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Spectrophotometric Determination of Silver (I) by Adsorption of its 1-Allyl-3-(5-Choloro-2-Pyridyl) Thiourea Complex on Microcrystalline Naphthalene

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The spectrophotometric determination of trace silver(I) with 1-allyl-3-(5-chloro-2-pyridyl) thiourea is described. A stable complex formed from silver and 1-allyl-3-(5-chloro-2-pyridyl) thiourea can not be directly extracted into benzene or chloroform, but can be easily adsorbed on microcrystalline naphthalene at room temperature. This complex is dissolved in dimethylformamide solution. The absorbance of solution was measured at 430 nm against the reagent blank. Beer's law was obeyed in the concentration range 7-120 μg of silver(I) in 10 ml of dimethylformamide. The molar absorptivity was found to be 3.18×10^4 l mol^{-1}cm^{-1} and sensitivity being 1.591×10^{-2} μg cm^{-2} of silver for the absorbance of 0.001.

INTRODUCTION

Thiourea and its derivatives have been introduced as useful analytical reagents by Yoe and Overhalser[1]. Since then a number of substituted thioureas have been reported as spectrophotometric and gravimetric reagents. The analytical application of substituted thioureas has extensively been investigated and reported from our laboratories.[2–11]

A new method called analysis of metals by solid-liquid seperation after liquid-liquid extraction[12–14] has been used for the photometric determination of trace amounts of Ag(I). The reagent, 1-allyl-3-(5-chloro-2-pyridyl) thiourea forms a water insoluble complex with Ag(I) which may be easily adsorbed on microcrystalline naphthalene. The traces of Ag(I) is determined spectrophotometrically.

EXPERIMENTAL

A stock solution (1000 ppm) or silver was prepared by dissolving requisite amount of silver nitrate (AR) in distilled water. A 10 ppm solution of silver (I) was prepared by diluting 10 ml of stock solution of silver nitrate to 1000 ml with distilled water. A 0.2% solution of 1-allyl-3-(5-chloro-2-pyridyl) thiourea was prepared by dissolving 0.2 gm of this reagent in 1000 ml of ethanol. 20%

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Naphthalene solution was prepared by dissolving 20 gm of naphthalene in 100 ml. of acetone. The buffer solutions of different pH values were prepared by mixing 1M acetic acid and 1M ammonium acetate solution (for pH range 3–6) and 1M aqueous ammonia and 1M ammonium acetate solution (for pH range 8–11).

A Toshniwal spectrophotometer model (CL-10) was used for all absorbance measurements. All pH measurements were taken with Toshniwal pH meter model (CL-43) equipped with glass and calomel electrodes.

Procedure

An aliquot of standard sample solution of silver(I) containing 1–120 μg of silver, was taken in a dry, clean tightly stoppered Erlenmeyer flask; pH of the solution was adjusted at 6.0 with 3.0 ml of acetate buffer solution and 3.0 ml of 0.2% 1-allyl-3-(5-chloro-2-pyridyl) thiourea solution was added. The contents of the flask were kept standing in hot water bath (50°–60°C) for $\frac{1}{2}$ hr. Then 3.0 ml of 20% naphthalene solution was added to the solution of silver(I) complex and shaken vigorously for 4 minutes. The silver(I) complex of 1-allyl-3-(5-chloro-2-pyridyl) thiourea was adsorbed on microcrystalline naphthalene and it was filtered off, washed with water and dried in an oven (50°–60°C). The silver complex adsorbed on naphthalene was dissolved in dimethylformamide and diluted to 10 ml. Absorbance of the solution was measured against the reagent blank.

RESULTS AND DISCUSSION

Absorption Spectra: The absorption spectra of the reagent blank and the silver-1-allyl-3-(5-chloro-2-pyridyl) thiourea complex in naphthalene-dimethylformamide solution shows that silver complex has one absorption peak at 430 nm. There is negligible absorbance due to reagent blank at 430 nm. Therefore, all the absorbance measurements were carried out at 430 nm.

Effect of pH: The effect of pH on absorbance of the silver(I) complex containing 90 μg of silver was investigated at different pH reanging between 2–10 at 430 nm. It was found that the absorbance of the silver (I) complex in dimethylformamide solution was dependent on pH. The maximum absorbance being obtained between 4.5–10.0 and decreased beyond pH 10.0 (Table 1). Hence the pH of the sample solution was adjusted to 6.0 for all absorbance measurements.

Effect of reagent concentration: In order to investigate the effect of the reagent concentration on the absorbance, varying amounts of 0.2% 1-allyl-3-(5-chloro-2-pyridyl) thiourea were added to the silver (I) solution (90 μg) and buffer solution at pH 6.0. The addition of 0.5 to 7.0 ml of the reagent solution gave the maxima and almost the same absorbance were recorded (Table 2). Therefore, 3.0 ml of the reagent solution was considered the appropriate quantity to be used for all absorbance measurements.

