorbance measurements. This spectrophotometer has a wavelength accuracy of ± 0.2 nm and a bandwidth of 2 nm in the wavelength range of 190–1100 nm. A TCC-140A mark temperature-controlled cell holder to this instrument was attached for absorbance measurements at a fixed wavelength. In order to control the temperature of reaction medium with an accuracy of $\pm 0.1^\circ\text{C}$ a Grant LTG-6G model thermostatic water bath regulated at the desired temperature was used (operating in the temperature range of -20 and 100°C). A stopwatch was used for recording the reaction time. A pH meter consisting of a glass-calomel electrode double was used to determine the pH values of solutions with an accuracy of ± 0.1 pH unit. Two standard buffer solutions of pH 7 ± 0.01 and pH 4 ± 0.01 (Sigma) were used for the calibration of pH meter. All solutions were preheated to a temperature of $25 \pm 0.1^\circ\text{C}$ shortly before the initiation of indicator

reaction with and without catalyst. All absorbance measurements were made at a working wavelength of 547 nm.

Experimental Procedure

An integral variant of tangent method [26] was used for processing the kinetic data, because a linear correlation exists between the absorbance (or the logarithm of the absorbance) and time during the first 5 min after mixing. The reaction rate was followed by the change in the values of the tangent of the angle ($\tan\alpha$) for the slope of the linear part of the kinetic curve to abscissa in the coordinates $A-t$ or $\log A-t$, because $\tan\alpha: dA/dt$ or $d\log A/dt$. The reaction parameters were investigated by measuring the reaction rates determined by calculating the initial linear parts of kinetic curves ($A-t$ graphs), $\tan\alpha: dA/dt$ and following the changes in absorbance of indicator dye as a function of time. The dA/dt quantity was used an analytical signal instead of reaction rate, dC/dt . After the preheating of 10 min, the preselected volumes of reagents participated into the indicator reaction were transferred to a flask of 10 mL in the sequence of pH 5.0 phosphate buffer, new fuchsin, 1,10-phenanthroline, $K_2S_2O_8$ and silver ion as catalyst. The mixture was completed to a final volume of 10 mL with distilled water and mixed thoroughly. An aliquot of the reaction mixture was immediately transferred to a cuvette and absorbance was recorded as a function of time. The catalyzed as well as uncatalyzed reaction was followed by monitoring the decrease in absorbance at 547 nm. Absorbance measurement was started exactly after 0.5 min of initiation up to 5 min to use as fixed time measurement of initial reaction rate. The initial rate of catalyzed reaction was calculated by subtracting the reaction rate corresponding to a blank solution containing no silver as uncatalyzed reaction. In order to eliminate any traces of metal ions coming from the glass surface, we cleaned the glassware used for this work scrupulously. Cuvettes were cleaned after using by immersion in HCl (1:1, v/v) and KOH (saturated solution with ethanol) for 15 min to remove traces of dye adsorbed on the walls.

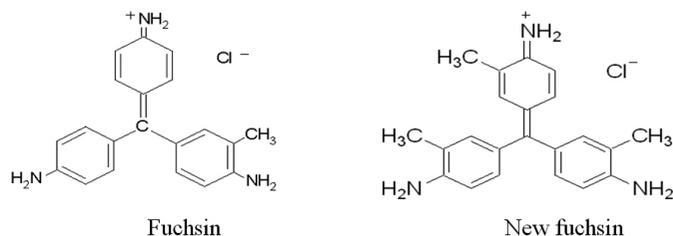
Analysis of real samples

Before analysis, all the water samples except tap water were filtered through a 0.45 mm membrane filter and the pH value was adjusted to approximately 5.0 with 0.1 M HCl and 0.1 M NaOH by using a pH meter. In order to minimize the effect of organic and inorganic interfering species present in sample and control the accuracy and precision of the method, a suitable amount of pond water sample (1 L) was treated with concentration nitric acid and sulfuric acid and then heated to dryness. Then aliquots of concentrated nitric acid were added and heated again. The residue was cooled to room temperature and dissolved by distilled deionized water. The solution was diluted to the desired volume. Then a suitable aliquot of the solution was analyzed by the developed kinetic method after adjusting pH to a value of 5.0. In order to suppress the possible serious interference of Hg(II) ions the 1 mL 0.001 M $S_2O_3^{2-}$ solution as a complexing agent was added to the reaction media if necessary before detection of Ag(I) ions. A known amount (approximately 1.5 g) of the developed panchromatic film was treated with 3 M NaOH solution until the gelatinous film separated from the rigid support, which was discarded after being washed. Then the proper amount of concentrated nitric acid was added and the solution was heated until silver dissolved completely. The solution was filtered and the filtrate was diluted to the desired volume with distilled deionized water. The suitable aliquot of the solution was analyzed by the proposed kinetic method after adjusting pH to a value of 5.0.

