

SPECTROPHOTOMETRIC REACTION RATE METHOD FOR THE DETERMINATION OF SILVER BASED ON ITS CATALYTIC EFFECT ON THE OXIDATION OF GALLOCYANINE BY PEROXYDISULPHATE

A.A. Ensafi* and K. Zarei

*Department of Analytical Chemistry, College of Chemistry, Isfahan University of Technology, Isfahan,
Islamic Republic of Iran*

Abstract

A sensitive and selective procedure was developed for the spectrophotometric determination of silver by its catalytic effect on the oxidation of gallocyanine by peroxydisulphate in acidic media at 540 nm. Silver can be determined in the range of 0.001-0.500 $\mu\text{g/ml}$ with a limit of detection of 0.0005 $\mu\text{g/ml}$, by a fixed-time method of 4.0 min from initiation of the reaction. The relative standard deviation for ten replicate determinations of 0.050 $\mu\text{g/ml}$ of Ag(I) is 1.4%. This method was used for the determination of silver in real samples.

Introduction

Many workers have reported the use of catalyzed reactions for the determination of trace silver ion. These methods include spectrophotometry [1,2], electrochemistry [3,4], and atomic spectroscopy [5-7]. Because of their simplicity, sensitivity and selectivity, kinetic methods, in particular those based on catalytic reaction, have continued to receive attention.

The silver-catalyzed oxidation of organic reagents by peroxydisulphate in the presence of an activator has been widely utilized [8-16] as can be seen in Table 1. But many of these methods are inadequate because of a small linear dynamic range and/or high limits of detection, and many have interfering species for the determination of silver.

Keywords: Catalytic; Silver; Gallocyanine

In this paper, we describe a kinetic spectrophotometric method for the determination of silver based on its catalytic effect on the oxidation of gallocyanine (GL) by peroxydisulphate using 1,10-phenanthroline as activator, as well as the optimum conditions, kinetic parameters and analytical characterization for determining trace amounts of silver in real samples. The method has a wider linear dynamic range and fewer interfering ions, with low limit of detection.

Experimental Section

Apparatus

A Shimadzu model 240 spectrophotometer with 1.0 cm glass cell was used for recording the absorbance spectra. A Perkin-Elmer model 35-spectrophotometer with a 1.0 cm glass cell was used for the absorbance measurements at 540 nm. A thermostat bath (Gallenkamp Griffin, BGL-240 V) was used to keep the reaction temperature at 30°C.

*To whom all correspondence should be addressed

Reagents

All the solutions were prepared from doubly distilled water. Working solutions were all kept in a water bath at 30°C, and analytical-reagent grade chemicals were used.

Standard silver solution (1000 µg/ml) was prepared by dissolving 0.1580 g of silver nitrate (Merck) in water, following which the solution was diluted to the mark in a 100-ml standard flask with water. A working standard solution was prepared daily from stock solution.

Potassium peroxydisulphate solution (0.1125 M) was prepared by dissolving 3.0411 g $K_2S_2O_8$ (Merck) in water and the solution was diluted to the mark with water in a 100-ml standard flask.

1,10-Phenanthroline solution (0.0450 M) was prepared by dissolving 0.892 g of 1,10-phenanthroline (Merck) in ethanol in a 100-ml standard flask.

Gallocyanine solution (GL) (8.33×10^{-4} M) was prepared by dissolving 0.0252 g of gallocyanine (Aldrich) in 50 ml of 10^{-5} M sodium hydroxide and the solution was diluted to the mark with water in a 100-ml standard flask.

Recommended Procedure

The reaction was followed spectrophotometrically by measuring the change in absorbance at 540 nm by a fixed-time method for the first 4.0 min from initiation of the reaction.

Transfer a sample solution containing not more than 1.00 µg of Ag(I) to a 10-ml standard flask. Add, in the following order, 1.0 ml of 0.060 M sulphuric acid (or buffer, pH = 2), 1.0 ml of 0.045 M 1,10-phenanthroline and 1.0 ml of 8.33×10^{-4} M GL. Dilute the solution to ca. 8 ml with water and then add 1.0 ml of 0.112 M potassium peroxydisulfate. Then dilute the solution to the mark with distilled water and mix well. Measure the time after addition of last drop of peroxydisulphate solution. Then transfer a portion of the solution to the cell within 30 sec after initiation of the reaction. Measure the absorbance against water at 540 nm for 0.5-4.0 min after initiation of the reaction. Label the decrease in absorbance of the sample and blank as ΔA_s and ΔA_b , respectively. The calibration graph can then be constructed by plotting $\Delta A_s - \Delta A_b$ at a fixed-time vs. Ag(I) concentration and slope (dA/dt) vs. Ag(I) concentration for fixed-time and slope methods, respectively. For a higher concentration of Ag(I) (0.100-0.500 µg/ml), 3.0 ml of 8.33×10^{-4} M GL solution, with the same concentration as the other reagents described above, was used.

