

Original Research Article

A Rapid Spectrophotometric Method for the Determination of Trace Level Silver Using 1, 5-Diphenylthiocarbazone in Aqueous Micellar Solutions

Abstract

A very simple, ultra-sensitive and fairly selective non-extractive spectrophotometric method is presented for the rapid determination of silver at ultra-trace level using 1,5diphenylthiocarbazone(dithizone) as a new micellar spectrophotometric reagent ($\lambda_{\text{max}} = 495 \text{ nm}$) in a slightly acidic (0.1-1.0 M H_2SO_4) aqueous solution. The presence of a micellar system avoids the previous steps of solvent extraction and reduces the cost, toxicity while enhancing the sensitivity, selectivity and molarabsorptivity. The average molar absorptivity of the Ag - dithizone complex formed in presence of anionic sodium dodecyle sulfate (SDS) surfactant was found to be $1.6 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ which was almost 10 times higher than the value observed ($1.0 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) in the standard method, resulting in an increase in the sensitivity of the method. The reaction is instantaneous and the absorbance remains stable for over 24 h. The Sandell's sensitivity was found to be 10 ng cm^{-2} of Ag. Linear calibration graphs were obtained for $0.07\text{-}10 \text{ mg L}^{-1}$ of silver ; the stoichiometric composition of the chelate is 1:1 (Ag : dithizone). The method is characterized by a limit of detection and limit of quantitation of $1 \text{ }\mu\text{g L}^{-1}$ and $10\mu\text{g L}^{-1}$, respectively of Ag . Large excess of over 50 cations, anions and complexing agents (e.g. EDTA, tartrate, oxalate, citrate, phosphate, azide) do not interfere in the determination. The method was successfully applied to a number of environmental water samples (potable and polluted), biological samples (human blood and urine), photographical samples and soil samples. The method has high precision and accuracy ($s = \pm 0.01$ for 0.1 mg L^{-1}).

Keywords: *Micellar spectrophotometry; silver; 1,5-diphenylthiocarbazone; sodium dodecyle sulfate; environmental; biological; photographical; soil samples.*

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36 **Introduction**

37 Silver is a useful element in many respects, it has an important role in electrical and electronic
38 applications, photographic film production and the manufacturing of fungicides¹. Silver
39 compounds and alloys have been widely used in dental and pharmaceutical preparations because
40 of their marked antibacterial properties². Silver is considered toxic for humans and the
41 recommendations of the World Health Organization (WHO) permit maximum concentrations
42 of 0.01 mg L⁻¹ of silver ions in drinking water disinfection, but the United States
43 Environmental Protection Agency (USEPA) recommends 0.05 mg L⁻¹ as maximum³. Silver is
44 both vital and toxic for many biological systems and its content in environmental samples is
45 increased with the increasing use of silver compounds and silver-containing products in
46 industry and in medicine⁴. Silver can enter into the environment via industrial waters and might
47 pose a potential risk as water pollutant. Thus, separation, pre-concentration and sensitive
48 determination of silver ion is of increasing interest⁵.

49 1,5-Diphenylthiocarbazone is one of the most widely used photometric reagents and forms
50 colored water-insoluble complexes with a large number of metal ions. Metal-dithizone
51 complexes are water insoluble and thus their determination requires a prior solvent extraction
52 step into CHCl₃ or CCl₄⁶⁻⁷, followed by spectrophotometric determinations. Since these methods
53 involve solvent extraction are lengthy and time-consuming and lack selectivity due to much
54 interference⁸, CHCl₃ and CCl₄ have been listed as toxic and as environmental pollutants⁹ i.e.
55 carcinogens by the ATSDR and EPA¹⁰, This problem has been overcome in recent years by
56 introducing a hydrophobic micellar system generated by a surfactant similar to that employed in
57 phase-transfer reactions¹¹⁻¹².

58 Micellar systems are convenient to use because they are optically transparent, readily available,
59 relatively non-toxic and stable¹³. Nevertheless, the addition of surfactants at concentrations
60 above the CMC to an aqueous medium to form a micellar solution is the most commonly
61 preferred procedure today. A non-ionic surfactant, like Triton X-100¹⁴⁻¹⁵ and Sweed 80¹⁶, have
62 been used for the spectrophotometric determination of several metal ions. Similarly, a few
63 anionic surfactants have been used¹⁷.

64 The aim of the present study is to develop a simpler direct spectrophotometric method for the
65 trace determination of silver with dithizone in the presence of inexpensive anionic micelles, such
66 as sodium dodecyl sulfate, in aqueous solutions. This method does not require a solvent-extraction
67 step; hence, the use of carcinogenic CCl₄ or CHCl₃ is avoided. The method described here has
68 recorded for the first time the non-extractive direct spectrophotometric determination of Ag in

69 aqueous media without the recourse of any “clean-up” step. This method is far more selective,
 70 sensitive, non-extractive, simple and rapid than all of the existing spectrophotometric
 71 methods¹⁸⁻²². This method is very reliable and a concentration in the ng g^{-1} range in an aqueous
 72 medium at room temperature ($25 \pm 5^\circ\text{C}$) can be measured in a very simple and rapid way.

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74 **Experimental Section**

75 ***Instrumentation***

76 Shimadzu (Kyoto, Japan) (Model-1800) double beam UV/VIS the recording spectrophotometer
 77 and a Jenway (England, U.K) (Model-30100) pH meter with a combination of electrodes were
 78 used for the measurements of absorbance and pH, respectively. A Varian (Australia) ICP – MS
 79 spectrophotometer was used for comparing the results.

80 **Chemicals and reagents**

81 All of the chemicals used were of analytical reagent grade or the highest purity available.
 82 Doubly distilled deionized water, which is non-absorbent under ultraviolet radiation, was used
 83 throughout. Glass vessels were cleaned by soaking in acidified solution of KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$
 84 followed by washing with concentrated HNO_3 and rinsed several times with deionized water.
 85 Stock solutions and environmental water samples (1000-mL each) were kept in polypropylene
 86 bottles containing 1-mL of concentrated HNO_3 . More rigorous contamination control was
 87 applied when the silver levels in the specimens were low.

88 ***Sodium dodecyl sulfate (SDS) solution (1%):***

89 A 100 mL of SDS solution was prepared by dissolving 1g of pure sodium dodecyl sulfate
 90 (SDS) (E. Merck, Darmstadt, Germany) in doubly distilled de-ionised water using ultrasonic
 91 bath.