RESULTS AND DISCUSSION

Fuchsin or rosaniline hydrochloride is a magenta dye with chemical formula $C_{20}H_{19}N_3 \cdot HCl$ [27,28]. There are other similar chemical formulations of products sold as fuchsine, and several dozen other synonyms of this molecule [27]. It becomes magenta when dissolved in water; as a solid, it forms dark green crystals. As well as dyeing textiles, fuchsine is used to stain bacteria and sometimes as a disinfectant. However, the triphenylmethane derivative, new fuchsin, also known as basic fuchsin and magenta III, is both a dye and an acid-base indicator. New fuchsin is a molecule that has three branched monomers and on polymerization forms a dendrimer. A dendrimer is a polymer that can be synthesized from regular, highly branched monomers leading to a nanometer-sized monodispersed, tree-like dendritic structure. New fuchsin has been used to determine sulfide ion concentrations by the kinetic spectrophotometric method [29], to determine sulfite ion concentrations using a full curve (PLS) and a fixed time method [30], to simultaneously determine sulfide and sulfite by PLS-GA model [31], as a copper corrosion inhibitor [32], and as a photosensitive reagent [33] whereas fuchsin is used for the determination of silver ions in real samples by the kinetic spectrophotometric method based on

its catalytic effect in the presence of 1,10-phenanthroline [34]. Two indicator species having similar chemical structure are exist in two forms, R^+ and ROH, depending on the pH of the solution too [35]. The open molecular structures of Fuchsin and New Fuchsin are given in Schema 1.



Scheme 1 The open molecular structures of Fuchsin and New Fuchsin.

It was observed that new fuchsin reacts with peroxodisulfate slowly and its absorbency is decreased. When a trace amount of silver is present, the reaction will proceed faster, but in the presence of 1,10-phenanthroline as an activator the reaction proceeds much faster. The catalytic effect of silver and the activating effect of 1,10-phenanthroline was used to develop a kinetic spectrophotometric method for the sensitive determination of silver. Thus, a change in the absorbance of new fuchsin with time at 547 nm as measure of the reaction rate was considered as an indication of amount of silver present in the sample.

Effect of reaction variables

In order to establish experimental conditions under which the catalytic effect of silver and therefore the sensitivity in its determination are at maximum, we studied the dependence of rate on pH, temperature and on the concentrations of indicator dye, 1,10-phenanthroline and peroxodisulfate and the effect of ionic strength. The change in the absorbance with time for the first 5 min was used to plot the graph for each variable and the optimum conditions were taken from the calculated slope of the linear parts of $A-t$ curves for the subsequent study of the variables. The reagent concentration optimization was carried out for the uncatalyzed and catalyzed reactions for a constant time of 5 min in the presence of 5 and 30 $\mu g L^{-1}$ of silver.

Effect of pH to sensitivity

The pH study was made by using phosphate buffer solutions in the pH range of 2-8. The effects of pH on the catalyzed-reaction rate are shown in Figure 1. It can be seen that the highest difference in the both reaction rates is obtained at pH 5.0. A greater and lower pH values than 5.0 would cause the sensitivity to decrease. In this experiment, pH value must be strictly controlled at 5.0 using buffer solution. Otherwise, the experimental error may be great and the accuracy of results may be questionable. For this reason the phosphate buffer solution at pH 5.0 was selected further experimental study. Additionally, the effect of buffer concentration on the reaction rate also was investigated. It was observed that a maximum buffer concentration responding to buffer volume of 1.5 mL was the best suitable concentration in Figure 2. From Figure 1 it appears that there is a linear relationship between pH and the reaction rates in the concentration range of 1×10^{-2} and 1×10^{-5} M. A similar linear relationship was found between $\log \tan\alpha$ and $\log C_{H^+}$ in the pH range of 2.0-5.0 for the catalyzed reaction. The order of the catalyzed reaction is 1 with respect to pH in the investigated pH interval from 2.0 to 5.0.

