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Spectrophotometric Determination of Gallium(III) as Bipyridylglyoxal *bis*(4-Phenyl-3-thiosemicarbazone) Derivative

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A new simple spectrophotometric method is developed for the determination of gallium. The reagent bipyridyl glyoxal *bis*(4-phenyl-3-thiosemicarbazone) reacts with Hg(II), V(V), Ru(IV), Ga(III), In(II), and Pt(II) to develop colour in aqueous N,N-dimethylformamide media with maximum absorbance within pH range 2-5. The composition of the metal chelates was examined by variation of the metal: ligand mole ratio. The molar absorptivity was observed within 1.8×10^{-3} to 4.6×10^{-4} L mol^{-1} cm^{-1} within 390-448 nm. The linear calibration curves were observed with 0.2 to 20 µg/mL. Highest molar absorpitivity was indicated by gallium(III) with detection limit 0.022 µg mL^{-1}. The proposed method was successfully applied for the determination of gallium(III) from semiconductor and medicinal drug.

Key Words: Gallium(III), Bipyridyl glyoxal *bis*(4-phenyl-3-thiosemicarbazone), Spectrophotometric determination.

INTRODUCTION

Gallium occurs at trace levels in the earth's crust, in silicate rocks, minerals and ores like bauxite, germanites and coal. Gallium is also obtained as a by-product of copper, zinc, lead and aluminum refining and is used in high temperature thermometers as a substitute of mercury, in arc lamps as a component of metal alloys, production of low melting alloys, inter-metallic compounds used in the electronic industry for manufacturing of semi conductors, lasers, special optical glasses and silicon replaced integrated circuits[1-3]. Gallium is a low-order toxic element and its citrate and nitrate salts are used as tumour-scanning and antitumoural agents. The toxicity of gallium and its role in pharmacokinetics have been reviewed[4-6]. The increasing use of gallium, especially in semiconductor industry has made it necessary to develop simple and sensitive method for specific and precise determination of gallium in environmental, biological and gallium containing alloys and minerals.

In recent years, various analytical techniques have been reported for the determination of gallium such as; atomic absorption spectrometry[7-10], graphite furnace atomic absorption spectrometry[11-17], flow injection[18], X-ray fluorescence spectrometry[19,20], fluorimetry[21-23], inductively coupled plasma mass spectrometry[24-26], inductively coupled plasma atomic emission spectrometry[27,28] and spectrophotometry[29-38]. The spectrophotometry is available in almost all analytical laboratories and is easily operatable, cheaper and less time consuming technique. For the spectrophotometric determination of gallium, chromazurol S[39], 4-(2-pyridylazo)resorcinol[40], 2-(2-pyridylazo)-5-monoethyl-amino-*p*-cresol[41], rhodamine B[42], N-*p*-chlorophenyl-2-furohydroxamic acid[43], 2-(2-(3,5-dibromopyridyl)azo)-5-diethylamino benzoic acid[44] and 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol[36] have been reported as chromogenic reagents for the determination of gallium.

Thiosemicarbazones and phenyl thiosemicarbazones are interesting complexing reagents, because they form highly stable and intensely coloured complexes immediately by binding through sulphur and hydrazine nitrogen atoms, which are ideally suited for spectrophotometric detection[45,46]. Studies on dithiosemicarbazones derived from glyoxal, biacetyl and benzil have been reported[47]. Gonzalez-Balairon *et al.*[48] have reported bipyridyl glyoxal *bis*(4-phenyl-3-thiosemicarbazone) (BGPT) for the spectrophotometric determination of zinc, cadmium and copper.

The present work examines the reaction of BGPT spectrophotometrically with a number of metal ions and determination of Ga(III) from medicinal drug and semiconductor.

EXPERIMENTAL

The reagent BGPT was prepared as reported[48] by heating together 4-phenyl-3-thiosemicarbazide and 1,2 diketone (pyridil) in 2:1 molar ratio in ethanol in the presence of a few drops of 1 N HCl. The reaction mixture was cooled at -5ºC for 24 h. The precipitate obtained was filtered and re-crystallized from ethanol. The compound melted at 222ºC.

The spectrophotometric studies were carried out on Hitachi 220 (Hitachi (pvt) Ltd. Tokyo) spectrophotometer. IR spectrum of the reagent BGPT was recorded in KBr on Perkin-Elmer 1360 IR spectrophotometer. The pH measurements were made on a digital (Orion model 420 A) pH meter.