92 ***1,5-diphenylthiocarbazone solution $1 \times 10^{-3} \text{ M}$:***

93 This solution was prepared by dissolving the requisite amount (0.025%) of 1,5-
 94 diphenylthiocarbazone (E. Merck, Germany) in a known volume of absolute ethanol. More
 95 dilute solutions of the reagent were prepared as required.

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97 ***Standard silver solution $9 \times 10^{-3} \text{ M}$:***

98 A stock solution (1000 mg L^{-1}) of Ag was prepared by dissolving 0.1575 g of silver nitrate (
 99 Merck, Germany) in 100 mL of doubly distilled deionized water. The working standard of
 100 silver solution was prepared by suitable dilutions of this stock solution.

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Tartrate solution:

A 100-mL stock solution of tartrate (0.01%) was prepared by dissolving 10 mg of A.C.S. grade (99%) potassium sodium tartrate tetrahydrate in (100-mL) deionized water.

Dilute ammonium hydroxide solution (NH₄OH) :

A 100-mL solution of dilute ammonium hydroxide was prepared by diluting 10-mL concentration. NH₄OH (28-30% A.C.S. grade) to 100-mL with deionized water. The solution was stored in a polypropylene bottle.

1,10-Phenanthroline solution:

A 0.1% 1,10-phenanthroline solution was prepared by dissolving 0.1 gm amount in 100-mL slightly hot deionized water.

Sodium azide solution:

A 100-mL sodium azide solution (2.5 % w/v) (Fluka purity > 99%) was freshly prepared by dissolving 2.5 gm in 100-mL of deionized water.

EDTA solution:

A 100-mL stock solution of EDTA (0.01%) was prepared by dissolving 10 mg of A.C.S. grade (≥90%) ethylenediaminetetraacetic acid, disodium salt dehydrate in (100-mL) deionized water.

Other solutions

Solutions of a large number of inorganic ions and complexing agents were prepared from their analytical grade or equivalent grade, water soluble salts. In the case of insoluble substances, special dissolution methods were adopted²³.

General Procedure

To 0.1-1.0 mL of a slightly acidic solution containing 0.7-100 μg of silver in a 10-mL volumetric flask was mixed with 1.0-4.0 (preferably 1.0 mL) of 1% sodium dodecyl sulfate (SDS) and 1.0– 4.0 (preferably 1.0 mL) of 1 M sulfuric acid followed by the addition of a 25 - 80 fold molar excess of a dithizone solution (preferably 1.0-mL of 1 x 10⁻³ M). The mixture was diluted up to the mark with deionized water. The absorbance was measured at 495 nm against a corresponding reagent blank. The silver content in an unknown sample was determined using a concurrently prepared calibration graph.

Results and Discussion

Factors Affecting the Absorbance

Absorption spectra

The absorption spectra of bluish yellow color of the silver - dithizone system in presence of 1-mL 1M sulfuric acid solution were recorded using a spectrophotometer. The absorption spectra of the silver - dithizone is a symmetric curve with maximum absorbance at 495 nm and an average molar absorptivity of $1.6 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ (**Fig. 1**). The reagent blank exhibited negligible absorbance, despite having a wavelength in the same region. In all instances, measurements were made at 495 nm against a corresponding reagent blank. The reaction mechanism of the present method is as reported earlier²⁴.

Effect of surfactant:

Of the various surfactants [nonionic { polyoxyethylenedodecylether (Briz-35) ; cationic {cetyltrimethylammonium bromide (CTAB) and anionic {cetylpyridinium chloride (CPC) , sodium dodecyl sulfate (SDS)] studied, SDS was found to be the best surfactant for the system. In the 1% SDS medium, however, the maximum absorbance was observed; hence, 1% SDS solution was used in the determination procedure.

Different volumes of 1% SDS solutions were added to a fixed metal ion concentration, in a 10 mL volumetric flask and the absorbance was measured according to the standard procedure. Effect of surfactant concentration was studied on the absorbance of 1 mg L^{-1} Ag-chelate complex, and 1.0-4.0 mL of 1% SDS solution produced a constant absorbance of the Ag-chelate. Outside this range of surfactant the absorbance decreased (**Fig. 2**). The effect may be due to inadequate interactions of surfactant at lower concentrations, while the micellar dilution effect is responsible for decreasing in the absorbance at higher surfactant concentrations. For all subsequent measurements, 1-mL of 1% SDS solution was added.

Effect of acidity

Of the various acids (nitric, sulfuric, hydrochloric and phosphoric) studied, sulfuric acid was found to be the best acid for the system. The variation of the absorbance was noted after the addition of 0.05-5.0-mL of 1M sulfuric acid to every 10-mL of test solution. The maximum and constant absorbance was obtained in the presence of 1-3.0-mL of 1 M sulfuric acid at room temperature $(25 \pm 5)^\circ\text{C}$. Outside this range of acidity, the absorbance decreased (**Fig. 3**). For all subsequent measurements 1-mL of 1 M sulfuric acid (pH 2) was added.

Effect of time:

The reaction is very fast. A constant maximum absorbance was obtained just after dilution within few seconds to volume and remained strictly constant for 24h (**Fig. 4**).

Effect of temperature

Effect of various temperatures (10-90°C) on Ag-dithizone system was studied. The Ag-dithizone system attained maximum and constant absorbance at room temperature ($25 \pm 5^\circ\text{C}$).

Effect of reagent concentration

Different molar excesses of dithizone were added to a fixed metal-ion concentration and the absorbance was measured according to the standard procedure. It was observed that a 1 mg L^{-1} of silver metal (optical path length 1 cm), the reagent molar ratios of 1:25 to 1:80 produced a constant absorbance of Ag - chelate (**Fig. 5**). A greater excess of the reagent was not studied. For all subsequent measurements, 1-mL of $1 \times 10^{-3} \text{ M}$ dithizone reagent was added.

Calibration graph (Beer's law and sensitivity)

The effect of the metal concentration was studied over $0.01\text{-}100 \text{ mg L}^{-1}$, distributed in four different sets ($0.01\text{-}0.1$, $0.1\text{-}1.0$, $1.0\text{-}10$ and $10\text{-}100 \text{ mg L}^{-1}$) for convenience of the measurement. The absorbance was linear for $0.07\text{-}10.0 \text{ mg L}^{-1}$ of silver at 495 nm. From the slope of the calibration graph, the average molar absorption co-efficient was found to be $1.6 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$. The Sandell's sensitivity (concentration for 0.001 absorbance unit) was found to be 10 ng cm^{-2} . Of these two calibration graphs, the one showing the limit of the linearity range is given in (**Fig. 6**). The next one was straight-line graph passing through the origin ($R^2 = 0.999$). The selected analytical parameters obtained with the optimization experiments are summarized in **Table 1**.