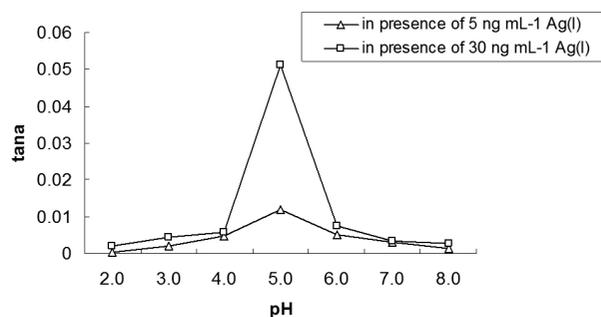


Fig. 1. Dependence of $\tan\alpha$ on the medium pH for the catalyzed-reaction. Initial conditions: $C_{\text{Fuchsin}}: 4.8 \times 10^{-5}$ M, $C_{K_2S_2O_8}: 0.015$ M, $C_{1,10\text{-phenanthroline}}: 2.0 \times 10^{-4}$ M, (Δ) 5 $\mu g L^{-1}$ and (\square) 30 $\mu g L^{-1}$ Ag(I) at $25 \pm 0.1^\circ C$

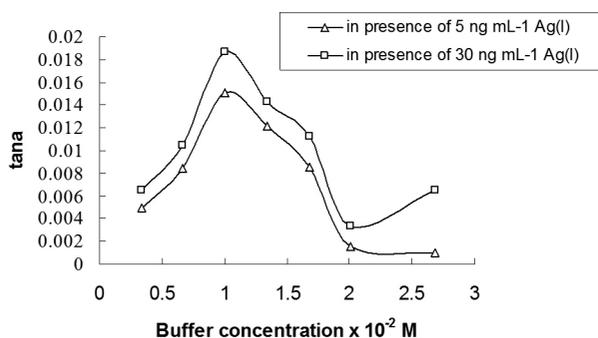


Fig. 2. Dependence of $\tan\alpha$ on the concentration of buffer solution for the catalyzed-reaction. Initial conditions: $C_{\text{New fuchsin}}: 4.8 \times 10^{-5} \text{ M}$, $C_{\text{K}_2\text{S}_2\text{O}_8}: 0.015 \text{ M}$, $C_{\text{1,10-phenantroline}}: 2.0 \times 10^{-4} \text{ M}$ in the presence of pH 5.0 phosphate buffer (Δ) $5 \mu\text{g L}^{-1}$ and (\square) $30 \mu\text{g L}^{-1}$ Ag(I) at $25 \pm 0.1^\circ\text{C}$

Effect of indicator dye concentration to sensitivity

The dependence of the reaction rates on the concentration of new fuchsin in the range of 6.4×10^{-6} – $6.4 \times 10^{-5} \text{ M}$ is shown in Figure 3. The results indicate that net reaction rates increased with increase in new fuchsin concentration up to $4.8 \times 10^{-5} \text{ M}$ for two different catalyst concentrations of 5 and $30 \mu\text{g L}^{-1}$. Higher concentration of indicator dye caused a decrease in analytical sensitivity. This effect is due to the fact that at higher concentration of indicator dye, the oxidation of indicator dye for the uncatalyzed reaction with peroxodisulfate is too fast to accurately detect the catalytic effect of Ag^+ ion. In addition to, a higher concentration of dye can not be used due to its molar absorption coefficient. Thus, a new fuchsin concentration of $4.8 \times 10^{-5} \text{ M}$ was used as optimal indicator concentration for further study. From Figure.3 it can be seen that the catalyzed reaction is first order with respect to the new fuchsin concentration from 6.4×10^{-6} to $4.8 \times 10^{-5} \text{ M}$ for the initial indicator concentration of $3.2 \times 10^{-4} \text{ M}$.