Determination of Silver in River Water

To 1000 ml of water sample, add 35 ml of concentrated nitric acid and 3 ml of sulphuric acid, and evaporate almost to dryness. Add 10 ml of concentrated nitric acid

and evaporate again. Cool to room temperature, add distilled water to dissolve the residue and make up to exactly 50 ml. Analyze suitable aliquot by the proposed method.

Determination of Silver in Developed Panchromatic Plates

Treat a known amount (about 1.0159 g) of the plate with 25 ml of 3 M sodium hydroxide until the gelatinous film separates from the rigid support, which is discarded after washing. Then add 25 ml of concentrated nitric acid and heat until the silver has dissolved completely. Filter and make up to volume in a 100-ml standard flask with water. Analyze suitable aliquot by the proposed method above.

Results and Discussion

GL is a dye that can be oxidized by peroxydisulfate in acidic media at a slow rate, but GL underwent rapid oxidation when Ag(I) at the ng/ml level was added. This process was monitored spectrophotometrically by measuring the decrease in absorbance of the characteristic band of GL (540 nm), due to consumption of the dye (Fig. 1). The rate equation for the uncatalyzed reaction can be written as:

$$(\text{rate})_{uc} = k_{uc} [\text{GL}]^a [\text{S}_2\text{O}_8^{2-}]^b \quad (1)$$

and for the catalyzed reaction as:

$$(\text{rate})_c = k_c [\text{GL}]^a [\text{S}_2\text{O}_8^{2-}]^b [\text{Ag(I)}] \quad (2)$$

where k_{uc} and k_c are rate constants for the uncatalyzed and catalyzed reactions, respectively. These equations also include the concentration of the activator, 1,10-phenanthroline. The letters a and b are the order for GL and $\text{S}_2\text{O}_8^{2-}$, and are equal to one at low concentrations of GL (3.58×10^{-5} - 8.0×10^{-5} M) and $\text{S}_2\text{O}_8^{2-}$ (2.5×10^{-3} - 9.0×10^{-3} M), respectively.

The concentration of $\text{S}_2\text{O}_8^{2-}$ is large when compared to Ag(I) and GL, thus equation (1) can be written as:

$$(\text{rate}) = k'_c [\text{GL}] [\text{Ag(I)}] \quad (3)$$

The kinetic equations of (1) and (2) are of the same type as those for the inactivated reaction, indicating that the activator does not change the reaction mechanism, but by only accelerates the rate-determining step of the reaction. Because of the reaction kinetic to be followed during the initial period of the reaction, equation (3) can be simplified by using Lambert-Beer's law for the change