GR grade chemicals: sodium acetate, acetic acid, sodium bicarbonate, sodium carbonate, boric acid, borax, ammonium chloride, ammonia (23 %), chloroform, acetonitrile, hydrochloric acid (37 %), perchloric acid (70 %), sulphuric acid (95-98 %) and nitric acid (65 %) (E-Merck, Germany) were used. Stock standard solution of Ga(III) was prepared by dissolving the appropriate amount of Ga_2O_3 in mixture of nitric acid and hydrochloric

acid. Freshly prepared doubly distilled water throughout the present studies was used. The buffer solutions in the pH range 1-10 at unit interval were prepared from the following: hydrochoric acid (0.1 M)-potassium chloride (1 M) pH 1-2; sodium acetate (1 M)-acetic acid (1 M) pH 3-6; ammonium acetate (1 M)-ammonia pH 7; boric acid (1 M)-borax (1 M) pH 8-9 and ammonium chloride (1 M)-ammonia (1 M) pH 10.

Analytical procedure

Dissolution method: The solution (1-5 mL) containing mercury(II) (20-80 µg), vanadium(V) (25-200 µg), ruthenium(IV) (40-200 µg), gallium(III) (2-10 µg), indium(III) (10-50 µg), or platinum(II) (10-50 µg) was transferred to 10 mL volumetric flask separately. The solution was added appropriate buffer solution 2 mL [pH 2 for vanadium(V), ruthenium (IV), indium(III) and platinum(II); pH 3 for gallium(III) and pH 5 for mercury(II)]. The reagent BGPT solution (3 mL) (0.025 % w/v in dimethylformamide) was added and volume was adjusted to the mark with methanol. The absorption spectra were recorded against reagent blank within 500-300 nm.

Solvent extraction: The solution (1 to 5mL) containing elements as described in analytical procedure (dissolution method) was transferred to the separating funnel and pH of the solution was adjusted. The reagent BGPT solution (3 mL) (0.025 % in dimethylformamide) was added followed by chloroform (3 mL). The contents were mixed well and layers were allowed to separate. The organic layer was collected in 10 mL volumetric flask. The extraction was repeated with chloroform (2 mL). The volume was adjusted to mark with methanol. The absorption measurements were made against reagent blank in same solvent system.

Spectrophotometric procedure for the determination of gallium(III) from medicinal drug: The sample medicinal drug 10 mL (Gallium A.P.Q) was concentrated to 1-2 mL and was heated at 550ºC for 4 h in furnace. The residue was allowed to cool and was added 3-4 mL aqua regia (HCl: HNO_3 3:1) and heated gently to clear solution. The solution was concentrated and re-dissolved in water and final volume was adjusted up to 10 mL, solution 2 mL was taken and solvent extraction procedure was followed. The quantization was made from external calibration curve.

Spectrophotometric procedure for the determination of gallium(III) from I.C semi conductor: An integrated circuit (I.C) sample was purchased from the local market of Hyderabad; 2.23 g was dissolved in aqua regi (HCl: HNO_3 3:1) (5 mL), most of the acid was evaporated on hot plate, 3 mL HCl was added and again heated near to dryness, residue was dissolved in 2 mL double distilled water and volume was adjusted to 25 mL with d.d water. Solution 2 mL was taken and procedure was followed as solvent extraction procedure.

Determination of gallium from medicinal drug and semiconductor by standard addition technique: 2 mL each from the solution of medicinal drug and the semiconductor solution was added gallium 0.5 µg and was processed as solvent extraction procedure. The amount of gallium from medicinal drug and semiconductor was calculated from the increase in the absorbance due to amount added.

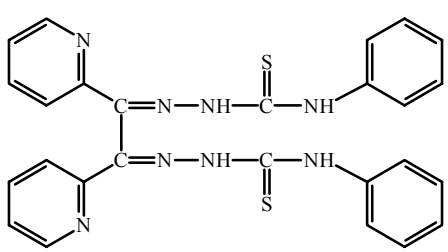

Fig. 1. Structural of bipyridyl glyoxal *bis*(4-phenyl-3-thiosemicarbazone)

RESULTS AND DISCUSSION

The reagent bipyridyl glyoxal *bis*(4-phenyl-3-thiosemicarbazone) (BGPT) reacts with a number of metal ions immediately to form coloured complexes in acidic to neutral media[48]. The reactions of the reagent BGPT were examined towards mercury(II), vanadium(V), ruthenium(IV), gallium(III), indium(III) and platinum(II). The elements developed yellow to reddish colour immediately in aqueous-methanol-dimethyl formamide in slightly acidic medium. The complexes were also extractable in chloroform. It was therefore the complexes were examined spectrophotometrically. The results of spectrophotometric study are summarized in Table-1 and the complexes indicated the absorbance within 390 to 448 nm with molar absorptivities of 1.8×10^3 to 4.6×10^4 L mol^{-1} cm^{-1}.