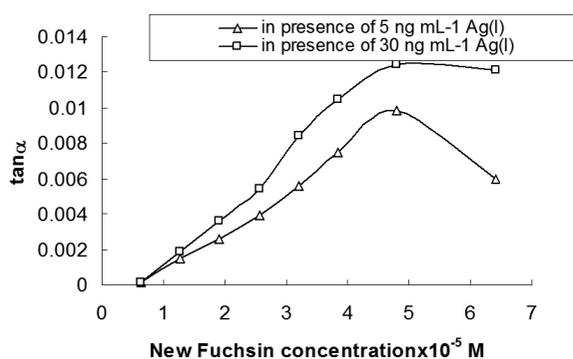


Fig. 3. Dependence of $\tan\alpha$ on the new fuchsin concentration for the catalyzed-reaction. Initial conditions: $C_{\text{K}_2\text{S}_2\text{O}_8}: 0.015 \text{ M}$, $C_{\text{1,10-phenantroline}}: 2.0 \times 10^{-4} \text{ M}$ in the presence of 1.5 mL pH 5.0 phosphate buffer (Δ) $5 \mu\text{g L}^{-1}$ and (\square) $30 \mu\text{g L}^{-1}$ Ag(I) at $25 \pm 0.1^\circ\text{C}$

Effect of the peroxodisulfate concentration to sensitivity

The dependence of the reaction rates on the concentration of peroxodisulfate in the range of 2×10^{-3} and $2 \times 10^{-2} \text{ M}$ is shown in Figure 4. The results indicate that net reaction rates increased with increase in peroxodisulfate concentration up to $1.5 \times 10^{-2} \text{ M}$ for two different catalyst concentrations of 5 and $30 \mu\text{g L}^{-1}$. Higher concentration of peroxodisulfate caused a decrease in analytical sensitivity. This effect is due to the fact that at higher reagent concentration, the oxidation of indicator dye for the uncatalyzed reaction or blank reaction with increasing peroxodisulfate concentration is too fast to accurately detect the catalytic effect of Ag^+ ion. Thus, a peroxodisulfate concentration of $1.5 \times 10^{-2} \text{ M}$ was adopted as optimal reactive concentration for further study. From Figure 4 it can be seen that the catalyzed reaction is approximately first order with respect to the peroxodisulfate concentration from $2 \times 10^{-3} \text{ M}$ to $1 \times 10^{-2} \text{ M}$ for the initial reactive concentration of 0.1 M.

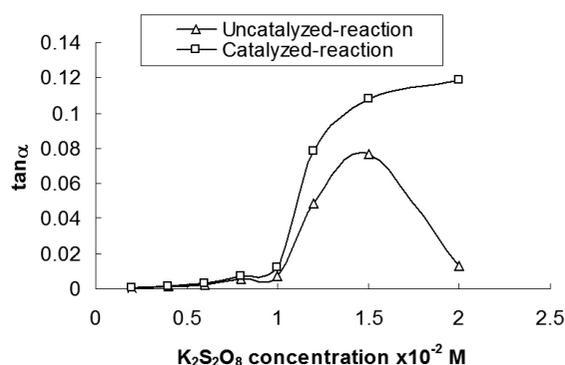


Fig. 4. Dependence of $\tan\alpha$ on the peroxodisulfate concentration for the catalyzed-reaction. Initial conditions: $C_{\text{New fuchsin}}: 4.8 \times 10^{-5} \text{ M}$, $C_{\text{1,10-phenantroline}}: 2.0 \times 10^{-4} \text{ M}$ in the presence of 1.5 mL pH 5.0 phosphate buffer (Δ) $5 \mu\text{g L}^{-1}$ and (\square) $30 \mu\text{g L}^{-1}$ Ag(I) at $25 \pm 0.1^\circ\text{C}$

Effect of 1,10-phenantroline concentration to sensitivity

The effect of the 1,10-phenantroline concentration on the catalyzed reaction was studied in the range of 5×10^{-5} – $6 \times 10^{-4} \text{ M}$ for the initial activator concentration of 0.01 M in the final solution. The dependence of the reaction rates on the concentration of activator in the concentration range of 5×10^{-5} – $6 \times 10^{-4} \text{ M}$ is shown in Figure 5. Analytical sensitivity or catalyzed reaction rate was increased by increasing the activator concentration up to $1 \times 10^{-4} \text{ M}$ and was decreased above this concentration. Thus, a concentration of $1 \times 10^{-4} \text{ M}$ was chosen as optimal activator concentration for further study.