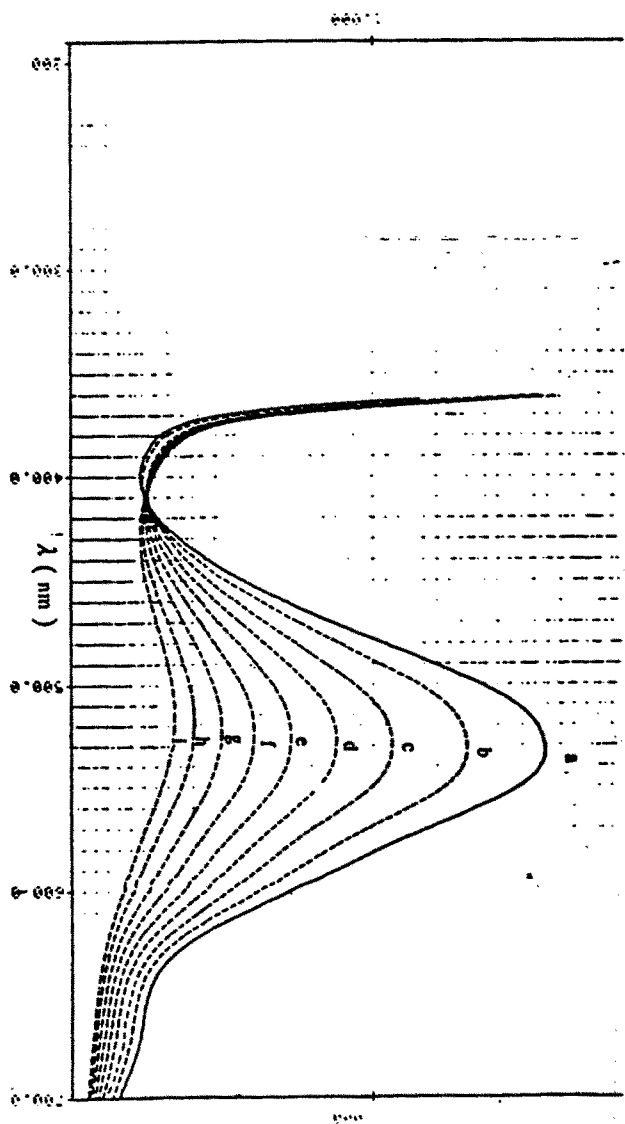


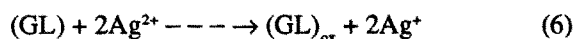
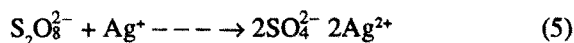
Figure 1. Variation of GL-S₂O₈²⁻-Ag(I) system with time. Conditions: H₂SO₄, 0.0060 M; GL, 8.33 × 10⁻⁵ M; 1,10-phenanthroline, 0.0045 M; S₂O₈²⁻, 0.0125 M; Ag(I), 0.050 μg/ml; at 30°C, and interval time of a: 75, b: 180, c: 240, d: 300, e: 400, f: 500, g: 600, and h: 700 sec from initiation of the reaction.

in concentration of GL for a period of a fixed time of reaction:

$$-d[GL]/dt = (\text{rate}) = \Delta A = k[Ag(I)] \quad (4)$$

Equation (4) was used for the determination of the reaction rate in the initial period of the reaction.

It is also known that the catalytic reactions are based on redox mechanisms in which the metal catalyst acts via a redox cycle [17, 18], according to the following scheme:



The overall reaction rate is dependent on the rate of the reaction step $Ag(I) \text{---} \rightarrow Ag(II) + e$, and an acceleration of this step causes an increase in the overall reaction rate. 1, 10-Phenanthroline is an organic reagent that accelerates the formation of Ag(II) [19], and for our system, 1,10-phenanthroline was found to be an activator of this step.

The initial reaction rate increases proportionally to the silver concentration, the log-log plots show a first-order dependence on the Ag(I) concentration. The apparent rate constants for the uncatalyzed and catalyzed reactions are 1.65 × 10⁻⁵ and 1.40 × 10² s⁻¹, respectively.

Effect of Variables

Ideally for kinetic-based measurements, the optimum concentration of each reacting constituent, except the analyte, will be the one which yields the smallest relative standard for the rate measurement and is in a region which is zero order with respect to that species. The latter conditions are desired so that small fluctuations in concentration will have no effect on the initial rate. Conditions should also be chosen so that the initial rate is first order with respect to the analyte. To obtain kinetic and optimization information and a calibration curve, each kinetic study was repeated at least three times to ensure the reproducibility of the results.

The dependence of the reaction rate on the acidity of the solution was studied in the pH range of 1.8-6.0. The acidity in the pH range of 1.8-2.5 was adjusted by the addition of a suitable amount of sulphuric acid. For the pH range 2.5-6.0, buffers were made from phosphoric acid/sodium hydroxide solution. The results are shown in Figure 2. Maximum and constant catalytic action is observed for pH = 2 with sulphuric acid. This pH value was achieved when 1.0 ml of 0.060 M H₂SO₄ solution was added to the mixture of the reaction in the final 10 ml solution. The reaction rate decreased at higher pH values (>2), because the activity of peroxydisulphate decreased by increasing pH. On the other hand, at higher acid concentrations, GL is protonated and the reaction rate was decreased.

