

DIRECT AND DERIVATIVE SPECTROPHOTOMETRIC DETERMINATION OF GOLD (III) USING 3,5-DIMETHOXY-4-HYDROXYBENZALDEHYDE BENZOYLHYDRAZONE(DMBBH) IN PRESENCE OF MICELLAR MEDIUMK.ARUNA BAI*¹, K.B.CHANDRASEKHAR ¹and N.DEVANNA ¹¹Department of Chemistry, JNTU College of Engineering, Anantapur-515002. Andhra Pradesh, India.

ABSTRACT: A simple and sensitive spectrophotometric method has been developed for the determination of Gold (III) using 3,5-Dimethoxy-4-hydroxy benzaldehyde benzoylhydrazone (DMBBH) in a neutral surfactant of Triton X-100(5%) (micellar medium). Gold (III) forms a wine red coloured water soluble complex with the reagent in acidic medium pH 5.0. The molar absorptivity and Sandell's sensitivity of coloured species are $2.32 \times 10^4 \text{ L.mol}^{-1} \text{ cm}^{-1}$ and $0.00862 \mu\text{g/cm}^2$ respectively. Beer's law is obeyed in the range $0.4925\text{-}5.91 \mu\text{g/ml}$ of Au(III) at λ_{max} at 380 nm. The developed derivative spectrophotometric method was employed for the determination of gold (III). This method has been satisfactorily applied for the determination of gold (III) in water samples and pharmaceutical samples.

Key words: Gold (III), 3,5-dimethoxy-4-hydroxybenzaldehyde benzoylhydrazone(DMBBH), Micellar Medium, derivative spectrophotometry.

INTRODUCTION

Gold, in its pure state is considered the most beautiful and hence most valuable of the pure metals. It is metallic, having a yellow colour when in mass, though when finely divided it may be black, ruby or purple. Gold is soft, ductile and the most malleable of metals, and because of this is usually alloyed to give improved strength and durability. Green gold(an alloy of gold, silver and copper-14 to 18 karats) is generally used for jewellery. Coinage gold contains gold and copper in slightly varied amounts. Australian gold contains silver instead of copper.

Gold is used in textile industry, gold flake is used for a radiation control coating for space craft. Used as a plating material. Gold alloys have a number of applications like gold-gallium and gold-antimony alloys are used in electronic industry, gold-silver or gold-platinum alloys have dental applications, used as a rejuvenator and for anti cancer treatments.

The potential analytical applications of hydrazone derivatives have been reviewed by Singh et al.¹. Hydrazones are important class of known analytical reagents²⁻⁷. They react with many metal ions forming colour complexes and act as chelating agents. In general the technique of solvent extraction is widely used in the spectrophotometric determination of metal ions. However, organic solvents such as benzene and chloroform are often carcinogenic, toxic and cause environmental pollution. It is significant to develop a method which does not involve solvent extraction. A micellar solution has the ability to enhance the stability of metal complex and has been utilized as a medium for the spectrophotometric determination of the metal chelate⁸⁻¹¹.

The present paper describes a new, very simple, rapid, sensitive and derivative spectrophotometric determination of Gold (III) in micellar medium is proposed. The method consists of the formation of wine red coloured metal complex using 3,5-dimethoxy-4- hydroxyl benzaldehyde benzoyl hydrazone (DMBBH) with gold (III) and the stability of the complex in presence of micellar solution of Triton X-100(5%) is presented.

EXPERIMENTAL

A Shimadzu 160A, microcomputer based UV-VIS spectrophotometer equipped with 1.0cm quartz cells was used for all spectral measurements. The instrumental parameters are optimized and the best results were obtained with scan speed fast, slit width of 1nm and $\Delta\lambda=2\text{nm}$ for first order derivative mode in the wavelength range 350-650nm. ELICO L1-120 digital pH meter was used for the pH adjustments.

