Silver-Enhanced Reduction of 2,3,5-Triphenyl-2H-tetrazolium by Semicarbazide for the Spectrophotometric Determination of Traces of Silver(I)

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A sensitive spectrophotometric method for the determination of silver is described. The reaction involves a silver-enhanced reduction of 2,3,5-triphenyl-2H-tetrazolium chloride by semicarbazide hydrochloride to yield a pink-colored product with maximum absorption at 510 nm. Beer's law is obeyed in the concentration range of 0.02 – 0.34 $\mu\text{g cm}^{-3}$ of silver, and the molar absorptivity is $4.51 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$. The optical parameters, optimum reaction conditions and interference studies have been described. The method has been applied to the determination of silver in photographic film waste water and in synthetic samples.

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Introduction

Many spectrophotometric methods have been reported for the determination of silver.¹⁻³ Among the very recent methods, the spectrophotometric determination of silver with 5,10,15,20-tetrakis-(4-bromophenyl)-21H,23H-porphine⁴ and using 1,10-phenanthroline and tetrabromophenolphthalein ethyl ester⁵ has been reported. 2,3,5-Triphenyl-2H-tetrazolium chloride (TTC)⁶ is used as a sensitive reagent for reducing sugars, used in histochemical studies and in the determination of antibiotics. TTC is also used to oxidize aldoses and ketoses. The chlorophyll-photosensitized reduction of TTC by hydrazine hydrate has been reported.⁷ The colorimetric determinations of iron(III), chromium(VI), thallium(III), aromatic and α,β -unsaturated aldehydes by using an equimolar mixture of isonicotinic acid hydrazide and TTC have been reported.⁸ A colorimetric micro determination of 2-deoxy-D-glucose with TTC has been described.⁹ Ramesh *et al.*¹⁰ have recently reported the extractive separation of selenium and tellurium using TTC. An excellent review on the tetrazolium salts and formazans has been reported.¹¹

In the present investigations, a highly sensitive spectrophotometric method for the determination of silver, that is, a new route involving the reduction of TTC by semicarbazide hydrochloride (SCH) using silver(I) in the presence of sodium hydroxide and nitric acid to produce a pink-colored product, is described. Interference studies involving various diverse species have been made. The results of applying the present method for the determination of silver in the photographic film waste water, and also in synthetic samples, compare favorably with the reported method.¹²

Experimental

Instrument

A JASCO Model UVIDE-610 spectrophotometer with 1.0 cm matched cells was used for electronic spectral measurements.

Reagents

2,3,5-Triphenyltetrazolium chloride (TTC), semicarbazide hydrochloride (SCH) and silver nitrate were obtained from Sigma (St. Louis, USA). Sodium hydroxide pellets (BDH grade) and nitric acid (AR grade) were used. All of the other reagents were of analytical grade, and deionized water was used throughout the experiment.

Solutions

A 0.1575 g portion of dried silver nitrate was dissolved in water containing 1 cm³ of concentrated HNO₃; the solution was made up to the mark with water in a 100 cm³ standard flask and stored in the dark. Solutions of lower concentrations were prepared by appropriate dilution of the stock solution. A 0.1% solution of TTC in water was used. Freshly prepared solutions were always used, and the solution of TTC was stored in the dark. A 0.5% solution of SCH in water was prepared, and a solution of 5 mol dm⁻³ NaOH was prepared by dissolving NaOH pellets in 1 l of water; 500 cm³ of concentrated nitric acid was diluted to 1 l with water to give a final concentration of 8 mol dm⁻³.

Recommended procedure

An aliquot of a standard solution containing 0.5 – 8.5 μg of silver(I) was transferred to a 25 cm³ calibrated flask. Then, 0.5 cm³ of a 0.1% TTC solution was added, followed by the addition of 1 cm³ of a 0.5% SCH solution with swirling. Then, 3 cm³ of a 5 mol dm⁻³ NaOH solution was added followed by

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Fig. 1 Absorption spectra of the pink product (1) and the reagent blank (2). The final concentration of silver: $0.16 \mu\text{g cm}^{-3}$.

