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SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF TRACE AMOUNT OF BISMUTH IN ALLOY SAMPLES USING 4-HYDROXYBENZALDEHYDE THIOSEMICARBAZON

Satheesh K. Padmanabha [1,*] and Suryanarayana V. Rao [2]
[1]Department of Chemistry, Veltech Dr.R.R. & Dr.S.R. Technical University,
Avadi Chennai-600062, India
[2]Department of Chemistry, Sri Krishnadevaraya University,
Anantapur-515003, Andhra Pradesh, India
*E-Mail: satheeshvasista@gmail.com

ABSTRACT

The reagent 4-Hydroxy benzaldehyde thiosemicarbazone (4-HBTS) has been synthesized and characterized and its analytical applications were investigated. The reagent 4-HBTS reacts with aqueous solution of Bi(III) ion in the pH range of 5.5-6.5 at room temperature and forms a green coloured 1:2 [Bi(II):4-HBTS] complex with stability constant $2.04x10^{11}$. The complex has maximum absorption at 356 nm. The molar absorptivity and sandell's sensitivity for the coloured solution are found to be $1.3X10^4$ M^{-1} cm^{-1} and 0.016075 µg cm^{-2} respectively. Beer's law is obeyed in the range of 0.835-8.359 µg/mL. The interference of various diverse ions has been studied. The procedure was successfully applied to the determination of bismuth in water, industrial waste water samples and also in different alloy samples.

Keywords: Bismuth (III), 4-Hydroxy benzaldehyde thiosemicarbazone, Spectro Photometry, alloy samples, industrial waste water.

INTRODUCTION

Bismuth and its compounds came to be known in the fourteenth century. However the metal at first could not be distinguished from lead and tin. Its properties were first described towards the middle of the eighteenth century. It occurs in free state as well as in the combined form. The important sources of bismuth are bismuth glance Bi_2S_2, bismuth telluride Bi_3Te_3 and bismuth oxide (Bi_2O_3). Bismuth is found in earth's crust, up to 0.0002%. It is least toxic among the heavy metals. Bismuth has been used in the form of sub carbonates and subgalletes for the treatment of diarrhea, dysentery and ulcers. Bismuth is also used in the manufacture of low melting alloys which finds application in the fusible elements in automatic sprinklers, special solders, safety plugs in compressed gas cylinders and automatic shutoffs for gas and electric water heating systems.

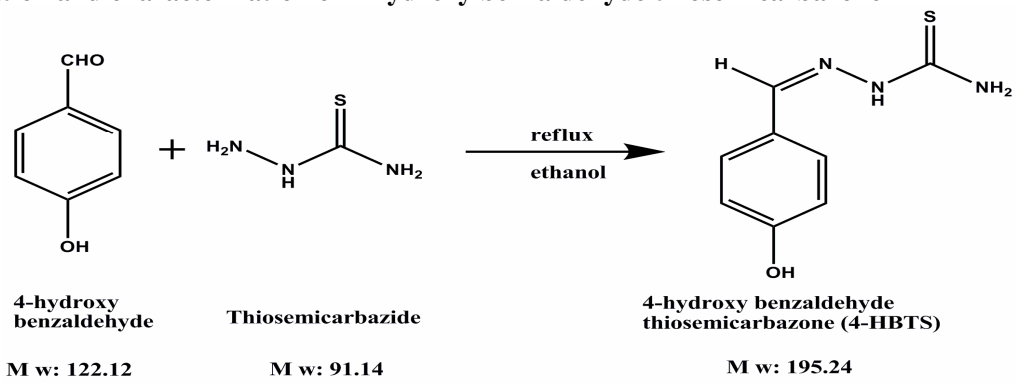
Number of organic compounds such as, 2-(4-antipyridyazo)-4,5-dicarboxy methoxybenzoic acid[1], Thiourea[2,3], mesotetra(4-Trimethyl ammonium phenyl)porphyrin, Di antipyril thiourea and P-methyldibromo-arsenazo, have been reported as a sensitive spectrophotometric reagents for the determination of bismuth(III) ion.[4-6] However these determination methods were suffered from critical pH range and low tolerance limit of associated metal ions. Other reagents like, N-methyl piperazone4-carbothioic acid, Morpholine-4-carbdithioate, potassium propylxanthate, N,N´-bis(2-hydroxy methyl)glycine and Rivanol in presence of iodine, 2,4,6-triphenyl pyrylium perchlorate and N-(2-acetamide)iminido acetic acid are useful for the determination of bismuth in the pharmaceutical and alloy samples.[7-13]