TABLE-1
QUANTITATIVE SPECTROPHOTOMETRIC DATA OF METAL CHELATES OF BGPT

Metal chelates	λ_{max} (nm)	pH of maximum derivatization	Composition of chelate metal:ligand	Σ (L mol^{-1} cm^{-1})	Calibration range (µg mL^{-1})
Hg(II)	390	5	1:2	1.8×10^4	2-8
V(V)	448	2	1:3	1.8×10^3	2.5-20
Ru(IV)	395	2	1:2	2.2×10^3	4-20
Ga(III)	422	3	1:3	4.6×10^4	0.2-1
In(III)	415	2	1:3	1.7×10^4	1-5
Pt(II)	390	2	1:2	2.5×10^4	1-5

The effect of pH, reagent concentration and extracting solvent on the colour reaction were examined. The effect of pH was varied within 1 to 10 at an interval of unit pH. Vanadium(V), ruthenium(IV), indium(III) and platinum(II) indicated maximum absorbance at pH 2 and KCl-HCl buffer covered the pH range satisfactory. Gallium(III) and mercury(II) indicated maximum absorbance at pH 3 and pH 5 respectively (Fig. 2) and sodium acetate-acetic acid buffers pH 3 and 5 were used. The reagent BGPT is only slightly soluble in water and methanol, therefore its solution (0.025 % w/v) was prepared in dimethyl formamide.

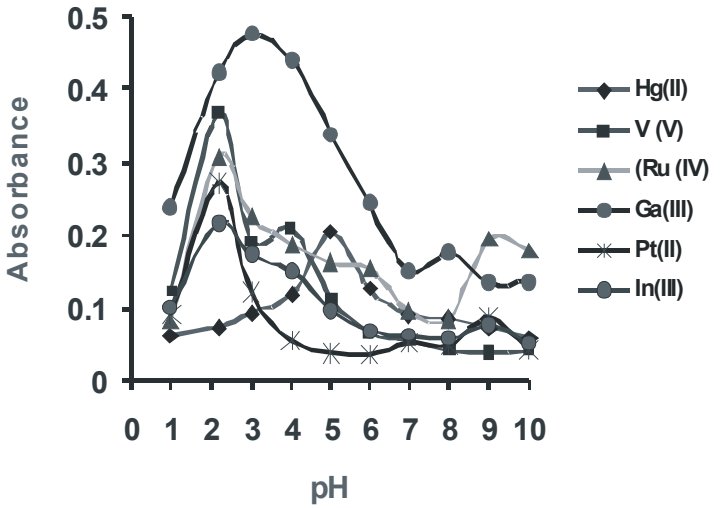

Fig. 2. Effect of pH on Hg(II), V(V), Ru(IV), Ga(III), In(III) and Pt(II) as BGPT chelates

The solution 1-4 mL at an interval of 1 mL was added for each element. Same colour was developed when solution 2 mL and above was added and solution 3 mL was added for each determination to ensure the excess of the reagent was present. The complexes were observed soluble in water-methanol-dimethyl formamide, but for possible preconcentration solvent extraction procedure was examined. Chloroform, dichloroethane and carbon tetrachloride solvents were examined. However because of the ease of the extraction chloroform was selected as solvent. At the optimized conditions the vanadium(V) indicated lowest sensitivity with molar absorptivity 1.8×10^3 L mol^{-1} cm^{-1} at 422 nm. The composition of the complexes was examined by variation in mole ratio of metal to ligand (Fig. 3) and it was observed that Hg(II), Pt(II) and Ru(IV) formed the complexes with metal: ligand (1:2) and V(V), Ga(III) and In(III) with metal : ligand (1:3). The V(V) indicated the linear calibration range within 4-20 µg mL^{-1}, but for

Ga(III) it was 0.2 to 1.0 μg mL^{-1} (Table-1). The coefficient of determination were observed within 0.991 to 0.999. All the complexes indicated high colour stability and did not indicate any change in absorbance up to 24 h.