Effect of foreign ions

The effect of over 50 cations, anions and complexing agents on the determination of only 1 mg L^{-1} of silver was studied. The criterion for interference²⁵ was an absorbance value varying by more than 5% from the expected value for silver alone. There was no interference from the following 10,000-fold amount of EDTA and tartrate, a 100-fold amount of acetate, chloride or ammonium. EDTA prevented the interference of a 10-fold excess of Al, 10-fold excess of Bi(III), 20-fold excess of Cr (VI), 100-fold excess of Pb (II), 100-fold excess of Na or a 10-fold excess of Sn (II) and tartrate prevented the interference of a 10-fold excess of V (V) or Zn. During interference studies, if a precipitate was formed, it was removed by centrifugation.

The quantities of these diverse ions mentioned were the actual amounts studied but not the tolerance limit. However, for those ions whose tolerance limit has been studied, their tolerance ratios are mentioned in **Table 2**.

Composition of the complex:

Job's method²⁶ of continuous variation and the molar-ratio²⁷ method were applied to ascertain the stoichiometric composition of the complex. A Ag : dithizone (1:1) complex was indicated by both methods.

Precision and accuracy

The precision of the present method was evaluated by determining different concentration of silver (each analyzed at least five times). The relative standard deviation (n=5) was 2-0% for 0.7-100 µg of silver in 10-mL, indicating that this method is highly precise and reproducible. The detection limit (3s/S of the blank) and Sandell's sensitivity (concentration for 0.001 absorbance unit) for silver were found to be 1 µg L⁻¹ and 10 µg L⁻¹, respectively. The reliability of our Ag-chelate procedure was tested by recovery studies. Regression analysis of Beer's law plots at 495 nm revealed a good correlation ($R^2 = 0.999$). The method was also tested by analyzing several synthetic mixtures containing silver and diverse ions (**Table 3**). The results for silver recovery were in good agreement with added values (**Table 4**). The average percentage recovery obtained for the addition of silver spike to some environmental water samples and real (certified reference materials) samples were quantitative, as shown in (**Table 4 and 5**). The result of biological samples analyses by the spectrophotometric method were in excellent agreement with those obtained by ICP-MS (**Table 6**). The method was also tested by analyzing several soil samples (**Table 8**). Hence, the precision and accuracy of the method were found to be excellent.

Applications

The present method was successfully applied to the determination of silver in series of synthetic mixtures of various compositions (**Table 3**) and also in a number of real samples (**Table 4**). The method was also extended to the determination of silver in a number of environmental water samples, biological, photographic and soil samples. In view of the unknown composition of environmental water samples, the same equivalent portions of each sample was analyzed for silver content; the recoveries in both 'spiked' (added to the samples before the mineralization and dissolution) and the 'unspiked' conditions are in good agreement

(**Table 5**). The results of biological analyses by spectrophotometric method were found to be in excellent agreement with those obtained by ICP-MS (**Table 6**). The results of photographic samples and soil samples analyses by the spectrophotometric method are shown in (**Table 7 and Table 8**).

Determination of silver in synthetic mixtures

Several synthetic mixtures of varying compositions containing silver and diverse ions of known concentrations were determined by the present method using EDTA as a masking agent and the results were found to be highly reproducible. The results are shown in **Table 3**. The accurate recoveries were achieved in all solutions.

Determination of silver in alloys, steels and brass (Certified Reference Materials)

A 0.1g amount of an alloy or steel or brass sample containing different composition of metals was accurately weighed and placed in a 50-mL Erlenmeyer flask. To it, 10-mL of concentrated HNO_3 and 1-mL of concentrated H_2SO_4 were carefully added and then covered with a watch-glass until the brisk reaction subsides. The solution was heated and simmered gently after the addition of another 5-mL of concentrated HNO_3 until all carbides were decomposed. The solution was carefully evaporated to dense white fumes to drive off the oxides of nitrogen and then cooled to room temperature (25 ± 5) $^\circ\text{C}$. After suitable dilution with deionized water, the contents of the Erlenmeyer flask were warmed to dissolve the soluble salts. The solution was then cooled and neutralized with a dilute NH_4OH solution in the presence of 1-2-mL of 0.01% (w/v) tartrate solution. The resulting solution filtered, if necessary, through Whatman no. 40 filter paper into a 25-mL calibrated flask. The residue (silica and tungstic acid) was washed with a small volume (5-mL) of hot (1:99) sulfuric acid, followed by water, the filtration and washing were collected in the same calibrated flask and the volume was made up to the mark with deionized water.

A suitable aliquot (1-2-mL) of the above solution was taken into a 10-mL calibrated flask and the silver content was determined as described under general procedure using citrate or fluoride as masking agent. Based on five replicate analyses, the average silver concentration determined by spectrophotometric method was in good agreement with the spiked values. The average percentage recovery obtained for addition of a silver spike to some certified reference material was quantitative as shown in **Table 4**.

Determination of silver in environmental water samples

Each filtered (with Whatman No. 40) environmental water sample (1000-mL) was mixed with 10-mL of concentrated HNO_3 and 1-mL of concentrated H_2SO_4 in a 2000-mL distillation flask.

The sample was digested in the presence of an excess potassium permanganate solution following a method recommended by Greenberg *et al.*²⁸. The solution was then cooled and neutralized with dilute NH₄OH solution. The resulting solution was then filtered and quantitatively transferred into a 25-mL calibrated flask and made up to the mark with deionized water.

An aliquot (1-2-mL) of this solution preconcentrated environmental water was pipetted into a 10-mL calibrated flask and the silver content was determined as described under the general procedure using EDTA or tartrate as a masking agent. The results of analyses of environmental water samples from various sources for silver are given in **Table 5**.

Determination of silver in biological samples

Regarding human blood (3-5 -mL) and urine (20-50 -mL) were collected in polyethane bottles from the affected persons. The samples were taken into a 100-mL micro-Kjeldahl flask. A glass bead and 10 mL of concentrated nitric acid were added and the flask was placed on the digester under gentle heating following a method recommended by Stahr.²⁹ When the initial brisk reaction was over, the solution was removed and cooled. 5 mL of concentrated HNO₃ was added carefully, followed by the addition of 0.5 mL of 70 % HClO₄, and heating was continued to dense white fumes, repeating HNO₃ addition if necessary. Heating was continued for at least 30 min; followed by cooling. The content of the flask was filtered and neutralized with dilute ammonia. The resultant solution was then transferred quantitatively into a 10-mL calibrated flask and made upto the mark with de-ionised water.