The effect of GL concentration on the rate of reaction for a range of 3.58 × 10⁻⁵ - 1.79 × 10⁻⁴ M GL concentration was studied in the presence of 0.100 μg/ml Ag(I). Figure 3 shows that the sensitivity increases up to 8.33 × 10⁻⁵ M GL concentration, whereas at higher concentrations, the reaction rate decreased. This effect may be due to the change in reaction mechanism. Thus 8.33 × 10⁻⁵ M GL concentration was selected for the study.

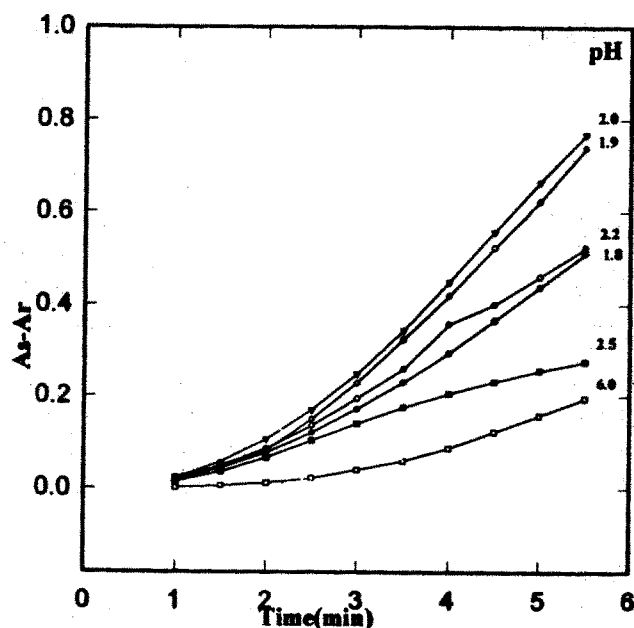


Figure 2. Effect of pH on the reaction rate. Conditions: $S_2O_8^{2-}$, 0.0125 M; GL, 1.19×10^{-4} M; 1,10-phenanthroline, 0.0050 M; Ag(I), 0.100 $\mu\text{g/ml}$; temperature 30°C and 4.0 min from initiation of the reaction.

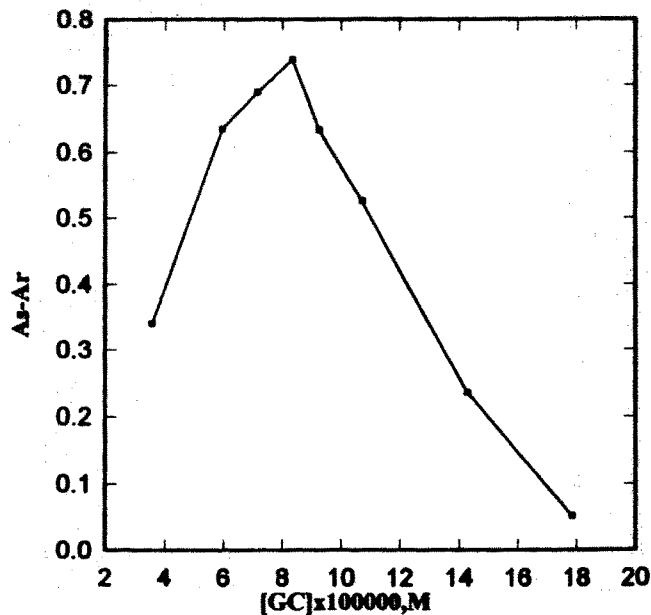


Figure 3. Effect of GL concentration on the reaction rate. Conditions H_2SO_4 , 0.0060 M; $S_2O_8^{2-}$, and others as in Figure 2.

The effect of potassium peroxydisulphate concentration for the reaction was studied in the presence of 0.100 $\mu\text{g/ml}$ Ag(I) (Fig. 4). The results show that the sensitivity increases up to 0.01125 M $S_2O_8^{2-}$. At higher

