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Extractive Spectrophotometric Determination of Silver(I) in Photo Films Waste Water

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A sensitive and rapid spectrophotometric method has been developed for the determination of microgram amounts of silver(I) using benzildithiosemicarbazone (BDTSC) after extraction into chloroform. The influence of various foreign ions on the extraction of silver has also been studied. This method obeys Beer's law in the range of 0.3–5.5 μg/mL. The method has been successfully applied for the determination of silver in photo film waste water samples and the results are compared with atomic absorption spectrophotometric method.

INDRODUCTION

Thiosemicarbazones have been extensively employed as reagents in the chemical analysis for separation and quantitative determination of different transition metal ions. But the literature survey reveals that only a few thiosemicarbazones[1–3] are used for the spectrophotometric determination of silver(I). Benzildithiosemicarbazone (BDTSC) has not so far been utilised as a reagent for the extractive spectrophotometric determination of silver. Hence, in the present investigation, an extractive spectrophotometric method has been developed for the determination of silver (I), using BDTSC as a reagent.

EXPERIMENTAL

Absorbance measurements were recorded on a Shimadzu model UV 240 recording spectrophotometer, supplied by Shimadzu Corporation Japan, The wave-length range was 190–900 nm, with a resolution of 0.10 nm and its accuracy was ± 0.3 nm. Comparison of results was made on Hitachi, Model 170–30 atomic absorption/flame spectrophotometer, manufactured by Hitachi Limited, Japan. The wavelength range of the instrument was 190–900 nm with a resolution of ± 0.5 nm. A digital pH meter Model LI-120 (ELICO) was used for pH measurements.

All the reagents and solvents used were of analytical grade. Silver(I) stock solution of 1.0 mg/mL was prepared by dissolving 1.575 g of silver nitrate in 1 litre of double distilled water. The solution was further diluted to obtain the required concentration. 0.1 M Lithium sulphate solution was prepared with double distilled water and used as a salting out agent.

1.0 M sodium acetate and 1.0 M acetic acid solutions were prepared in double distilled water and suitable portions of these solutions were mixed to get the desired pH using pH meter.

BDTSC was prepared[4] and recrystallised from ethyl alcohol. Reagent solution of suitable concentration was prepared by using 40% DMF solution.

Photo film washings were collected from local studios in Tirupati (India). 1.0 mL each of such washing solution was treated with a few drops of nitric acid and then diluted. The solution was filtered and made up to 25 mL. This solution was further diluted to get desired concentrations.

Procedure

An aliquot of a solution containing 20 μg of silver (I) is transferred into a 25 mL separating funnel. To it, 4.0 mL of sodium acetate-acetic acid buffer (pH, 5.0), 3.0 mL of 4.635×10^{-5} M reagent and 1.0 mL of 0.1 M lithium sulphate solution are added. The total volume of the aqueous phase is brought to 15.0 mL with double distilled water. The contents are shaken with 5.0 mL of chloroform for about two minutes. The greenish yellow coloured organic layer is transferred into a 10 mL standard flask and made up to the mark with chloroform. The absorption spectrum of the complex is recorded against the reagent as blank.