Thiosemicarbazones are good analytical reagents.[14-18] In this present note a simple, selective and sensitive spectrophotometric method was developed for the determination of trace amount of Bismuth in alloy samples using 4-Hydroxybenzaldehydethiosemicarbazone.

EXPERIMENTAL

The absorbance and pH measurements were made on a Shimadzu UV-Visible spectrophotometer (model UV-160A) fitted with 1.0cm quartz cells and Elico digital pH meter (modelLI20) respectively.

Preparation and characterization of 4-hydroxy benzaldehyde thiosemicarbazone



Scheme-1: Preparation of 4-HBTS

The reagent was prepared by the simple condensation of 4-hydroxy-benzaldehyde(1.22gm) with (0.91gm) of thiosemicarbazide in a clean 250ml round bottomed flask. 4-hydroxybenzaldeyde was dissolved in 100 mL of methanol and thiosemicarbazide was dissolved in hot water. The solutions were mixed and refluxed for two hours. On cooling brown colored product was formed which was collected by filtration. It was recrystallized using methanol and dried in vacuum.

The yield was 80% by weight and the M.P. is 207-209 $^{\circ}$C. The structure of the compound was established using both IR and NMR spectra.

Characterization

The IR spectrum of the compound was recorded using Perkin-Elmer 137 IR spectrometer in KBr. The peaks observed at 3458 cm^{-1} and 3342 cm^{-1} may be assighned to symmetric and assymetric (–N-H) steching frequency of primary amino group. The peak observed at 3028 cm^{-1} may be assighned to Ar-H stretching frequency of benzene ring, and the C=N stretching frequency of azomethine was observed at 1595cm^{-1}. The peak observed at 3218-3092 cm^{-1} has assighned for –OH group stretching frequency. The observed strong peak at 1056 cm^{-1} may assigned to C=S stretching frequency. The peaks observed in the range of 1530-1360 cm^{-1} frequency were charecteristic aromatic ring stretching frequency.

The ^{1}H-NMR spectrum of the compound was recorded with DRX300 NMR spectrometer in DMF solvent. The peak observed at δ value 10.74(H) was charecterstic of phenolic –OH group. The peak found at δ value 7.86(4H) may be due to aromatic protons, the peak observed at δ value 6.8 (2H) may be due to $–NH_2$ protons attached to thionylgroup (C=S) and the peak observed at δ value 9.0 is due to aldehydic proton. The peak at δ value 11.5 may be due to –NH proton (azomethine).

Preparation of the solutions

Bi (III) solution

1.2126 g of bismuth nitrate (AR, BDH, India) was dissolved in doubly distilled water in a 250 mLl volumetric flask to get 1 x 10^{-2} M solution and standardized. The stock solution was suitably diluted to get the required concentration

Stock solution of the reagent

0.195 g of recrystallized sample of the reagent 4-hydroxybenzaldehyde thiosemicarbazone was dissolved in DMF in a 100 mL volumetric flask to obtain the stock solution (0.1 M), and it was suitably diluted to get the required concentration. Fresh reagent solutions were prepared as and when required.

Buffer solutions

The buffer solutions are prepared by mixing 1M hydrochloric acid and 1M Sodium acetate (pH 1.0-3.0) and 0.2M acetic acid and 0.2M sodium acetate (pH 3.5-7.0). Exact pH of the solution was measured using a pH meter.