An aliquot (1-2 -mL) of this digested biological sample was pipetted into a 10-mL calibrated flask and the silver content was determined as described under the general procedure using EDTA and tartrate as a masking agents. The results of the biological sample analyses by the spectrophotometric method were found to be in excellent agreement with those obtained by ICP-MS. The results are given in **Table 6**.

Determination of silver in photographic samples

20 mL of photographic sample was transferred into a 50 mL flask to which 2 mL of H₂O₂ and 10 mL of concentrated HNO₃ were added. The solution was heated on a hot plate and evaporated to dryness. The residue was dissolved with 10 mL 5% HNO₃. The resulting solution was then neutralized with NH₄OH and filtered and quantitatively transferred into a 25-mL calibrated flask and made up to the mark with deionized water³⁰.

An aliquot (1-2 -mL) of this digested photographic sample was pipetted into a 10-mL calibrated flask and the silver content was determined as described under the general procedure

using EDTA or tartrate as a masking agent. The results of analyses of photographic samples for silver are given in **Table 7**.

Determination of silver in soil samples

An air-dried homogenized soil sample (100g) was accurately weighed and placed in a 100-mL micro-Kjeldahl flask. The sample was digested in the presence of an oxidizing agent following a method recommended by Jackson³¹. The content of flask was filtrated through Whatman No. 40 filter paper into a 25-mL calibrated flask, and neutralized with dilute ammonia in the presence of 1-2-mL of a 0.01% (w/v) EDTA solution. It was then diluted up to the mark with deionized water.

Suitable aliquots (1-2-mL) were transferred into a 10-mL calibrated flask and the silver content was determined as described under general procedure using fluoride or thiocyanide solution as a masking agent and quantified from a calibration graph prepared concurrently. The results are shown in **Table 8**.

Conclusions

In the present work, a simple, sensitive, selective and inexpensive micellar method with the Ag-dithizone complex was developed for the determination of silver in industrial, environmental, photographic, biological and soil samples. The presence of micellar system (altered environment) avoids the previous steps of solvent extraction and reduces the cost and toxicity while enhancing the selectivity, sensitivity and molar absorptivity. The average molar absorptivity of the Ag-dithizone complex formed in the presence of the anionic SDS surfactants is almost the ten-times $1.6 \times 10^5 \text{ L. mol}^{-1} \text{ cm}^{-1}$ the value obtained in the standard method ($1.0 \times 10^4 \text{ L. mol}^{-1} \text{ cm}^{-1}$); the maxima of absorption is shifted by about 15 nm when compared with standard method, resulting in an increase in the sensitivity of the method. With suitable masking, the reaction can be made highly selective. Although many sophisticated techniques, such as pulse polarography, HPLC, NAA, AAS and ICP- MS, are available for the determination of Ag at trace levels in numerous complex materials, factors such as the low cost of the instrument, easy handling, portable, lack of any requirement for consumables, and almost no maintenance, have caused spectrophotometry to maintain a popular technique, particularly in the laboratories of developing countries with limited budgets. The sensitivity in terms of molar absorptivity ($\varepsilon=1.6 \times 10^5 \text{ L. mol}^{-1} \text{ cm}^{-1}$) and precision in terms of relative standard deviation of the present method are very reliable for the determination of Ag in real samples down to (ng g^{-1} levels in an aqueous medium at room temperature ($25 \pm 5^\circ\text{C}$)).

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414 **Tables:**

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416 **Table 1:** Selected analytical parameters obtained with optimization experiments.

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Parameters	Studied range	Selected value
Wavelength / $\lambda_{\max}$ (nm)	200-800	495
Acidity/ M H ₂ SO ₄	0.03-5.0	1.0-3.5 (preferably 1.0)
pH	3.5 – 1.3	2.0 – 1.5 (preferably 2.0)
Surfactant / 1% SDS / mL	0.1-7.0	1.0-4.0 (preferably 1.0)
Time / h	0-72	1 min-24 h (preferably 1 min)
Temperature / °C	25±5	25±5
Reagent (fold molar excess, M:R)	1:1 – 1:80	1:25 - 1:80 (preferably 1: 30)
Linear range/mg L ⁻¹	0.01-100	0.07-10
Molar absorption coefficient/ L. mol. ⁻¹ cm. ⁻¹	0.6 x 10 ⁴ –2.6 x 10 ⁵	1.6 x 10 ⁵
Sandell's sensitivity/ ng. cm ⁻²	1-100	10
Detection limit / μ g L ⁻¹	0.01-10	1
Reproducibility (% RSD)	0-10	0-2 %
Regression co-efficient (R ²)	0.9890-0.9999	0.9998

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Table 2. Tolerance limits^a of foreign ions, tolerance ratio [Species(x)]/Ag (w/w)

Species x	Tolerance ratio [Species (x) / Ag (w/w)]	Species x	Tolerance ratio [Species (x) / Ag (w/w)]
Acetate	100	Iodide	20
Aluminum	10 ^b	Iron(II)	100
Ammonium	100	Iron(III)	100
Arsenic (III)	100	Lead (II)	100 ^b
Arsenic (V)	50	Magnesium	100
Ascorbic acid	100	Mercury (I)	200
Azide	100	Mercury (II)	200
Barium	50	Molybdenum (VI)	100
Beryllium	50	Nickel (II)	100
Bismuth	10 ^b	Nitrate	20
Bromide	100	Oxalate	100
Cadmium	50	Phosphate	100
Calcium	20	Potassium	10
Cerium (III)	200	Selenium (IV)	100
Chloride	20	Selenium (VI)	50
Chromium (III)	200	Sodium	100 ^b
Chromium (VI)	20 ^b	Strontium	20
Citrate	100	Tartrate	10000
Copper (II)	50	Titanium(IV)	10
Cyanide	50	Tin (II)	10 ^b
EDTA	1000	Vanadium (V)	10 ^c
Fluoride	20	Zinc	10 ^c

^aTolerance limit defined as ratio that causes less than 5 percent interference.

^bwith 1000 mg L⁻¹, EDTA,

^cwith 50 mg L⁻¹ tartrate

Table 3. Determination of silver in some synthetic mixtures.