TABLE 1
EFFECT OF pH ON ABSORBANCE

pH	Absorbance 430 nm
2.0	0.375
2.5	0.385
3.0	0.425
3.5	0.435
4.0	0.480
4.5	0.510
5.0	0.545
5.5	0.562
6.0	0.560
6.5	0.561
7.0	0.565
7.5	0.567
8.0	0.564
8.5	0.565
9.0	0.563
9.5	0.565
10.0	0.565
10.5	0.546

Silver (I): 90 μg; Naphthalene: 0.6 gm.

TABLE 2
EFFEFT OF REAGENT CONCENTRATION

0.2% Reagent ml.	Absorbance 430 nm.
0.5	0.245
1.0	0.482
1.5	0.560
2.0	0.562
2.5	0.565
3.0	0.567
3.5	0.561
4.0	0.568
4.2	0.564
4.5	0.572
4.8	0.574
5.0	0.577
5.3	0.576
5.5	0.535
5.8	0.478
6.0	0.465

Silver: 90 μg; pH:6.0; Naphthalene: 0.6 gm.

Effect of naphthalene concentration: The effect of naphthalene concentration on the absorbance measurements was determined by adding varying amounts of 20% naphthalene acetone solution to the solution containing silver(I) complex of 1-allyl-3-(5-chloro-2-pyridyl) thiourea. The absorbance increased with the addition of naphthalene solution upto 1.5 ml and achieved its maximum value in the range 1.5–6.0 ml. Hence, 3.0 ml of 20% naphthalene solution was taken for all absorbance measurements.

Effect of digestion time: The solution of silver(I) complex of 1-allyl-3-(5-chloro-2-pyridyl) thiourea containing 90 μg of silver was digested for different time periods at 50°–60°C and the absorbance were measured at 430 nm to investigate the effect of digestion time on the absorbance. It was observed that absorbance increased slowly upto 10 minutes, digestion time, in the range of 10–45 minutes it remained almost constant and above *ca.* $\frac{3}{4}$ hr. it decreases slowly. Therefore, the digestion time of $\frac{1}{2}$ hr. was selected for the absorbance measurements.

Calibration curve for silver (I): Under the optimum conditions as specified in the recommended procedure, the calibration curve was obtained. The absorbance of the complex showed a linear relationship to the concentration of silver over the range 7–120 μg per 10 ml of dimethylformamide. The molar absorptivity was found to be 3.185×10^4 l mol^{-1}cm^{-1} at 430 nm and sensitivity being 1.595×10^{-2} μg cm^{-2} of silver for the absorbance of 0.001.

Choice of solvent: Tests were made with various organic solvents to dissolve the mixture of the silver complex and naphthalene. The mixture is easily soluble in acetonitrile and dimethylformamide at room temperature. Therefore, dimethyl formamide was chosen as the solvent.

Precision: The precision of the proposed method was estimated with ten samples of silver(I) complex solution containing 90 μg of silver, which gave a mean absorbance of 0.566 with a standard deviation of 0.027%.

Effect of Diverse Ions: The possible interference due to the presence of alkali metal salts and metal ions were also examined and summarised in Tables 3 and 4.

TABLE 3
EFFECT OF DIVERSE ALKALI METAL SALTS

Alkali Metal Salts	Amount Added mg	Found μg
KCl	50	90.6
	100	91.1
	150	91.3
NH_4Cl	75	89.8
	100	90.1
	120	90.2
NaCl	50	89.8
	75	89.9

TABLE 3 (*Contd.*)

Alkali Metal Salts	Amount Added mg	Found μg
	150	90.6
Na_2CO_3	75	90.5
	150	90.7
	200	90.9
Na_2HPO_4	100	90.4
	150	90.7
	200	90.9
$(NH_4)_2SO_4$	50	90.8
	150	90.9
	250	91.4

Silver: 90.0 μg; pH: 6.0; Naphthalene: 0.6 gm.

TABLE 4
EFFECT OF DIVERSE METAL IONS

Ions	Amount of Ion Added mg.	Found μg
Fe(III)	30	90.4
	60	90.7
Ni(II)	50	91.1
	100	89.6
Cu(II)	40	91.3
	100	91.6
Zn(II)	40	90.2
	100	90.5
Al(III)	20	90.5
	50	90.7
Co(II)	50	91.1
	100	91.4
Mn(II)	70	89.3
	150	90.6
Cd(II)	50	90.9
	150	91.2
Mg(II)	90	92.3
	150	92.7
Bi(III)	50	91.3
	100	91.8

Silver: 90.0 μg; pH: 6.0; Naphthalene: 0.6 gm.

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