Indian J.Sci.Res. 6(2): 215-218, 2015 ISSN: 0976-2876 (Print)
ISSN: 2250-0138(Online)

PHOTOMETRIC DETERMINATION OF BISMUTH (III) BY ADSORPTION OF ITS 1-ALLYL-3-(5-CHLORO-2-PYRIDYL) THIOUREA COMPLEX ON MICROCRYSTALLINE NAPHTHALENE

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ABSTRACT

The photometric determination of bismuth (III) by adsorption of its 1-ally1-3-(5-chioro-2-pyridyl) thiourea complex on microcrystalline naphthalene is described. Bismuth (III) formed a stable water insoluble complex with 1-ally1-3-(5-chloro-2-pyridyl) thiourea. This complex was adsorbed on microcrystalline naphthalene. The adsorbed complex was dissolved in dimethylformamide. The absorbance was measured at 485 nm, against the reagent blank. Beer's law was obeyed in the concentration range10-110 µg of bismuth in 10 ml of dimethylformamide. The molar absorptivity was found to be 3.821 x 104 1 mol-1 cm-1 at 485 nm and sensitivity being 1.21 x 10^{-2}µg cm^{-2} ofbismuth for the absorbance of 0.001. The optimum conditions of the present study were investigated by examining the effect of various parameters viz. pH, reagent concentration, amount of naphthalene etc. on absorbance measurements.

KEYWORDS: Pyridyl Substituted Thiourea, Bismuth (III) Complex, Absorbance

Yoe and Overholser (Yoe and Overholser; 1942) have investigated the application of thiourea and its substituted derivatives. These compounds react with many cations and anions to give color reactions of analytical importance. Morgen and Burstell (Morgan and Brustell; 1928) suggested that the presence of three coordinating groups, two amino groups and one thiocarbonyl group in thioureas lead to the formation of polynuclear complexes. amino group acts as a bridging unit. However, various workers (Mawarta and Mann; 1943, Prasad and Srivastava; 1958) have suggested the coordination through sulphur atom. (Sidhanta and Banerjee ; 1951) have considered the bridging in thiourea molecule through sulphur atom. The smaller electron density and greater ionization potential of nitrogen in amino group than sulphur in thiocarbonyl group and also due to steric effect of the substituents in the amino group of thiourea molecule suggests that the co-ordination should be through sulphur rather than nitrogen.

Thiocarbamide CS $(NH_2)_2$ reacts with the bismuth ion in nitric or sulphuricacid solution to form a bright yellow compound (Busev; 1953) Thiocarbamide is a highly selective reagent for the detection and photometric determination of small quantities of bismuth in various materials (Lurie et al. 1949, Busev & Zav; 1950, Busev and Korets ;1979). Derivatives of thiocarbamides are even more sensitive and selective e.g. 0-tolylthiocarbamide which is used for the extractive photometric determination of bismuth (Busev *et al.*; 1969) Diethylthiophosphoric acid is used in the form of its nickel salt for extraction and photometric determination of bismuth in the presence of some elements (Ivanyutin and A.I. Busev; 1958).

1,5-Diphenylthiocarbazone (dithizone), dinaphthyl-thiocarbazone and their numerous derivatives react with the bismuth ion to form intensely colored compounds extractable with chloroform and other organic solvents (Busev and L.A.; 1961).

Bismuthol I and bismuthol II react with the Bi^{3+} ion in an acid medium to form a red precipitate. The ions of other metals form a precipitate of other colors. The reagents are used for the determination of bismuth in the presence of some elements (Majumdar and Chakrabartty; 1957).

A large number of substituted thioureas have been reported in literature as analytical regents. The analytical application of pyridyl substituted thioureas have extensively been studied and reported from our laboratories (Yamamoto *et al.* 1973; Hohar ; 1974, Mathur; 1974).