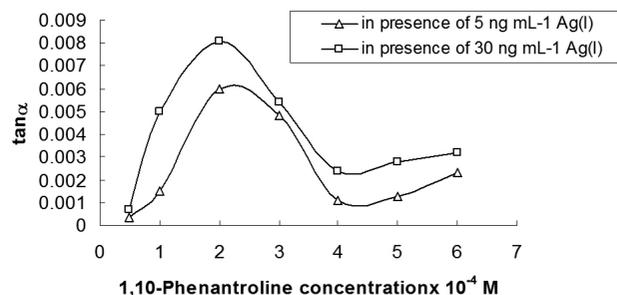


Fig. 5. Dependence of $\tan\alpha$ on the 1,10-phenantroline concentration for the catalyzed-reaction. Initial conditions: $C_{\text{New fuchsin}}: 4.8 \times 10^{-5} \text{ M}$ and $C_{\text{K}_2\text{S}_2\text{O}_8}: 0.015 \text{ M}$ in the presence of 1.5 mL pH 5.0 phosphate buffer (Δ) $5 \mu\text{g L}^{-1}$ and (\square) $30 \mu\text{g L}^{-1}$ Ag(I) at $25 \pm 0.1^\circ\text{C}$

Effect of the reaction temperature to sensitivity

A study of the effect of the temperature on the catalyzed reaction rate in the optimal reagents and activator concentrations for the silver concentrations of 5 and $30 \mu\text{g L}^{-1}$ was made in the temperature range of 20 – 60°C . The increase in the reaction rate with increasing temperature for the catalyzed reaction is shown in Figure 6. According to the results, the reaction rate increased with increasing temperature up to 25°C , whereas at the higher temperatures the reaction rate decreased for the catalyzed reaction. The reason of this decrease in sensitivity is the increase in the rate of uncatalyzed reaction with increasing temperature at higher temperatures than 25°C . Thus, a temperature of 25°C was chosen as optimal temperature due to both give maximum sensitivity and its application facility for further study.

Calibration graph and detection limit

The calibration graph was obtained under the optimized working conditions and with 547 nm as the determination wavelength and the initial rate method was applied to the change in the reaction rate, $\tan\alpha$ during the first 5 min passed just after the initiation of indicator reaction. The measurements were made for the time of first 5 min passed just after the initiation of uncatalyzed- and catalyzed- reactions so that they would provide the maximum sensitivity and the best correlation between analytical signal and catalyst concentration. Under the selected optimal conditions described above ($[\text{New fuchsin}]: 4.8 \times 10^{-5} \text{ M}$, $[\text{S}_2\text{O}_8^{2-}]: 0.017 \text{ M}$, $[\text{1,10-phenantroline}]: 4 \times 10^{-4} \text{ M}$ and 1.5 mL pH: 5.0 phosphate

buffer), Ag⁺ ions can be determined in the concentration range of 2–20 µg L⁻¹ Ag⁺; $\tan \alpha = 9.18 \times 10^{-3} + 4.32 \times 10^{-4} C_{Ag(I)}$ (with a correlation coefficient of 0.9850 for five replicate measurements, N: 5) and for the concentration range of 20–50 µg L⁻¹ Ag⁺ under the selected second optimal conditions ([New fuchsin]: 4.8 × 10⁻⁵ M, [S₂O₈²⁻]: 0.013 M, [1,10-phenantroline]: 2 × 10⁻⁴ M and 1.5 mL pH: 5.0 phosphate buffer), $\tan \alpha = -5.83 \times 10^{-3} + 7.94 \times 10^{-4} C_{Ag(I)}$ (with a correlation coefficient of 0.9950 for five replicate measurements, N: 5) where C_{Ag(I)} is the silver concentration in µg L⁻¹ and tan α is the change in the net reaction rate and/or catalytic reaction rate for the initial rate method. The relative standard deviation for five replicate determinations of 15 and 35 µg L⁻¹ Ag⁺ is 5.27% and 3.32%, respectively. The experimental detection limit, calculated as three times the standard deviation of the blank divided by the slope of the calibration graph and theoretical detection limit, defined as the concentration giving a signal equal to the average of the blank value plus three times its standard deviation of the developed kinetic method were found as 0.475 µg L⁻¹ Ag⁺ and 1.50 µg L⁻¹ Ag⁺ [36].