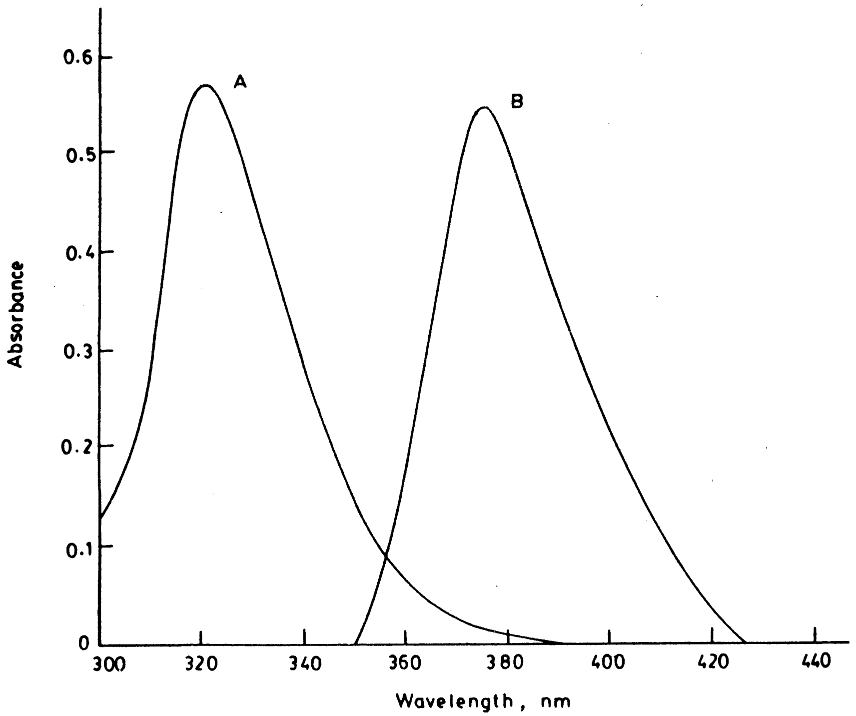

Fig. 1. Absorption spectra of (A) BDTSC and (B) Ag-BDTSC complex.

Similarly, the absorption spectrum of the reagent is also recorded against solvent as blank (Fig. 1).

The spectra revealed that Ag-BDTSC complex has a maximum absorbance at 375 nm, whereas the reagent at 320 nm. The reagent has negligible absorbance at 375 nm. Hence further absorbance measurements of the complex are made at 375 nm.

Calibration

Known aliquots of 15.0 mL solutions each containing constant volumes of 4.0 mL of buffer (pH, 5.0), 5.0 mL of 4.635×10^{-5} M BDTSC and 1.0 mL of 0.1 M lithium sulphate solutions and varying amounts of silver (I) (3.0–55.0 µg) are prepared. Each solution is shaken with two 4.0 mL portions of chloroform in two stages and the organic phases are taken into a 10 mL standard flask and finally made upto the mark with chloroform. The experiment is repeated with other aqueous solution also. The absorbances of all the organic phases are taken at 375 nm and a plot is drawn between the amount of silver (I) and absorbance as shown in Fig. 2.

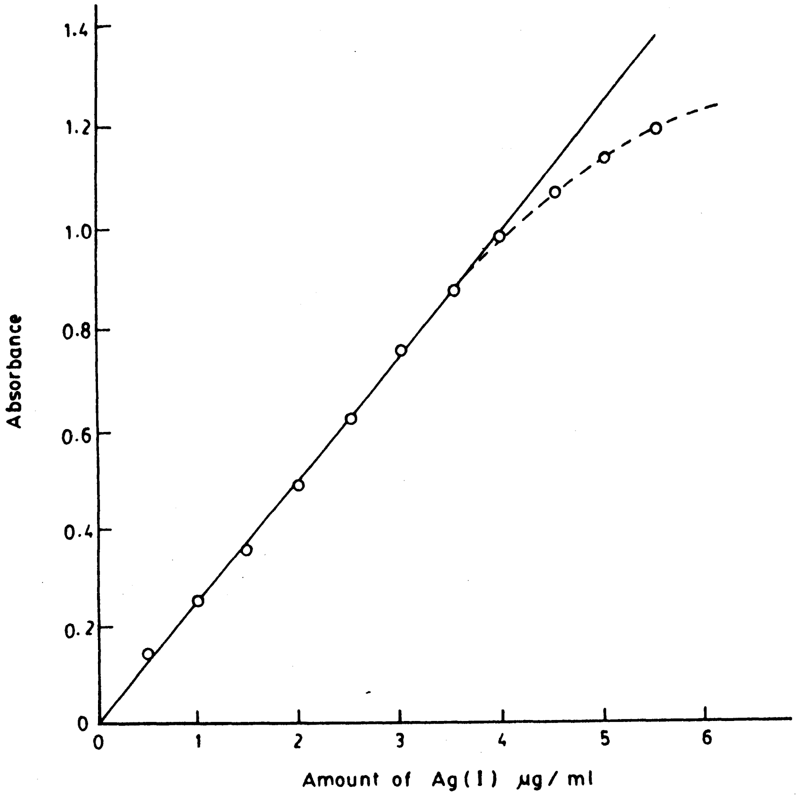

Fig. 2 Calibration plot of Ag-BDTSC complex.