Sample	Composition of mixtures (mg L ⁻¹)	Silver / mg L ⁻¹		
		Added	Found ^a	Recovery $\pm s^b$ (%)
A	Ag ⁺	0.50	0.49	98 $\pm$ 0.5
		1.00	1.00	100 $\pm$ 0.0
B	As in A + As ³⁺ (25) + Co ²⁺ (25)	0.50	0.49	98 $\pm$ 0.6
		1.00	0.99	99 $\pm$ 0.3
C	As in B + Cr ³⁺ (25) + Fe ³⁺ (25)	0.50	0.50	100 $\pm$ 0.0
		1.00	0.98	98 $\pm$ 0.5
D	As in C + Mg ²⁺ (25) + Ni ²⁺ (25)	0.50	0.49	98 $\pm$ 0.6
		1.00	0.97	97 $\pm$ 0.8
E	As in D + NH ₄ ⁺ (25) + Mo ^{VI} (25) + EDTA (100)	0.50	0.48	96 $\pm$ 1.2
		1.00	0.95	95 $\pm$ 1.5

^a Average of five analyses of each sample

^b The measure of precision is the standard deviation (SD).

Table 4. Analysis of high-speed steel and alloys

Sample	Certified reference material (Composition, %)	Silver / mg L ⁻¹		
		Added	Found ^a	Recovery $\pm$ s ^b (%)
1	BAS – 5 g, high-speed steel (C, Si, Mn, Mo, V, Ni, Cr, W and Cu)	1.0	1.02	102 $\pm$ 1.0
		5.0	5.15	103 $\pm$ 0.8
2	BAS – 10 g, high tensil brass (Cu, Fe, Pb, Ni, Sn, Al, Zn and Mn)	1.0	1.05	105 $\pm$ 1.5
		5.0	5.30	106 $\pm$ 1.0
3	Brass – 5 f (Cu, Zn, Pb, Sn, Fe, Ni, Mn and P)	1.0	1.03	103 $\pm$ 1.0
		5.0	5.25	105 $\pm$ 1.2
4	GSBH – 40101 – 96 Cr ₁₂ MoV – Dies steel (Cr, Ni, Cu, Mo, V and Co)	1.0	1.06	106 $\pm$ 1.5
		5.0	5.35	107 $\pm$ 1.4
5	YSBC – 1013 – 1 – 95 9 Cr ₁₇ MoV - high tensil steel (C, Si, Mn, Cr, Mo, V and Co)	1.0	1.08	108 $\pm$ 1.7
		5.0	5.45	109 $\pm$ 1.8

^a Average of five analyses of each sample

^b The measure of precision is the standard deviation (SD).

467 **Table 5.** Determination of silver in some environmental water samples.

Sample		Silver / $\mu\text{g L}^{-1}$		Recovery $\pm$ s (%)	s_r^b (%)
		Added	Found ^a		
Tap water		0 100 500	15.00 116.0 520.0	100.8 $\pm$ 0.5 100.9 $\pm$ 0.6	0.25 0.28
Well water		0 100 500	12.0 115.0 520.0	102.7 $\pm$ 0.6 101.6 $\pm$ 0.4	0.13 0.15
Rain Water		0 100 500	5.00 106.00 510.00	100.9 $\pm$ 0.5 100.9 $\pm$ 0.6	0.18 0.24
River water	Karnafuly (upper)	0 100 500	25.00 125.00 530.0	100 $\pm$ 0.0 100.9 $\pm$ 0.8	0.00
		0 100 500	28.00 130.00 535.00	101.5 $\pm$ 1.0 101.3 $\pm$ 1.2	0.16 0.12
	Halda (upper)	0 100 500	10.00 110.00 515.00	100 $\pm$ 0.0 100.9 $\pm$ 1.3	0.00 0.15
		0 100 500	12.00 110.00 520.00	98 $\pm$ 1.3 101.5 $\pm$ 1.5	0.18 0.26
	Bay of Bengal (upper)	0 100 500	5.00 106.00 510.00	100.9 $\pm$ 0.8 100.9 $\pm$ 1.0	0.39 0.49
		0 100 500	6.00 108.00 510.00	101.9 $\pm$ 0.8 100.8 $\pm$ 0.6	0.33 0.46
	Bay of Bengal (lower)	0 100 500	45.00 150.00 540.0	103 $\pm$ 1.5 99 $\pm$ 1.6	0.42 0.44
		0 100 500	35.00 138.00 540.00	102 $\pm$ 1.5 100.9 $\pm$ 1.8	0.45 0.56
	Jewellery ^e	0 100 500	23.00 125.00 520.0	101.6 $\pm$ 1.6 99 $\pm$ 1.7	0.35 0.46
		0 100 500	45.00 150.00 540.0	103 $\pm$ 1.5 99 $\pm$ 1.6	0.42 0.44
		0 100 500	35.00 138.00 540.00	102 $\pm$ 1.5 100.9 $\pm$ 1.8	0.45 0.56
		0 100 500	23.00 125.00 520.0	101.6 $\pm$ 1.6 99 $\pm$ 1.7	0.35 0.46

468 ^aAverage of five replicate determinations.

469 ^bThe measure precision is the relative standard deviation (s_r)

470 ^cEstern Cables, Patenga, Chittagong.

471 ^dElite Paint, Nasirabad, Chittagong.

472 ^eJewellery Shop, Comilla.

Table 6. Concentration of silver in blood and urine samples.

Serial No.	Sample	Silver / $\mu\text{g L}^{-1}$				Sample sources ^a
		ICP - MS (n = 5)		Proposed method (n = 5)		
		Found	RSD, %	Found	RSD, %	
1	Blood	13.80	1.0	13.75	1.0	Diabetes patient (Female)
	Urine	3.53	1.2	3.45	1.3	
2	Blood	79.00	1.0	75.50	1.2	Rheumatoid Arthritic patient (Female)
	Urine	13.79	1.5	13.55	1.5	
3	Blood	7.55	1.3	7.45	1.5	Lupus Gramutosis patient (Male)
	Urine	1.94	1.8	1.88	1.9	
4	Blood	2.58	1.3	2.55	1.2	Normal adult (Male)
	Urine	0.65	2.0	0.68	1.8	

^aSamples were from Chittagong Medical College Hospital, Chittagong.

494 **Table 7.** Determination of silver in photographic (X-ray) samples.