A number of methods (Sunderarajan and Subbaiyan; 1983, Donaldson 1989, Ortuno *et al*. 1987, Jain *et al*. 1988) are available for the photometric determination of metal ions.

1-ally1-3-(5-chloro-2-pyridyl) thiourea has been chosen as complexing reagent for the determination of bismuth (III).

EXPERIMENTAL

Standard Bismuth (III) Solution

A standard stock solution of bismuth (III) (1000 ppm) was prepared by dissolving requisite amount of bismuth carbonate in distilled water and volume was made upto one litre. A 10 ppm working standard solution of bismuth (III) was obtained by diluting 10 ml of sock solution to 1000 ml with distilled water.

Amount of bismuth was determined gravimetrically.

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1-ally1-3-(5-chloro-2-pyridyl)thioureas Solution

A 0.2% solution of 1-ally1-3-(5-chloro-2-pyridyl) thiourea was prepared by dissolving 0.2 g of reagent in 100 ml of ethanol.

Naphthalene-Acetone Solution

A 20% naphthalene solution was prepared by dissolving 20g. of naphthalene in 100 ml of acetone.

Buffer Solution

Buffer solutions of different pH values were prepared by mixing 1M acetic acid and 1M ammonium acetate for pH range of 3-6 and 1M aqueous ammonia and 1M ammonium acetate solution for pH range of 8-11.

Chemicals used throughout the experimental work were of analytical reagent grade.

Apparatus

A Toshniwal spectrophotometer (Model Cl-10) was used for all absorbance measurements.

The pH measurements were made with Toshniwal pH meter (Model Cl-43) equipped with glass and calomel electrodes.

Procedure

An ali1quot of standard sample solutions of bismuth (III) containing 50-90 µg of bismuth was taken in a dry clean, tightly stoppered Erlenmeyer flask. To it, 3 ml of acetate buffer solution was added to adjust the pH of the solution to 5.0 and then 3 ml of 0.2 1-ally1-3-(5-chloro-2-pyridyl) thiourea solution was mixed. The contents of the flask were kept standing in hot waterbath (50^0-60^0C) for 20 minutes. Then 2.5 ml of 20% naphthalene solution were added to the solution of bismuth (III) complex and shaken vigorously for 5 minutes. The Bismuth (III) complex of 1-allyl-3-(5-chloro-2-pyridyl) thiourea was adsorbed on microcrystalline naphthalene. It was filtered off, washed with water and dried in oven at 55^0C. This dry solid was dissolved in dimethylformamide and diluted to 10 ml. The absorbance measurements of bismuth (III) complex were taken at 485 nm wave length against the reagent blank which was prepared similarly.

RESULTS AND DISCUSSION

Absorption Spectra

A sample containing 70 µg of bismuth (III), 3.0 ml of 0.2% 1-allly-3-(5-chloro-2-pyridyl) thiourea solution and 3.0 ml of acetate buffer solution (pH 5.0) was prepared according to the recommended procedure. The bismuth (III) complex so formed was adsorbed on microcrystalline naphthalene on vigorous shaking for 6 minutes. The solid mixture of naphthalene and bismuth (III) complex was dissolved in dimethylformamide and the absorbance of the solution was measured at wavelength between 360-700 nm. The data of absorbance was plotted against the wavelengths and absorption spectra of bismuth (III) complex solution was obtained against the reagent blank. The bismuth (III) complex had the maximum absorption at 485 nm wavelength whereas the reagent blank had negligible absorption at this wavelength. Therefore, all absorbance measurements were carriedout at 485 nm (γ max) wavelength.

Effect of pH

The different pH on the absorbance of the bismuth (III) complex containing 70 µg of bismuth was investigated at different pH ranging between 2-11 at 485 nm wavelength. The results are shown in Table 1. It was found that the absorbance of this bismuth (III) complex in dimethylformamide solution was very much dependent on pH. The maximum absorbance was obtained in the pH range 4.5-9.0 and decreased beyond pH 9.0. Therefore, the pH of the sample solution of bismuth (III) was adjusted to 5.0 for all absorbance measurements.