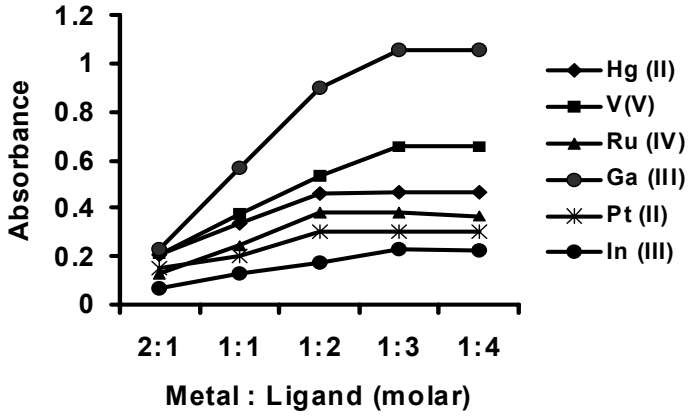

Fig. 3. Variation in metal: ligand ratio of Hg(II), V(V), Ru(IV), Ga(III), In(III) and Pt(II) as BGPT chelates

All the complexes indicated reasonable sensitivity and solution stability, but gallium(III) indicated highest sensitivity, was examined for spectrophotometric determination of gallium.

The effect of Cu(II), Ni(II), Ag(I), Hg(II), Al(III) and In(III) on the determination of gallium (0.5 μg mL^{-1}) was examined in the concentration range 0.5-2.0 μg mL^{-1} and % recovery of gallium was observed within 95-99.8 % (Table-2). The method was applied for the determination of gallium from the medicinal drug (Gallium A.P.Q), homeopathic drug present

TABLE-2
EFFECT OF FOREIGN IONS ON THE DETERMINATION OF 0.5 μg mL^{-1} GALLIUM AT pH 3

Foreign ion added	Amount of ion added (μg mL^{-1})	Amount of gallium found (μg mL^{-1})	Recovery (%)
Ni^{2+}	0.1	0.497	99.4
	0.2	0.491	98.2
	0.5	0.485	97.0
	1.0	0.483	96.6
	2.0	0.483	96.6
Cu^{2+}	0.5	0.492	98.4
	1.0	0.490	98.0
	2.0	0.487	97.4
	1.5	0.485	97.0
	2.0	0.485	97.0

Foreign ion added	Amount of ion added (μg mL^{-1})	Amount of gallium found (μg mL^{-1})	Recovery (%)
In^{3+}	0.5	0.499	99.8
	1.0	0.498	99.6
	1.5	0.494	98.8
	2.0	0.490	98.0
Ag^{+}	0.5	0.497	99.4
	1.0	0.494	98.8
	2.0	0.492	98.4
Hg^{2+}	0.5	0.499	98.0
	1.0	0.499	99.8
	1.5	0.495	99.0
	2.0	0.495	99.0
	3.0	0.492	98.4
Al^{3+}	0.2	0.492	98.4
	0.4	0.481	96.4
	0.8	0.480	96.0
	1.0	0.476	95.2
	2.0	0.475	95.0

in local market of Hyderabad, saled to increase the baby feed of women and an integrated circuit (IC) (semiconductor). The drug and IC was analyzed after acid digestion. The quantization was carried out from calibration curve and standard addition technique. The results are summarized in Table-3 and indicate RSD within 3.6 to 4.6 %.

TABLE-3
QUANTITATIVE SPECTROPHOTOMETRIC DETERMINATION OF Ga(III) FROM MEDICINAL DRUG AND INTEGRATED CIRCUIT (IC)

Sample	Amount found RSD (%) (n = 3)	Amount found by standard addition RSD (%) (n = 3)
Gallium drug (A.P.Q)	1.15 μg mL^{-1} (4.2)	1.2 μg mL^{-1} (3.6)
I.C semiconductor	0.172 mg g^{-1} (3.8)	0.174 mg g^{-1} (4.6)

Conclusion

The spectrophotometric characteristics of mercury(II), vanadium(V), ruthenium(IV), gallium(III), indium(III) and platinum(II) with BGPT were examined. The gallium(III) indicated highest sensitivity and was applied for the determination of gallium from a drug and Integrated circuit (IC) and RSD was observed with 4.6 %.

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