All chemicals used were of A.R grade unless stated. All solutions were prepared with doubly distilled water. The standard gold (III) solution (0.01M) was prepared by dissolving accurately weighed 0.34 g of Hydro Auric chloride (HAuCl_4) in a few ml. of doubly distilled water and made up to the mark in a 100-ml of volumetric flask. The stock solution was standardised by standard procedure. The working solutions were prepared by diluting the stock solution to an appropriate volume. Aqueous solution of 5% Triton X-100 was prepared by diluting 5ml of Triton X-100 (A.R Merck) to 100ml with doubly distilled water. Buffer solutions (phosphate buffers) were prepared by using 0.1M HCl, 0.1M NaOH, 0.1M disodium hydrogen phosphate and 0.1M potassium dihydrogen phosphate. Solutions of various ions of suitable concentrations were prepared using AR grade chemicals.

The reagent 3,5-dimethoxy-4-hydroxybenzaldehyde benzoylhydrazone (DMBBH) was synthesized by refluxing equimolar amounts of 3,5-dimethoxy-4-hydroxybenzaldehyde and benzhydrazide. In a 250 ml round bottomed flask hot ethanolic solution of 3,5-dimethoxy-4-hydroxybenzaldehyde (1.8217g, 0.01 mole) and hot ethanolic solution of benzhydrazide (1.3615g, 0.01mole) were mixed and refluxed using water condenser for 3 hours. On cooling the reaction mixture, a yellow coloured product separated out, which was collected by filtration and washed with double distilled water. The resulting hydrazone was recrystallized using 50% ethanol (yield, 76%, mp 225°C). The structure of DMBBH is shown in figure-1.

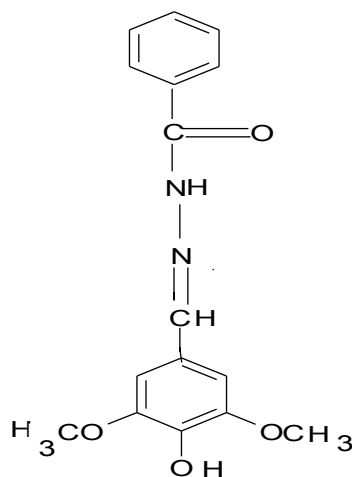


Fig.1. Structure of 3,5-Dimethoxy-4-hydroxybenzaldehyde benzoylhydrazone (DMBBH)

The reagent solution (0.01 M) was prepared by dissolving 0.30032 g of DMBBH in 100 ml of Dimethylformamide (DMF). The reagent solution is stable for 48 hours.

The reaction of some important metal ions were tested at different pH values. The samples were prepared in 10ml volumetric flasks by adding buffer solution 3.0 ml (pH 1-11), metal ion 0.5 ml of $1 \times 10^{-3}\text{M}$, Triton X-100 (5%) 0.5ml and DMBBH 0.5 ml of $1 \times 10^{-2}\text{M}$ solution. The mixture was diluted up to the mark with distilled water. The absorbance was measured in 300-700nm range against reagent blank. The colour reactions of some important metal ions with DMBBH are summarized in Table-1.

Table-1: Analytical Characteristics of 3,5-Dimethoxy-4-hydroxybenzaldehyde benzoylhydrazone

Metal ion	pH	λ_{\max} (nm)	Molar absorptivity (ϵ) ($L \cdot mol^{-1} \cdot cm^{-1}$)
Cu(II)	9.0	435	3.16×10^4
Pd (II)	4.25	376	1.86×10^4
Au(III)	5.0	380	$2.32 \times 10^{4*}$
Co(II)	6.0	439	2.69×10^4

*Present work

For the spectrophotometric determination of gold (III), an aliquot of the solution containing 0.4925-5.91 $\mu g/ml$ of gold (III), 3.0ml of buffer solution (pH 5.0), 0.5ml of 5% Triton X-100 and 0.5ml of $5 \times 10^{-3} M$ DMBBH reagent solution were taken in 10 ml volumetric flask and the solution was diluted up to the mark with doubly distilled water. The absorbance was read at 380 nm in a 1.0cm cell against reagent blank prepared in the same way. The measured absorbance was used to compute the amount of gold (III) from the predetermined calibration curve.

The first-order derivative spectrum was recorded with scan speed fast having a degree of freedom 9, in the wave length range from 350-650nm. The first order derivative peak height was measured at 439nm. The peak height was plotted against the amount of gold (III) to obtain the calibration curve. The second order derivative spectrum of [Au (III)-DMBBH] system was recorded with reference to the reagent blank in a wave length range 350-650nm. In the second order derivative spectrum peak height at 446 nm was measured from the zero line of spectrum. Calibration plot was constructed by plotting the derivative amplitude against the amount of gold (III).