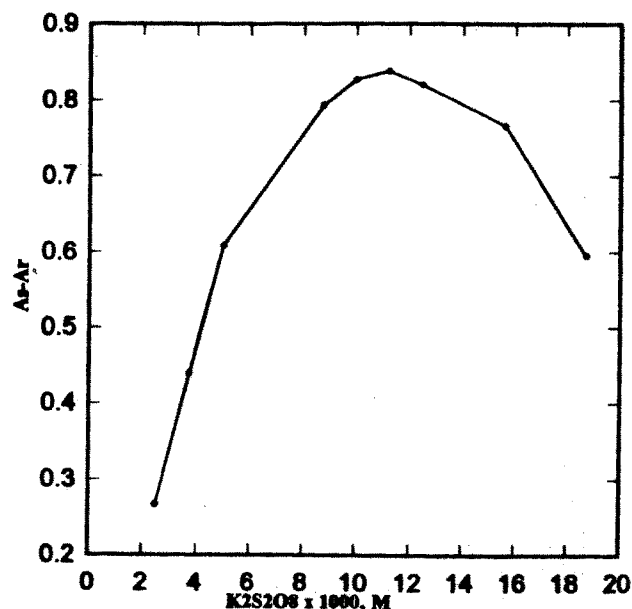


Figure 4. Effect of peroxydisulphate concentration on the rate of reaction. Conditions as in Figure 3 with 8.33×10^{-5} M GL.

concentrations of the reagent, the sensitivity was decreased, owing to the rate increases for the blank reaction. Thus 0.01125 M peroxydisulfate was used for the study.

The effect of some N-donor substances previously employed for activation of Ag(I)-catalyzed oxidation reaction [18,19] was examined, and their efficiency was found to decrease in order: 1,10-phenanthroline, 4-aminopyridine, 2,2-bipyridine and ammonia. Thus 1,10-phenanthroline was chosen, and it was found that with the addition of 1.0 ml of 0.045 M 1,10-phenanthroline to the reaction mixture, maximum sensitivity was achieved (Fig. 5). According to Bontschev and co-workers [8,12], activators of 2,2-bipyridyl type accelerate the rate-determining step of the process, the oxidation of Ag(I) to Ag(II).

The temperature dependence of the reaction rate was studied in the range of 0-50°C at optimum pH and reagent concentrations. The results show that 30°C gives maximum sensitivity. At a higher temperature, the sensitivity decreased owing to the decrease in $\Delta A_c - \Delta A_b$; this means that at temperatures greater than 30°C, the rate of the uncatalyzed reaction increases with temperature to a great extent, thus the difference between the rate of reaction with and without silver ion ($\Delta A_c - \Delta A_b$) diminished at higher temperatures. Therefore, 30°C was used for the study.

The effect of ionic strength on the rate of reaction

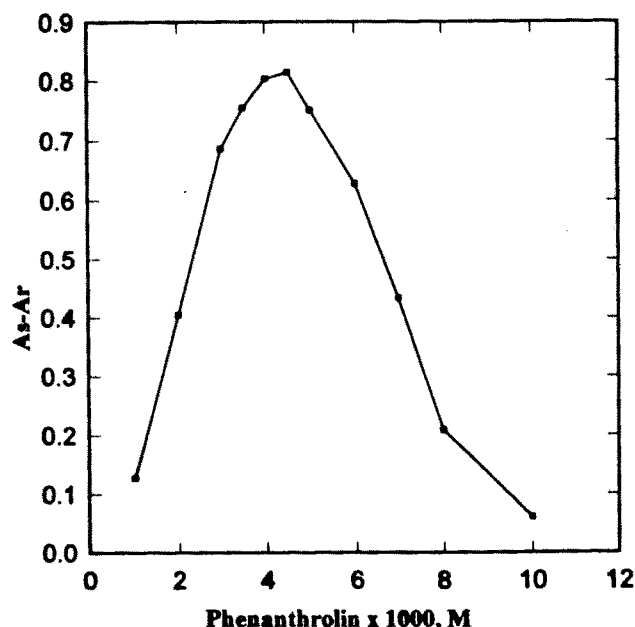


Figure 5. Effect of 1,10-phenanthroline concentration on the rate of reaction. Conditions as in Figure 4 with 0.0125 M S₂O₈²⁻.

under optimum conditions with and without Ag(I) was studied using NaNO₃ solution (3.0 M). The results show that the reaction rate decreased by slowly increasing ionic strength.

Calibration Graphs

Calibration graphs were obtained by applying the fixed-time and initial rate (slope) methods.