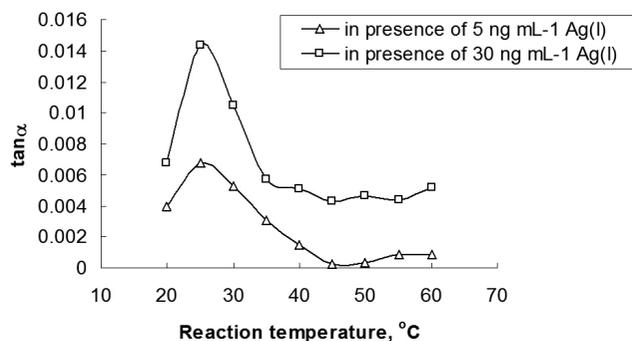


Fig. 6 Dependence of tan α on the temperature of reaction medium for the catalyzed-reaction. Initial conditions: C_{New fuchsin}: 4.8 × 10⁻⁵ M, C_{K₂S₂O₈}: 0.015 M and C_{1,10-phenantroline}: 2.0 × 10⁻⁴ M in the presence of 1.5 mL pH 5.0 phosphate buffer (Δ) 5 µg L⁻¹ and (□) 30 µg L⁻¹ Ag(I)

Interference study

The influence of interfering foreign ions on the analytical system was examined on the determination of 20 µg L⁻¹ Ag⁺. The results are summarized in Table 1. The tolerance limit was defined where the concentration of interfering ions caused less than 5.0% relative error. Most of the cations and anions had no measurable interfering effect on the determination of Ag⁺ ion as catalyst, even when present in 100-1500 fold excess over silver. The most serious

interference is originated from Br⁻, I⁻, SO₃²⁻ and CN⁻ anions due to the formation of insoluble metal salts or metal complexes. The tolerance limit of Br⁻, I⁻, SO₃²⁻ ions and even CN⁻ ion can be increased up to a tolerance ratio of 75 by addition of 1.0 mL of conc. HNO₃ solution into 10 ml of the Ag-catalyzed solution and heating to dryness. Also, it was observed that the V⁵⁺ and Hg²⁺ ions interfered into the catalyzed reaction rate with a tolerance ratio changing in the range of 1-5. The interfering effect of Hg²⁺ ion can be removed by addition of 1 mL 0.001 M S₂O₃²⁻ ion as masking reagent up to 25 fold. The interfering effect of VO₂⁺ ion can be suppressed by addition of 1.25 mL 0.025% (w/v) citric acid or tartaric acid solution as masking reagent up to 35 fold.

Table 1 Influence of different interfering ions on the determination of 20 µg L⁻¹ of silver in the optimal conditions.

Interfering species	Tolerance ratio of interfering ions to silver ion
CH ₃ COO ⁻ , Citrate, Tartrate, SO ₄ ²⁻ , Se(IV), Se(VI), ClO ₃ ⁻ , Ca ²⁺ , Ba ²⁺ , Sr ²⁺ , NO ₃ ⁻ , Al ³⁺ , K ⁺ , Na ⁺ and NH ₄ ⁺	500-1500
Cl ⁻ , F ⁻ , CO ₃ ²⁻ , C ₂ O ₄ ²⁻ , IO ₃ ⁻ and NO ₂ ⁻	250-350
PO ₄ ³⁻ , Cd ²⁺ , Pd ²⁺ and S ₂ O ₃ ²⁻	100-200
Zn ²⁺ , Ni ²⁺ , CN ⁻ , Cu ²⁺ , Sn ²⁺ , Fe ²⁺ and Mn ²⁺	50-75
Co ²⁺ and SO ₃ ²⁻	25, 30 (75)*
Br ⁻ and I ⁻	5 (75)*
V ⁵⁺	5 (35)**
Hg ²⁺	1 (25)***