Serial No.	Sample	Silver / mg L ⁻¹ or µg g ⁻¹		
		Found (n = 5)	RSD, %	Sample sources ^a
1	X-ray fixer	4.89 (mg L ⁻¹)	1.5 (mg L ⁻¹)	Photographical solution
2	X-ray develop	2.81 (mg L ⁻¹)	2.0 (mg L ⁻¹)	Photographical waste solution
3	X-ray hypo	6.25 (µg g ⁻¹)	1.0 (µg g ⁻¹)	Photographical solid material

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497 ^aSamples were from Studio University, Chittagong University campus, Chittagong.
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Table 8. Determination of silver in some surface soil samples

Serial no.	Silver / $\text{mg kg}^{-1} \pm s^a$ (n = 5)	Sample sources
S ₁ ^b	41.8 $\pm$ 1.0	Jewellery soil
S ₂	104.2 $\pm$ 1.2	Silver Industry soil
S ₃	105.8 $\pm$ 1.5	Elite Paint soil
S ₄	58.9 $\pm$ 1.0	Marine soil
S ₅	10.5 $\pm$ 0.5	Agriculture soil (Chittagong University Campus)

^aThe measure of precision is the standard deviation.

^bComposition of the soil samples: C, N, P, K, Na, Ca, Mg, Cu Fe, Pb, Zn, Mn, Mo, Co, NO₃, SO₄ etc.

Figures:

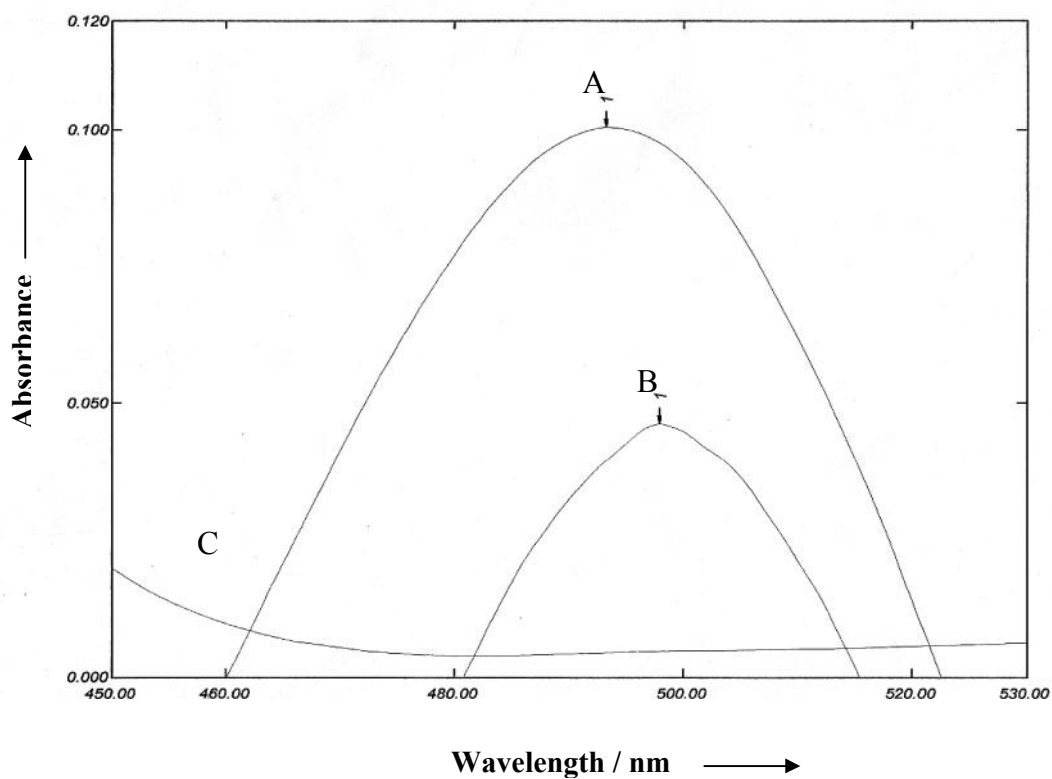


Fig. 1. A, B and C absorption spectra of Ag-dithizone system in anionic micellar media of sodium dodecyl sulfate, carbon tetrachloride media and the reagent blank ($\lambda_{\text{max}} = 495 \text{ nm}$), respectively.

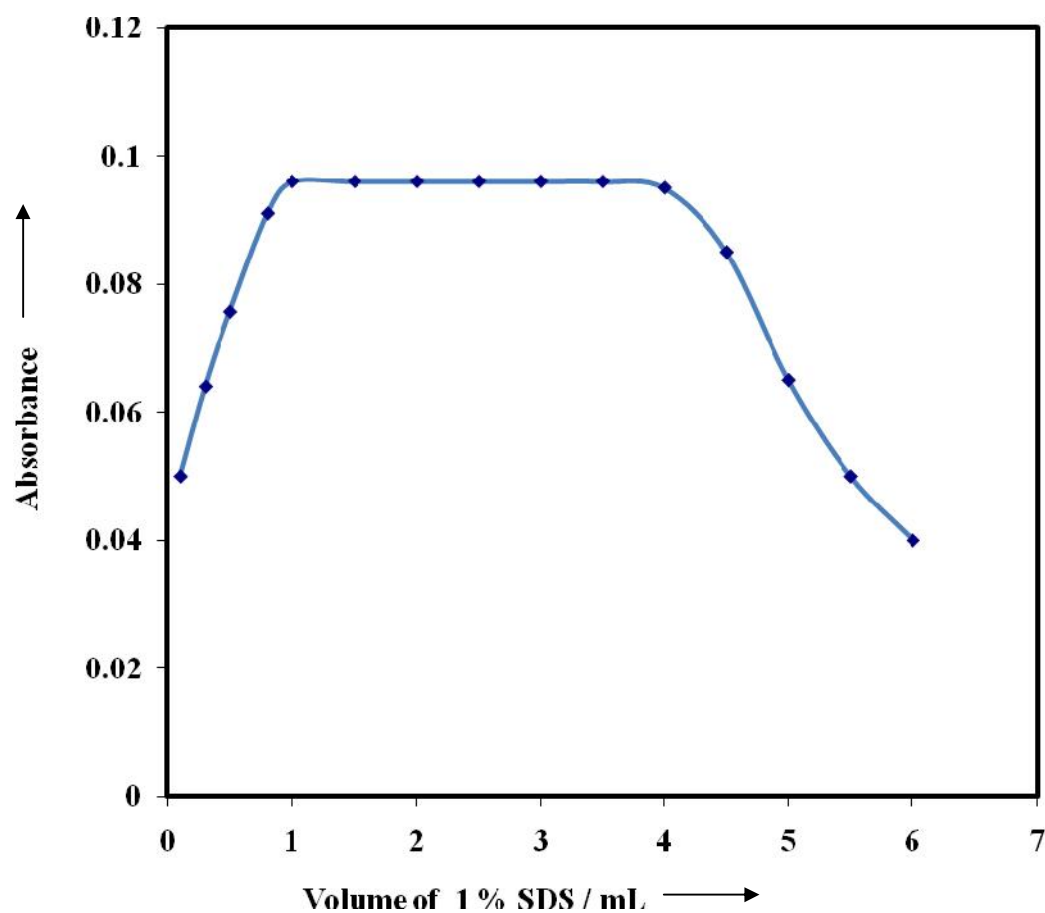


Fig. 2. Effect of a surfactant on the absorbance of the Ag-dithizone system.