Fixed-Time Method

Under the optimum conditions described above, the effect of time to give the best sensitivity and regression coefficient was studied. From the results, a fixed-time of 4.0 min from initiation of the reaction was selected due to its reproducibility and its speed. With 0.0060 M H₂SO₄, 8.33 × 10⁻⁵ M GL, 0.01125 M S₂O₈²⁻ and 0.0045 M 1,10-phenanthroline, for the concentration range of 0.001-0.100 µg/ml Ag(I), the following regression equation was obtained: ΔA = -0.0016 + 7.55C with r = 0.9985 and variance of 1.82 × 10⁻⁴; and with 2.51 × 10⁻⁴ M GL, 0.01125 M S₂O₈²⁻, 0.0045 M 1,10-phenanthroline, and 0.0060 M H₂SO₄, for the range of 0.100 -0.500 µg/ml silver ion, the following regression equation is obtained: ΔA = -0.0098 + 0.1899C with r = 0.9989 and variance of 6.686 × 10⁻⁶ where C is µg/ml Ag(I) and ΔA is the absorbance change for the sample reaction minus absorbance change for the blank reaction for 0.5-4.0 min from initiation of the reaction (A_s-A_b).

Initial Rate Method

A plot of reaction rate (first 240 sec) vs. silver concentration under optimum conditions for the concentration range of 0.010-0.100 µg/ml silver ion,

Table 1. Characteristics of the kinetic photometric methods for silver determination (S₂O₈²⁻ as the oxidant)

Substrate	pH	Activator	Range of applicability (ng/ml)	Detection limit (ng/ml)	Ref.
Sulphanilic acid	4.35	2,2'-Bipyridyl	0.4-3.0	0.4	8
1,2-Diaminoethane	---	---	0.4-70.0	---	9
Pyrocatechol derivative	8.0	1,10-Phenanthroline	10.0-80.0	---	10
Pyrogallo Red	2.0	1,10-Phenanthroline	0.26-0.88	0.26	11
Ce(IV)*	1.6	Starch	0-16	---	12
Ce(IV)*	1.6	2,2'-Bipyridyl	0-4	---	13
Carmin	5.0	---	0.2-24	0.1	14
2-Hydroxybenzaldehyde					
Thiosemicarbazone	ammonia	---	50-400	50	15
Phloxin	5.0	---	3-100	1	16

*: Chlorine was used as an oxidant

with 0.0060 M H_2SO_4 , 8.33×10^{-5} M GL, 0.01125 M $S_2O_3^{2-}$ and 0.0045 M 1,10-phenanthroline, the following regression equation was obtained: Slope = $0.0193 + 2.498 C$ with $r = 0.9991$ and variance of 5.676×10^{-5} ; and with 2.51×10^{-4} M GL, 0.01125 M $S_2O_3^{2-}$, 0.0045 M 1,10-phenanthroline, and 0.0060 M H_2SO_4 , for 0.100-0.500 $\mu g/ml$ Ag(I): Slope = $2.70 \times 10^{-3} + 0.0988C$ with $r = 0.9992$ and variance of 4.37×10^{-6} , where C is the concentration of Ag(I) in $\mu g/ml$.

The tolerance limit of Br, Cl, I, and $S_2O_3^{2-}$ can be increased to 1000-fold by addition of 1.0 ml of concentrated HNO_3 into 10 ml of the sample solution and heated to dryness.

Determination of Silver Ion in River Water and in Developed Panchromatic Plates

As a practical application, the methods were applied to the determination of silver in river water and in

Table 2. Determination of silver in real samples

Sample	Silver found					
	Proposed method	S_1 (n=q)	Atomic absorption method*	S_2 (n=5)	t**	F**
River water (1)	8.75 ng/ml	0.20	8.85 ng/ml	0.40	0.15	3.06
River water (2)	2.38 ng/ml	0.40	2.45 ng/ml	0.45	0.20	1.28
Photographic plate	0.0051%	9.2×10^{-5}	0.0052%	9.0×10^{-5}	0.47	1.04

*: After preconcentration by boiling of 1000 ml of sample to reduce its volume to 10 ml

**: Theoretical values for t and F at the 5% level are 2.18 and 8.98 respectively

The experimental limit of detection is 0.0005 $\mu g/ml$ and 0.003 $\mu g/ml$ of Ag(I) for a fixed-time and slope method, respectively. The relative standard deviation for ten replicate determinations of silver ion with a fixed-time method is 2.2% and 1.4% for 0.050 and 0.200 $\mu g/ml$ Ag(I), respectively.