*After pretreatment with concentrated HNO₃ solution
 **After pretreatment with 1.25 mL 0.025 % (w/v) citric acid or tartaric acid solution
 ***After pretreatment with 1 mL 0.001 M S₂O₃²⁻ solution

Analytical application of the developed kinetic method

In order to verify the analytical usefulness of the proposed kinetic method, we applied to the method was to determination of silver in a sample of pond water and in several drinking-water samples. The pond water and drinking water samples were analyzed by the method of the well-known standard addition. The determination of silver in a photographic solution was also performed, and the results obtained by the proposed kinetic method and FAAS method were compared. Table 2 also shows the results of analyses of different real samples. The good agreements between the results obtained by two methods show the applicability of the method to real sample analyses from analytical point of view.

Table 2: Determination of Ag(I) in some real water samples (results of recoveries of spiked samples) and photographic solution using the proposed kinetic method and atomic absorption method.

Samples	Silver added (µg L ⁻¹)	Proposed kinetic method		Standard method ^e		Student t-test ^b	F-test ^c
		Silver found±SD ^a (µg L ⁻¹)	Recovery %	Silver found±SD ^a (µg L ⁻¹)	Recovery %		
Tap water ^d	5.0	4.98±0.02	99.6	4.96±0.03	99.2	1.87	2.24
	10.0	9.97±0.03	99.7	9.98±0.02	99.8	1.37	1.76
Drinking water samples							
DW ₁	-	2.93±0.04	-	2.95±0.04	-	0.89	1.78
	5.0	7.84±0.03	98.2	7.90±0.03	99.0	0.77	2.78
	10.0	12.94±0.03	100.1	12.97±0.02	100.2	1.01	4.00
DW ₂	-	2.85±0.02	-	2.87±0.03	-	1.05	1.56
	5.0	7.84±0.03	99.8	7.86±0.03	99.8	1.56	1.96
	10.0	12.88±0.03	100.3	12.89±0.02	100.2	0.62	2.25
DW ₃	-	2.95±0.03	-	2.92±0.03	-	0.62	2.25
	5.0	7.87±0.02	98.4	8.02±0.03	102.0	1.24	2.25
	10.0	12.97±0.03	100.2	12.93±0.02	100.1	1.24	2.25
Pond water	-	23.5±0.04	-	24.0±0.03	-	0.74	2.30
	10.0	33.8±0.02	103.0	34.2±0.02	102.0	1.27	2.38
Photographic solution	-	21 µg L ⁻¹	-	23 µg L ⁻¹	-	0.76	2.34

^a Mean±standard deviation (n:5); ^b Tabulated t-value for 8 degrees of freedom at confidence level of 95% or probability level of 0.95 is 2.306; ^c Tabulated F-value for (4,4) degrees of freedom at probability level of 0.95 is 6.39; ^d Tap water gave no detection test for silver ion and ^e The values obtained by using standard atomic absorption spectrometric method.

Table 3 A few various analytical methods used for the determinations of silver at trace and/or ultra trace levels.