Procedure

1 mLof 1 x 10^{-3} M bismuth nitrate solution, 10 mLof buffer solution of required pH, 1 mL of 1 x 10^{-2} M 4-hydroxy benzaldehyde thiosemicarbazone are taken in a 25 mL standard flask. The contents of the flask were made up to the mark with doubly distilled water. The solution has shaken well for uniform concentration. The blank solution is also prepared on the same lines but without containing the metal ion. The spectrum of the experimental solution is recorded in the wavelength range 350 to 700 nm against the respective blank solution.

RESULTS AND DISCUSSIONS

Bi (III) reacts with 4-HBTS in weak acidic pH to give a green coloured water soluble species. The colour reaction between Bi (II) and 4-HBTS is instantaneous even at room temperature. The maximum absorbance λ_{max} of the green coloured species (complex) was observed at 356 nm which remains constant for 24 hours. Studies on the effect of pH on the absorbance revealed that the maximum colour was formed in a solution of pH 6.5. A tenfold excess of the reagent is adequate for complete colour development. Addition of excess of reagent has no adverse effect on absorbance.

The studies relating to the effect of Bi (III) revealed that a linear relationship exists between the metal ion concentration and the absorbance in the range of 0.837-8.359 µg/mL. The molar absorptivity and sandell's sensitivity are $1.2x10^4$ L.mol $^{-1}cm^{-1}$ and $1.64x10^{-3}$ µg/cm^2 respectively. The effect of the reagent on absorbance is also studied, linear relationship has not found between the reagent and the absorbance. As the metal ion Bi (III) forms a coloured complex with reagent, an attempt is made to determine the composition and the stability of the complex. Job's method and mole ratio method are conducted to make these determinations. It is noticed that the Bi(III) ions form a stable green coloured 1:2 [M:L_2] complex with 4-hydroxy benzaldehyde thiosemicarbazone. The stability constant of the complex was found to be $2.04x10^{11}$.

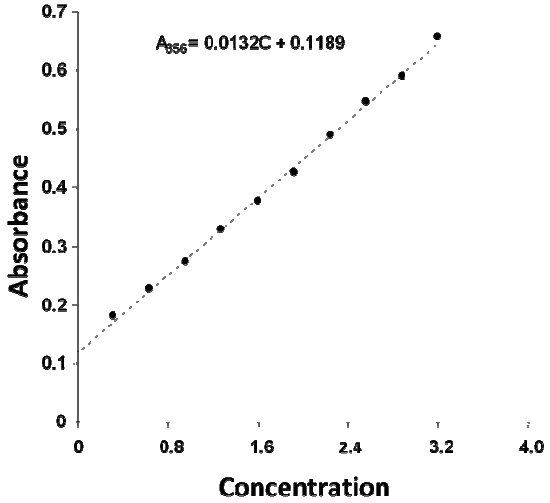


Fig.-1: (a) Beer's Law verification;

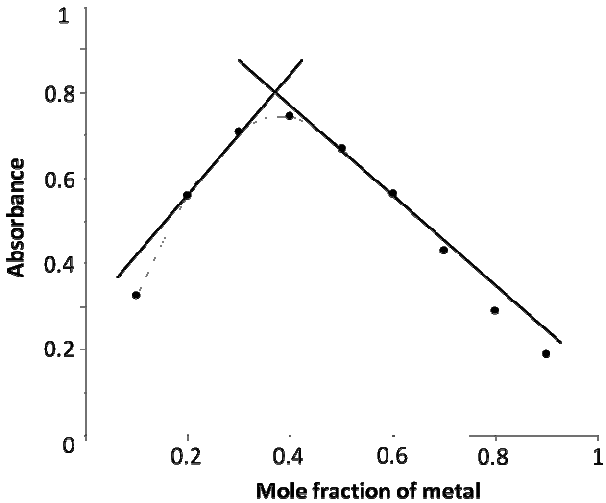


Fig.-1: (b) Job's method for the determination of Composition of the complex (M:L)

