Indian J.Sci.Res. 07 (1): 221-224, 2016 Research Article ISSN: 0976-2876 (Print)
ISSN: 2250-0138 (Online)

DIVERSE ION STUDIES AND EFFECT OF DIGESTION TIME IN THE PHOTOMETRIC DETERMINATION OF BISMUTH (III) BY 1-ALLYL-3-(5-CHLORO-2-PYRIDYL) THIOUREA

SUBHASH P.D.[1]

Department of Chemistry, St. Andrew's College, Gorakhpur, 273001, India

ABSTRACT

The effect of diverse ions, and digestion time in the 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 range 10-110 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} of bismuth for the absorbance of 0.001. The optimum conditions of the present study were investigated by examining the effect of various parameters viz. diverse ions, digestion time, shaking time and amount of naphthalene etc. on absorbance measurements.

KEYWORDS: Pyridylthiourea, Bismuth (III) Complex, Digestion Time

INTRODUCTION

The application of thiourea and its substituted derivatives have widely studied (J H Yoe *et al.*, 1942). These compounds react with many cations and anions to give color reactions of analytical importance The significance of the presence of three coordinating groups, two amino groups and one thiocarbonyl group in thioureas lead to the formation of polynuclear complexes (Morgan and Brustel 1928),the amino group acts as a bridging unit. However, various workers (Mavarata and Mann 1942; Prasad and Shrivastava, 1956) 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 sulphuric acid solution to form a bright yellow compound (A I Busev *et al.*, 1942). Thiocarbamide is a highly selective reagent for the detection and photometric determination of small quantities of bismuth in various materials. Derivatives of thiocarbamides are even more sensitive and selective e.g. o-tolylthiocarbamide which is used for the extractive photometric determination of bismuth (A I 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 (M N Ivanyutin, 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(A I Busev 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 (AK Majumdar, 1951).

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 (Y Yamamoto *et al.*, 1973).

A number of methods (J Sunderarajan and M Subbaiya, 1983) 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.

---

[1]**Corresponding author**

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 aliquot 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 water bath (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 carried out at 485 nm (γ max) wavelength.

Effect of Digestion Time

The solution of Bismuth (III) complex of 1-allyl-3-(5-chloro-2- pyridylthiourea) containing 70µg of bismuth was digested for different time periods at 50-60^0C and absorbance was measured at 485 nm to investigate the effect of digestion time on the absorbance. Results are given in Table 1. It was observed that absorbance increased slowly up to 10 minutes digestion time, in the range of 10-45minutes, the absorbance remained almost constant and above 45 minutes, it decreased slowly. Hence digestion time of 25 minutes was selected for all absorbance measurements.

Table 1: Effect of digestion time

Digestion Time	Absorbance 485 nm
2	0.452
5	0.498
8	0.543
10	0.575
15	0.577
20	0.571
25	0.579
30	0.575
35	0.578
40	0.573
45	0.574
50	0.520
55	0.457
60	0.413
65	0.356
70	0.308
Bismuth(III) :70µg; pH :56.0; 0.2% reagent: 3ml	

Effect of Shaking Time

To study the effect of shaking time on the absorbance 2.5 Ml of 20% naphthalene solution were added to the bismuth (III) complex solution containing 70µg of bismuth at pH 5.0 and shaken vigorously for

different periods of time. The absorbance were measured at 435 nm .Results are given in Table 2.

Table 2: Effect of shaking time

Shaking Time (sec)	Absorbance 485 nm
5	0.570
10	0.573
15	0.576
20	0.576
25	0.578
30	0.571
35	0.574
40	0.570
45	0.573
50	0.575
55	0.576
60	0570
65	0.579
70	0.576
80	0.574
85	0.568
90	0.556
95	0.542
100	0.547
Bismuth(III) : 70 µg; pH : 5.0; 0.2% reagent 3ml	

Absorbance remained practically constant up to 8 minutes .Beyond 8 minutes absorbance were decreased gradually. Therefore, shaking time of 5 minutes was chosen for the 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 3. The absorbance increased slightly with the addition of naphthalene solution up to 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.

Table 3: Effect of Naphthalene concentration

20%Naphthalene, mL	Absorbance 435 nm
0.5	0.515
1.0	0.543
1.5	0.572
2.0	0.576
2.5	0.571
3.0	0.573
3.2	0.577
3.5	0.576
3.7	0.578
4.0	0.571
4.3	0.574
4.5	0.574
4.8	0.570
5.0	0.578
5.3	0.574
5.5	0.576
6.0	0.579

Effect of Diverse Ions

Interference due to the presence of alkali metal salts and metal ions are summarized in table 4 and 5 respectively

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 4: Effect of Diverse Alkali metal Ions

Alkali Metal Salts	Amount Added mg	Found µg
KCl	100	70.6
	150	70.2
	200	70.8
NH_4Cl	70	71.3
	100	71.5
	200	71.8
NaCl	60	71.4
	120	71.6
	200	71.9

Na_2CO_3	80	71.4
	150	72.1
	250	72.3
Na_2HPO4	80	71.5
	160	71.6
	250	71.9
$(NH_4)_2SO_4$	50	69.8
	150	70.2
	250	70.4
	Bismuth(III) : 70 µg; pH : 5.0; Naphthalene:0.5gm	

Table 5: Effect of Diverse Metal Ions

Metal Ions	Amount of Ion Added mg.	Found µg
Fe(III)	20	71.2
	50	71.6
Ni(II)	30	70.1
	60	70.3
Cu(II)	50	71.5
	100	71.7
Zn(II)	60	70.5
	120	70.8
Co(II)	50	71.2
	100	71.5
Ag(I)	100	71.6
	150	71.8
Cd(II)	70	71.8
	150	71.6
Mg(II)	80	72.23
	120	72.6
Mn	60	71.2
	100	71.6
	Bismuth (III) :70 µg; pH :5.0 ; Naphthalene :0.5g	

REFERENCES

J.H. Yoe and L.G. Overholser., 1942. Ind. Eng. Chem. Anal., Ed. 14: 435.

Morgan and Brustell., 1928. J. Chem., 143.

Mawarta and Mann., 1943: J. Chem. Soc., 661.

Prasad and Shrivastava.,1958. J. Ind. Chem. Soc., 35:793..

S.K. Sidhanta and S.N. Banerjee., 1951. J. Am. Chem. Soc., 73: 765.

A.I. Busev, Analytical Chemistry of Bismuth., 1953.Mascow, 12d. AN USER.

A.I. Busev, N.V. Shvedovaaa, V.K. Akomov and E.G. Fursova., 1969zh Akh, 24: 1833.

M.I. Ivanyutin and A.I. Busev., 1958. Reports of Higher School. Chemistry and Chem. Technology., 1: 73.

A.I. Busev and L.A. Bazhanova., 1961.zh Akh, 6: 2210.

A.K. Majumdar and M.M. Chakrabartty., 1957. 2. anal. Chem. Bd. 154: 2805.

Y. Yamamoto, K. Horiuchi, K. Yoda K. Kuko and Y. Murakami., 1973. Kyritus. Yakka Diagaku, Kenyu, Nemp., 18: 64.

G. Sunderarajan and M. Subbaiyan., 1983. J. Ind. Chem. Soc., 60: 1182.