No	Reagents	Activator	Concentration range of determination Ag^+ ($\mu\text{g mL}^{-1}$)	Detection limit ($\mu\text{g L}^{-1}$)	Observations	Reference
1	Fuchsin- $\text{S}_2\text{O}_8^{2-}$	1,10-phenantroline	0.002-0.020	0.7	At pH 5.0 Fixed-time method	[34]
2	Antipyrine 8-hydroxyquionilone + $\text{S}_2\text{O}_8^{2-}$ ^{azo}	2,2'-Bipyridyl	(1-10) $\times 10^{-2}$	0.5	pH 3.06	[37]
3	1,2-Diaminoethane + $\text{S}_2\text{O}_8^{2-}$	-	(5.4-860) $\times 10^{-3}$	5	-	[38]
4	Pyrocatechol-1-aldehyde 2-pyridylhydrazone + $\text{S}_2\text{O}_8^{2-}$	1,10-phenantroline	(1-8) $\times 10^{-2}$	2	pH 8.2	[39]
5	Oxine-5-sulfonic acid + $\text{S}_2\text{O}_8^{2-}$	-	(6-30) $\times 10^{-3}$	3	Dithizone extraction pH 2.2	[40]
6	$[\text{Fe}(\text{CN})_6]^{4-}$ +HMBPTS ^a	-	0.004-0.13	0.87	In acidic medium	[41]
7	Thionine+ $\text{S}_2\text{O}_8^{2-}$	1,10-phenantroline	0.0002-0.01	0.098	In diluted H_2SO_4 medium, fixed-time method	[42]
8	$[\text{Fe}(\text{CN})_6]^{4-}$ +TPTZ ^b	-	0.005-0.41 at 405 nm and 0.01-0.61 at 600 nm	1.6	pH 2.0	[43]
9	Salicylic acid+ $\text{S}_2\text{O}_8^{2-}$	2,2'-bipyridyl	0.0043-0.0388	0.384	At pH 5.0 and 40°C, fixed-time method	[44]
10	Indigo carmine+ $[\text{Fe}(\text{CN})_6]^{3-}$	-	0.0-2.0, 0.0-70.0 and 0.0-100.0	130, 2300 (2400) and 5400 (5500)	At pH 6.0, Fixed-time method, initial rate method	[45]
11	New fuchsin+ $\text{S}_2\text{O}_8^{2-}$	1,10-phenantroline	0.002-0.02 and 0.020- 0.05	0.475	At pH 5.0 and 25°C, initial rate method	The present method

^a2-Hydroxy-4-methoxybenzophenone thiosemicarbazone^b2,4,6-tripyridyl 1,3,5-triazine

CONCLUSIONS

In the present study, a new catalytic Ag(I) determination method based upon the oxidation of new fuchsin with peroxodisulphate in presence of 1,10-phenantroline as activator at pH 5.0 has been proposed. Under the optimum conditions, the calibration curves were obtained for two different concentration ranges. These calibration curves are as follows: $\tan\alpha: 9.18 \times 10^{-3} + 4.32 \cdot 10^{-4} C_{\text{Ag(I)}}$ in the concentration range of 2–20 $\mu\text{g L}^{-1}$ Ag^+ and $\tan\alpha: -5.83 \times 10^{-3} + 7.94 \cdot 10^{-4} C_{\text{Ag(I)}}$ in the concentration range of 20–50 $\mu\text{g L}^{-1}$ Ag^+ with correlation coefficients (r) of 0.9850 and 0.9950. The proposed kinetic method offers several distinct advantages: high selectivity, sensitivity, ease of operation and rapidity. The developed kinetic method is recommended to analyze photographic developing solutions and different water samples because the cheaper reagents are necessary and the instrument needs only minimum maintenance. The advantages of the present kinetic method over the previously reported methods [34,37-45] are summarized in Table 3. Especially it can clearly be seen that new fuchsin gives a wider linear range of 2-50 $\mu\text{g L}^{-1}$ and a lower detection limit of 0.475 $\mu\text{g L}^{-1}$ for determination of Ag(I) when it is compared with those of Fuchsin having a detection limit of 0.7 $\mu\text{g L}^{-1}$, a narrower linear range of 2-20 $\mu\text{g L}^{-1}$ and a similar molecular structure [34] and other studies except for those of reference [42]. This increase in sensitivity can be explained the fact that electron-donor methyl groups locating at o-position according to basic amine groups causes to shift the measurement wavelength of indicator substance to a red region of $\Delta\lambda: 3$ nm at pH 5.0. Another reason of this increase in sensitivity is the fact that initial rate method used in the present study, gives a more sensitive responds to the fast indicator reactions according to the fixed-time method. Although the catalytic reaction between Salicylic acid and $\text{S}_2\text{O}_8^{2-}$ in the presence of 2,2'-bipyridyl as an activator [44] has a low detection limit of 0.384 $\mu\text{g L}^{-1}$, it has a narrow linear range of 9 fold and high reaction temperature of 40°C at pH 5.0 when it was compared with those of the present kinetic method.

ACKNOWLEDGEMENTS

The authors are very grateful to Prof. Dr. Mehmet AKÇAY for providing laboratory facilities to do the relevant scientific study during the preparation of this paper. They are especially indebted to the authorities of Chemistry

Department for their generous help in supplying instrumental tools and all chemicals including indicator dye and other chemical reagents in analysis.

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