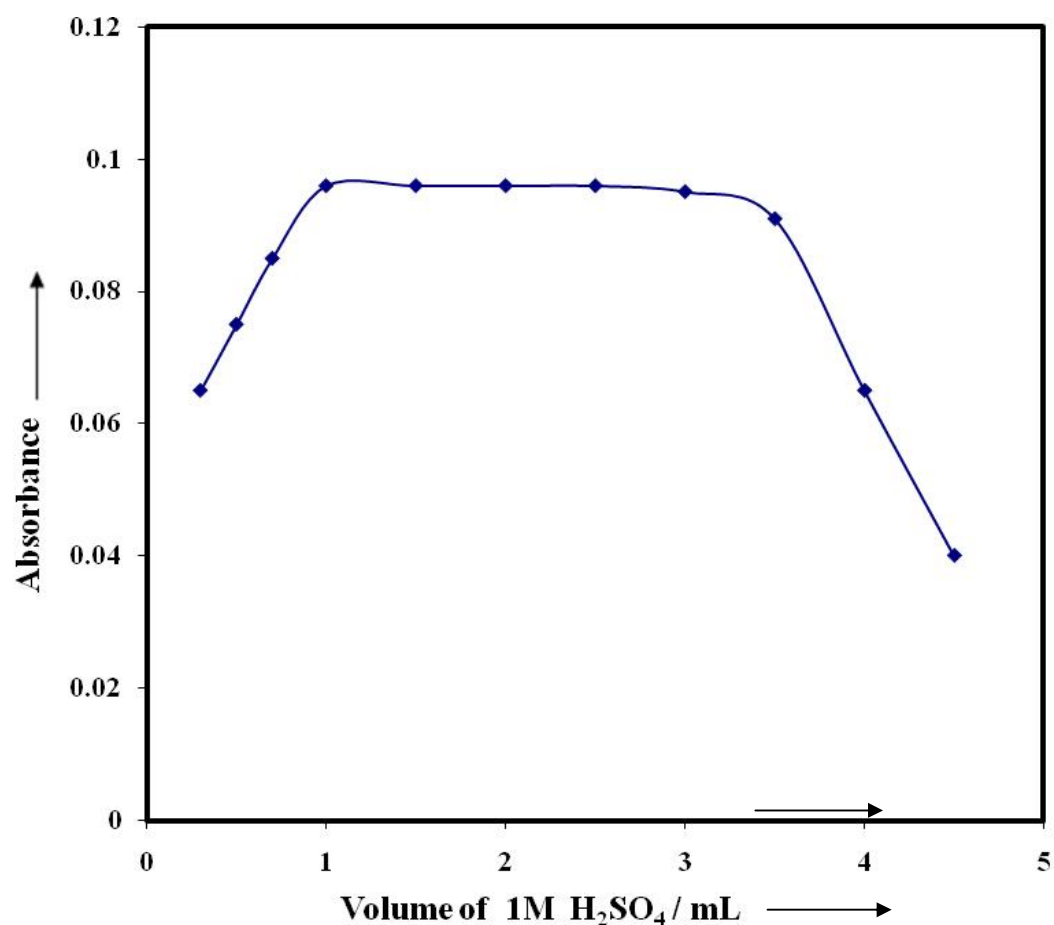


Fig. 3. Effect of the acidity on the absorbance of the Ag-dithizone system

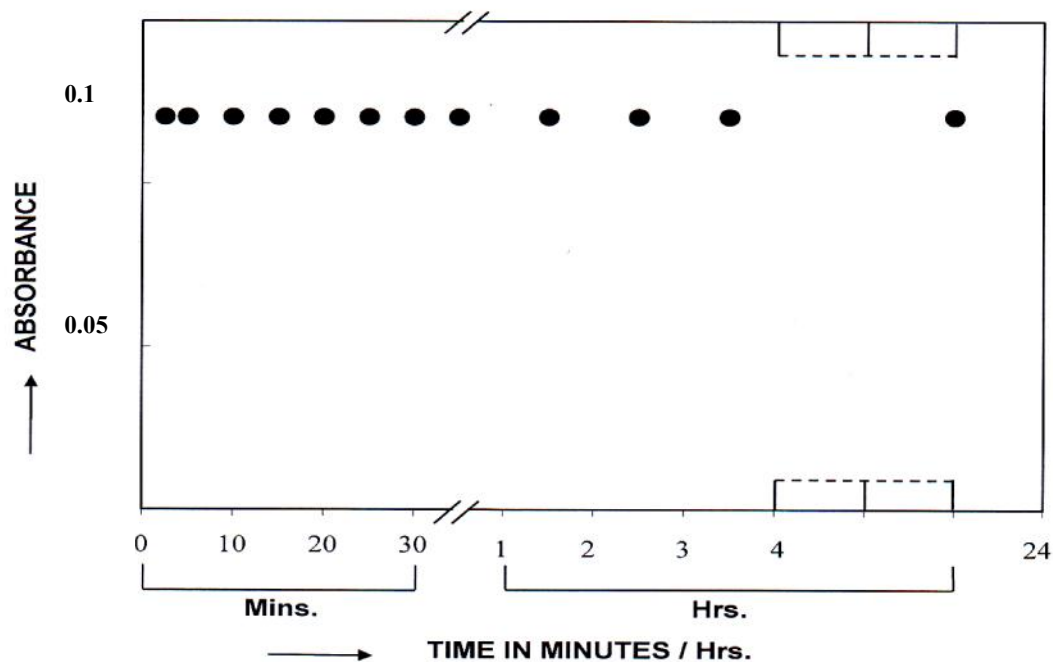


Fig. 4. Effect of the time on the absorbance of the Ag-dithizone system