Interferences

More than forty substances in the solution were studied for their possible influence on the determination of 0.100 $\mu g/ml$ of silver ion by the proposed method. The results show that large amounts of alkali and alkaline earth metal cations did not interfere. There were no effects from a 1000-fold Al(III), NH_4^+ , La(III), $C_2O_4^{2-}$, ClO_4^- , BrO_3^- , ClO_3^- , $B_4O_7^{2-}$, PO_4^{3-} , HCO_3^- , $P_2O_7^{2-}$, SO_3^{2-} , acetate and citrate and 500-fold of U(VI), Cd(II), and SCN⁻; 10-fold of Ni(II), V(III), Co(II), Ce(IV), Zn(II), Hg(II), Mn(II), F⁻, NO_2^- ; 50-fold of Cl⁻, Th(IV), and Fe(III) do not interfere. But more than 10-fold of Cu(II), Br⁻, I⁻, $S_2O_3^{2-}$ interfere. The interference of these ions is due to the reaction of silver ion with anions or the catalytic effect of Cu(II) on the reaction.

developed panchromatic plates used in offset printing. Samples were taken from exposed and unexposed parts of each plate, and suitable aliquots of solutions were analyzed by the proposed method, and also by atomic absorption spectrometry after preconcentration for river water. Table 2 shows the agreement between the results, these were also compared with standard atomic absorption spectrometric by statistical methods.

Conclusion

The suitability of the GL- $S_2O_3^{2-}$ -Ag(I) system for the development of a kinetic spectrophotometric method for determining ultratracess of Ag(I) as low as 0.0005 $\mu g/ml$ which is sensitive, precise, rapid, and relatively selective has been demonstrated. The method is more sensitive and selective than other catalytic methods and can be used for the determination of Ag(I) in real samples. The method was accurate and precise when compared with the standard method (Table 2). The fixed-time method has a low limit of detection when compared with the slope method.

References

1. Escobar, R. and Perez, A.G. *Analyst*, **111**, 1297, (1986).
2. Al-Jabari, C. and Jaselskis, B. *Talanta*, **34**, (5), 497, (1987).
3. Elsner, U. and Mark, H.B. *J. Electroanal. Chem.*, **24**, 345, (1970).
4. Wang, J. and Martinez, T. *Anal. Chim. Acta*, **207**, 95, (1988).
5. Nakashima, R., Sasaki, S. and Shibata, S. *Ibid.*, **77**, 65, (1975).
6. Howlett C. and Taylor, A. *Analyst*, **130**, 916, (1978).
7. Ferreira, N.P. and Butler, L.R.P. *Ibid.*, **103**, 607, (1978).
8. Bontscheve, P.R., Alexiev, A. and Dimitrova, B. *Talanta*, **16**, 597, (1969).
9. Jonnalagadda, S.B. *Anal. Chim. Acta.*, **144**, 245, (1982).
10. Afonso, A.M., Santana, J.J. and Garcia, F. *Talanta*, **33**, 779, (1986).
11. Sevillano-Cabeza, A., Medina-Esrich, J., Bat-Estelles, M.L. and Martin-Penella, M. *Analyst*, **111**, 1417, (1986).
12. Zhu, H., Peng, A. and Yang, X. *Fenxi Huaue*, **20**, 742, (1992). (*Chem. Abstr.*, **117**, 142468a, (1992)).
13. Zhu, H., Peng, A. and Wu, Z. *Fenxi Shiyanshi*, **11**, 31, (1992). (*Chem. Abstr.*, **118**, 138804b, (1993)).
14. Wang, X. and Zhang, X. *Guijinshu*, **12**, 58, (1991). (*Chem. Abstr.*, **117**, 39331t, (1992)).
15. Moreno, A., Silva, M. and Bendito, D.P. *Anal. Letters*, **16**, 747, (1983).
16. Cordoba, M.H., Sanchez-Pedreno, C. and Vinas, P. *Quim. Anal.*, **4**, 159, (1985).
17. Latinen, H.A. and Harris, W.E. *Chemical analysis*, (2nd edn), p. 308. McGraw-Hill, (1975).
18. Anderson, J.M. and Kochi, J.K. *JACS.*, **25**, 1651, (1970).
19. Bontchev, P.R. and Aleksiev, A.A. *Teor. Eksp. Khim.*, **9**, 191, (1973).