Table 1 Optical characteristics and precision data

Optical characteristics and precision	Parameter
Color	Pink
λ_{max} (nm)	510
Stability (min)	30
Beer's law range ($\mu\text{g cm}^{-3}$)	0.02 – 0.34
Molar absorptivity ($\text{l mol}^{-1} \text{cm}^{-1}$)	4.51×10^5
Sandells' sensitivity ($\mu\text{g cm}^{-2}$)	0.00024
Optimum photometric range ($\mu\text{g cm}^{-3}$)	0.04 – 0.30
Detection limit ($\mu\text{g cm}^{-3}$)	0.008
Regression equation (Y^a)	
Slope (b)	3.3204
Intercept (a)	-0.0108
Correlation coefficient (r)	0.994
Relative standard deviation ^b (%)	0.2227
Range of error ^b	± 0.3090

a. $Y = bx + a$, where x is the concentration of silver in $\mu\text{g cm}^{-3}$.

b. Five replicates.

dilution to the mark with 8 mol dm^{-3} nitric acid; the solution was then mixed well. The absorbance of the resulting pink solution was measured at 510 nm within 30 min against a freshly prepared reagent blank (without silver) prepared in the same manner.

Determination of silver in photographic film waste water

After photographic film washings were collected from local studios of Mysore, 1 cm^3 of each solution was treated with one or two drops of concentrated nitric acid and diluted. The solution was filtered and made up to 25 cm^3 . The solution was further diluted to obtain lower concentrations. A known aliquot of this solution was pipetted into a 25 cm^3 calibrated flask and continued according to the recommended procedure, as mentioned above.

Determination of silver in synthetic samples

The recommended procedure was also followed for synthetic samples, by taking known amounts of a silver nitrate solution. To determine the precision and accuracy of the method, recovery experiments were performed using the method of additions, and analyzed within the Beer's law limits.

Scheme 1

Results and Discussion

Spectral characteristics of the colored product

A pink-colored product with maximum absorption at 510 nm was formed when TTC was reduced by SCH using silver nitrate. The absorption spectra of the reduced product as well as the reagent blank are shown in Fig. 1. The optical characteristics and the precision data are given in Table 1.

Optimization of reaction conditions

A 0.1% solution of TTC in the range of $0.5 - 2.0 \text{ cm}^3$, a 0.5% solution of SCH in the range of $0.5 - 2.0 \text{ cm}^3$, $2.0 - 5.0 \text{ cm}^3$ of a 5 mol dm^{-3} NaOH solution and $7 - 9 \text{ mol dm}^{-3}$ nitric acid were necessary to develop the maximum color intensity. For excellent results, 1.0 cm^3 of TTC, 1.0 cm^3 of SCH, 3.0 cm^3 of NaOH and 8 mol dm^{-3} nitric acid were required. The maximum absorbance readings were obtained in the above ranges. Above or below these ranges, a decrease in the absorbance readings was noted, and the pink product was not stable.

Stability of the colored product

The instantaneous formation of the pink-colored product was stable for up to 30 min at room temperature ($27 \pm 2^\circ\text{C}$). After this time interval, the absorbance readings steadily decreased. Also, the absorbance readings remained constant in the temperature range of $20 - 60^\circ\text{C}$. At temperatures above 60°C , the absorbance values decreased, indicating dissociation of the product. However, a time of 30 min was sufficient to complete the analysis.

Reaction mechanism

The reaction involves the reduction of TTC by SCH using silver(I). Under the present conditions, TTC is reduced to 1,3,5-triphenyltetrazolium formazan. The reaction mechanism is shown in Scheme 1. Without the addition of silver(I) ions, no color formation is noticed. With silver(I) ions and a NaOH solution, a purple precipitate of formazan is formed, which becomes clear pink upon the addition of nitric acid. Here, silver(I) ions enhance the reduction reaction. The plausible mechanism would be the reaction of two molecules of Ag(I) with three molecules of semicarbazide in an alkaline medium, leading to the oxidation of semicarbazide, liberating sixteen nascent hydrogen (eight nascent hydrogen per molecule of Ag(I)), which in turn reduces four molecules of tetrazolium to four molecules of formazan, per molecule of silver(I). This means that four molecules of formazan are formed per molecule of Ag(I) . Other acids and solvents were tried to increase the stability of the product, but were unsuccessful.