Table-1: Physico-chemical and analytical characteristics of Bi(III)- 4-HBTS

Characteristics	Results
Λ_{max} (nm)	356
p^H range (optimum)	5.5-6.5
Moles of the reagent required per mole of metal ion for complete colour development	10 folds
Molar absoptivity ($Lmole^{-1}cm^{-1}$)	$1.2x10^4 L.mol^{-1}cm^{-1}$
Sandell's sensitivity($\mu g/cm^2$)	$1.64x10^{-3}$
Composition of the complex (M:L 2ratio)	1:2
stability constant of the complex	$2.04x10^{11}$
Standard deviation in the determination of 1.17µg/ml of Bi(III) for ten determinations.	0.003447
RSD	0.0824

Interference studies

Influence of various cations and anions on the absorbance values is studied and the data is presented in the Table 2 the cations were chosen in such a way so that they either belong to the same group (or) same period. The effect of neighboring metals of bismuth in the periodic table is studied.

Table-2: Tolerance limit of foreign ions in the determination of bismuth in the determination of 0.15µg/ml of Bi (III).

Ion added (Anions)	Tolerance limit (µg/ml)	Ion added (Cations)	Tolerance limit (µg/ml)
Iodide	507.6	Manganese(II)	11.0
Bromide	319.6	Cobalt(II)	1.17
Chloride	141.8	Lead(II)	2.5
Nitrate	496.0	Cadmium(II)	4.5
Iso cyanide	232.0	Iron(II)	2.2
Fluoride	75.9	Nickel(II)	2.4
Tartarate	1104.0	Magnesium(II)	0.6
Thio urea	182.64	Zinc(II)	1.8

The tolerance limit in each case is expressed in µg/mL. Most of the general anions do not show much interference. It is seen from the data that all the metal ions interfere in the determination of bismuth as the tolerance limits are low.

Analysis of synthetic mixtures

In order to extend the utility of the proposed method, it was used for the determination of Bi (III) content in synthetic mixtures corresponding to alloys like lipowitz's and solder alloys. The results are reported in table-3. Comparision of present method with other reported spectrophotometric methods for the determination of Bismuth is presented in Table- 4

Table-3: Determination of Bi (III) in bismuth based alloys

Alloy Sample	Certified Composition (%)	Amount of Bi (III) (%) Present	found [a]	Relative error (%)
Bi Solder alloy	Bi-40, Pb-40,Sn-20	40	39.25	-1.875
Lipowitz's alloy	Bi-50,Pb-26.7,Sn-13.3, Cd-10	50	50.15	+0.3

a Average of five detrerminations.

Table-4: Comparision of present method with other reported spectrophotometric methods for the determination of Bismuth

Reagent name	pH	Λmax	Molar absorptivity (Lmole $^{-1}$cm $^{-1}$)	Beer's law range (µg/ml)/ppm.	Ref
1-amino-4,4,6-trimethyl(1H,4H) pyimidine-2-thiol	5M perchloric acid	470	$6.5x10^3$	7-24ppm	19
Semi –xylanol orange	-	540	$4.2x10^4$	10-30µg/ml	20
1(4′-Bromophenyl) 4,4,6-Trimethyl (1H,4H)-Pyrimidine-2-Thiol	0.3M HCl	410	$6.501x10^3$	7-24ppm	21
Di ethylene tri amine penta-acetic acid	1.6M perchloric acid	270	-	1-40 µg/ml.	22
4-Hydroxy benzaldeyde thiosemicarbazone	6.5	356	$1.2x10^4$	0.837-8.359µg/ml.	Present method

CONCLUSIONS

The methods described in this paper allows for the rapid, precise and reliable determination of trace amounts of Bismuth in some alloy samples using 4-Hydroxy benzaldehyde thiosemicarbazone. The main benefits of the procedure are the enhanced sensitivity of the spectrophotometric method, low cost, fairly easy operation and speed of analysis.

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