Effect of Buffer Solution

The effect of addition of varying amounts of the buffer solution on the absorbance of bismuth (III) complex was studied. The results are given in table 2. The addition of 1ml to 6 ml of the buffer solution broughtout the same absorbance and therefore, 3.0 ml of the buffer solution was chosen as the most suitable amount for our investigations.

Effect of 1-allyl-3-(5-chloro-2-pyridyl)thiourea Concentration

In order to investigate the effect of reagent concentration of the absorbance of bismuth (III) complex solution, different amounts of the reagent solutions were added to the sample solution containing 70 µg of bismuth (III) at pH 5.0. The results are shown in table 3. The absorbance increased upto 1 ml addition of the reagent solution and then remained almost constant upto 5 ml The absorbance decreased slightly beyond the 5 ml addition of the reagent solution. Hence 3.0 ml of the reagent solution was considered the appropriate concentration to be used for all absorbance measurements.

Effect of Concentrations of Naphthalene

The effect of naphthalene concentration on the absorbance measurement was determined by adding different amounts of naphthalene solution to the solution containing bismuth (III) complex of 1-allay1-3-(5-chloro-2-pyridyl) thiourea.

The results are given in table 4. The absorbance increased slightly with the addition of naphthalene solution upto 1.5 ml and achieved its maximum value in the range 1.5-6.0 ml. Hence 2.5 ml of 20% naphthalene solution was taken for all absorbance measurement.

Precision

The precision of the proposed method was estimated with ten samples of bismuth (III) complex solution containing 70 µg of bismuth, which gave a mean absorbance of 0.574 with a standard deviation of 0.15%.

Table 1: Effect of pH

pH	Absorbance 485 nm
2.0	0.414
2.5	0.438
3.0	0.480
3.5	0.502
4.0	0.525
4.5	0.571
5.0	0.574
5.5	0.573
6.0	0.578
6.5	0.570
7.0	0.572
7.5	0.577
8.0	0.57
8.5	0.576
9.0	0.579
9.5	0.535
10.0	0.524
10.5	0.506
11.0	0.497
Bismuth : 70 µg; Naphthalene : 0.5 gm	

Table 2 : Effect of Buffer solution

Buffer solution ml	Absorbance 485 nm
1.0	0.571
1.2	0.577
1.5	0.578
1.8	0.572
2.0	0.570
2.3	0.575
2.5	0.573
2.8	0.574
3.0	0.572
3.5	0.579
3.7	0.571
4.0	0.575
4.2	0.570
4.5	0.572
4.7	0.575
5.0	0.576
5.3	0.574
5.5	0.578
6.0	0.573
Bismuth : 70 µg; Naphthalene : 0.5 gm	

Table 3 : Effect of Reagent concentration

0.2% reagent ml	Absorbance 485 nm
0.0	0.378
0.5	0.473
1.0	0.555
1.5	0.574
2.0	0.578
2.5	0.571
3.0	0.572
3.5	0.579
4.0	0.573
4.2	0.578
4.5	0.576
5.0	0.579
5.3	0.547
5.5	0.536
5.8	0.525
6.0	0.513
6.5	0.465
7.0	0.446
Bismuth : 70 µg; pH : 5.0; Naphthalene : 0.5 gm	

Table 4 : Effect of Naphthalene Concentration

20% Naphthalene	Absorbance 485 nm
0.5	0.515
1.0	0.543
1.5	0.572
2.0	0.576
2.5	0.571
2.7	0.573
3.0	0.575
3.2	0.577
3.5	0.576
3.7	0.578
4.0	0.571
4.3	0.574
4.5	0.570
4.8	0.573
5.0	0.578
5.3	0.574
5.5	0.576
6.0	0.579
Bismuth : 70 µg; pH : 5.0; Naphthalene : 0.5 gm	

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