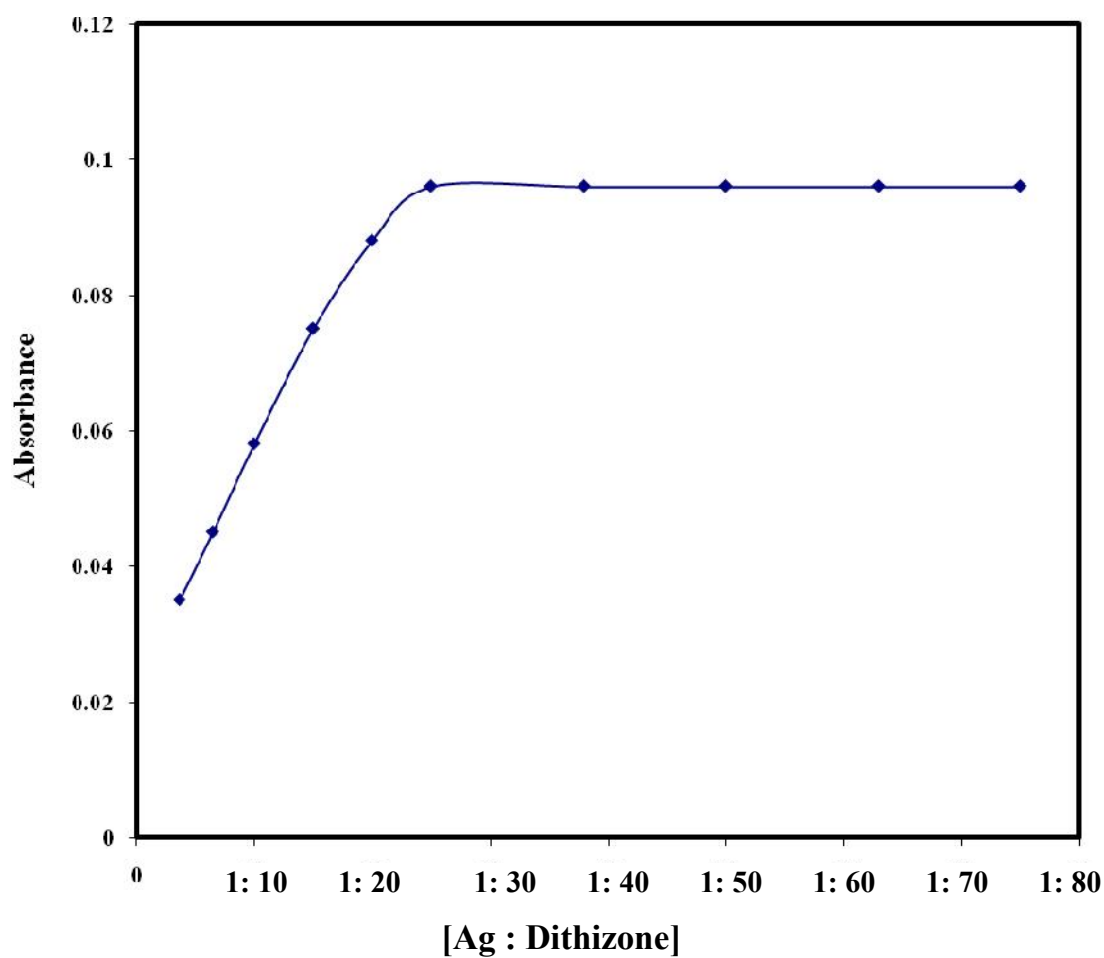


Fig. 5. Effect of reagent [Ag : dithizone molar concentration ratio] on the absorbance of Ag-dithizone system in micellar media

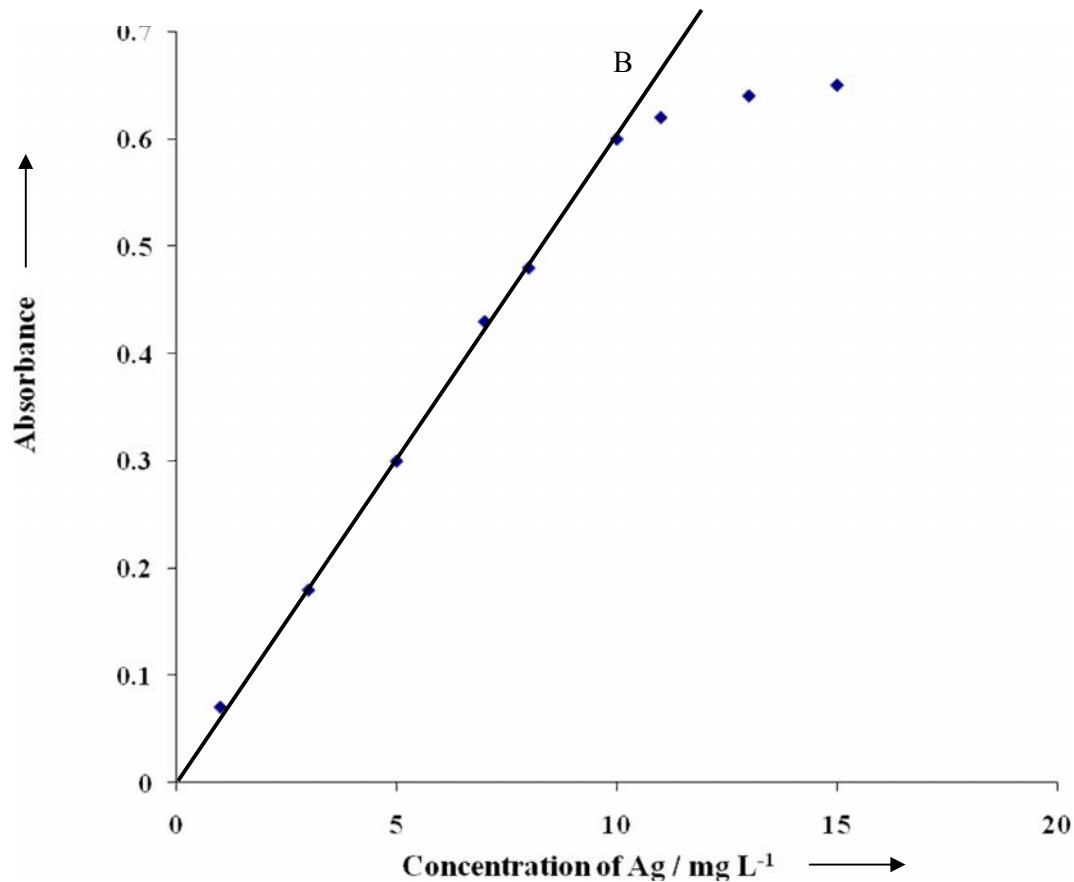


Fig. 6. Calibration graph : B, 1.0 -10 mg L⁻¹ of Ag