Interference studies

The effects of foreign ions and other substances were studied by taking $0.16 \mu\text{g cm}^{-3}$ of silver(I). An ion was considered to interfere if the obtained absorbance differed by more than $\pm 2\%$ of the absorbance value from that of silver alone. The main interfering species were NO_2^- , Hg^{2+} , Pb^{2+} , Mn^{2+} , Fe^{2+} , Cu^{2+} ,

Table 2 Effect of diverse species on the determination of 0.16 $\mu\text{g cm}^{-3}$ silver

Species	Tolerance limit/ $\mu\text{g cm}^{-3}$
EDTA, formaldehyde, sulfamic acid	2000
NO_2^- , ^a K^+ , CO_3^{2-} , Zn^{2+} , Na^+ , Ca^{2+} , CH_3COO^-	500
Tartarate, F^- , SO_4^{2-} , Mg^{2+} , Fe^{3+} , Al^{3+} , Se^{4+}	300
SO_3^{2-} , CN^- , ^b Ni^{2+} , Cl^- , V^{5+} , Cd^{2+}	100
Cu^{2+} , Fe^{2+} , Pb^{2+} , Mn^{2+}	50 ^c
$\text{S}_2\text{O}_3^{2-}$	20

a. Can be masked up to 500 $\mu\text{g cm}^{-3}$ by the addition of 1 cm^3 of 1% sulfamic acid solution.

b. Can be masked up to 100 $\mu\text{g cm}^{-3}$ by the addition of 1 cm^3 of 40% formaldehyde solution.

c. Can be masked up to 50 $\mu\text{g cm}^{-3}$ by the addition of 1 cm^3 of 1% EDTA solution.

SCN^- and CN^- . Hg^{2+} and SCN^- could not be masked using any masking agents, whereas the other ions could be masked. The tolerance limits and other details are given in Table 2.

Precision and accuracy

The precision of the proposed method was ascertained from the absorbance values of the actual determinations of five replicates of fixed amounts of the silver sample. The percentage relative standard deviation was calculated by the proposed method. To determine the accuracy of the proposed method, different amounts of samples containing silver were taken within the Beer's law limits and analyzed by the recommended method. The results are given in Table 1.

Application of the recommended method

The proposed method has been applied to the determination of silver(I) in a photographic film waste water and also in synthetic samples. The results of analysis by the present method and the reported method¹² agree favorably. The results are given in Table 3.

Conclusion

The proposed method for the determination of silver(I) is much simpler, and no critical conditions are necessary. The calibration curve can be precisely reproduced; extraction or heating is not necessary. The method has the advantages of being rapid, reproducible, selective and more sensitive than many other reported methods.

Table 3 Determination of silver in photographic film waste water and synthetic samples

Sample	Silver added/ $\mu\text{g cm}^{-3}$	Proposed method		Reported method ¹²	
		Silver found/ $\mu\text{g cm}^{-3}$	Mean recovery, %	Silver found/ $\mu\text{g cm}^{-3}$	Mean recovery, %
Photographic film waste water ^a	—	3.068	—	3.076	—
	—	3.412	—	3.42	—
	—	3.64	—	3.60	—
	—	4.80	—	4.82	—
Synthetic sample	0.02	0.0199	99.5	0.0196	98.0
	0.04	0.041	102.5	0.04	100.0
	0.12	0.1198	99.83	0.1195	99.58
	0.14	0.14	100.0	0.14	100.0
	0.20	0.196	98.0	0.198	99.0

a. Black & white film washings collected around Mysore city (India).

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