RESULTS AND DISCUSSION

Silver(I) reacts with BDTSC in sodium acetate-acetic acid buffer of pH 5.0 and forms a 1 : 1 complex. The complex is easily extractable into chloroform. It has maximum absorbance at 375 nm and is stable for about 36 h. Beer's law is obeyed in the range of 0.3–4.0 μg/mL of silver (I). The molar absorptivity of the complex is calculated as 2.704×10^4 lit mol^{-1} cm^{-1} and Sandell's sensitivity of the complex is 0.00399 μg cm^{-2}.

The method has got a good reproducibility. For a set of ten measurements of 1.0 μg/mL of silver(I), values such as standard deviation, relative standard deviation, confidence limit and standard error are found to be 0.00232 μg/mL, 0.928 %, ± 0.00165 and 0.0007 respectively. These values clearly indicate that the precision and accuracy of the method are good.

The composition of the complex is calculated from Job's method of continuous variation,[5] molar ratio method[6] and Asmus' method.[7] From all the three methods it is evident that the ratio of silver to ligand in the complex is 1 : 1 and represented as Ag-BDTSC. The instability constant of the complex is calculated from both Asmus' method and Edmonds and Birnbaum's method. Both the methods are in good agreement with each other and the value is found to be 4.7619×10^{-5} at 30°C.

Effect of Interfering Ions

The influence of various foreign ions on the extraction of 20 μg of silver(I) has been investigated. A change in absorbance of ± .01 is taken as tolerance limit for the interference.

Cations like Al(III), Be(II), Bi(III), Ce(IV), Cd(II). Cr(III), Cr(VI), Fe(III), Mo(VI), Pb(II), Se(IV), Ti(IV), U(VI), V(V), Zr(IV) and Zn(II) do not interfere even when present in twentyfold excess. Sb(V) and Hg(II) decrease the absorbance when present in more than tenfold excess. Cu(II), Co(II), Ni(II) and Pd(II) interfere seriously. Anions like ascorbate, bromide, chloride, iodide, fluoride, citrate, oxalate, phosphate, sulphate, tartrate, thiosulphate and thiourea do not interfere even when present up to fiftyfold excess. Tenfold excess of thiocyanate decreases the absorbance.

The interference of Cu(II) and Ni(II) can be avoided by using 1.0 mL of 2% sodium citrate solution and Co(II) and Pd(II) can be avoided by using 1.0 mL of 2% sodium thiosulphate solution as masking agents.

Application of the Method for Photo Film Waste Water

The method developed is successfully employed to determine the amount of silver present in prepared solutions of photo film waste water. The results of the determinations of test samples and photo film waste water samples are reported in Table-1. The results obtained for photo film waste waters are compared with atomic absorption spectrophotometric method and they are in good agreement, showing reliability of the present method.

TABLE-1
(a) DETERMINATION OF SILVER (I) IN TEST SOLUTIONS

Amount of Silver(I) taken, μg/mL		Amount of Silver(I) found, μg/mL
0.5	—	0.498
1.0	—	0.996
1.5	—	1.495
2.0	—	1.982
2.5	—	2.497
3.0	—	2.999

Average error = 0.004333

(b) DETERMINATION OF SILVER(I) IN PHOTO FILM WASTE WATER SAMPLES

Sample	Amount of silver(I) determined, μg/mL	
	BDTSC method	AAS method
Black and White film washings*	3.068	2.076
Colour film washings*	3.412	3.420

*Average of four determinations.

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