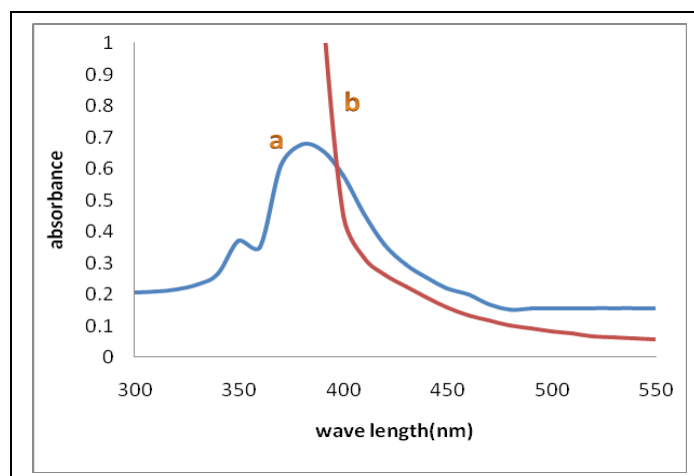
RESULTS AND DISCUSSION

The reagent 3,5-dimethoxy-4-hydroxyl benzaldehyde benzoylhydrazone(DMBBH)was easily synthesized as any other Schiff base reagent. The new chromogenic reagent DMBBH was used for the spectrophotometric determination of gold (III).

The absorption spectrum of DMBBH and its gold (III) complex under the optimum conditions are shown in Figure-2. The [Au (III)-DMBBH] complex shows the maximum absorbance at 380 nm, where the reagent blank does not absorb appreciably. Gold (III) reacts with DMBBH in acidic buffer to give wine red coloured water soluble species. The colour reaction between gold (III) and DMBBH was instantaneous even at room temperature in pH range 3.0-6.0, the maximum colour intensity was observed at pH 5.0 in presence of neutral surfactant Triton X-100(5%).A slow decrease in absorbance was observed for the coloured species after 15 min. The stability of the complex was increased by adding neutral surfactant Triton X-100. The absorbance of [Au (III) –DMBBH] remain constant for more than 2 hours. The effect of surfactants such as Triton X-100, Sodium dodecyl benzene sulphonate (SDBS) and Cetyl trimethyl ammonium bromide (CTAB) on the absorption profiles of the system has been investigated and presented in Table-2. In presence of Triton X-100(5%) the complex is more stable and exhibited maximum absorbance. Hence Triton X-100(5%) has been selected for further studies.

Table-2. Influence of different surfactants on the [Au (III)-DMBBH] complex.

Surfactant	Type	Absorbance at 380 nm
None	-	0.517
Tritonx-100(5%)	Neutral	0.612
CTAB(5%)	Cationic	0.413
SDBS(5%)	Anionic	0.358



**Fig.2. Zero order Absorption spectra. (a) Au(III)-DMBBH complex .
(b) Reagent (DMBBH) Vs DMF blank.**

When varying amounts of 5% Triton X-100 solution from 0.5ml to 4.0 ml, the constant absorbance was obtained from 0.5ml. The absorbance remains constant up to 4.0ml of 5% Triton X-100. Hence 0.5ml of 5% Triton X-100 was sufficient in all analytical studies. Triton X-100 serves to stabilize and sensitize the metal complex. Similarly when varying the volume of reagent DMBBH from 0.5ml to 4.0ml, the constant absorbance was obtained from 0.5 ml. therefore a 10 fold molar excess of reagent is adequate for full colour development.

The order of addition of buffer solution, metal ion, Tritonx-100 and reagent has no adverse effect on the absorbance of [Au(III)-DMBBH] complex. Beer's law obeyed in the range 0.4925-5.91 $\mu\text{g/ml}$. The molar absorptivity and Sandell's sensitivity of [Au(III)-DMBBH] complex was obtained from the Beer's law. The linear regression analysis of absorbance at λ_{max} of the complex against metal ion ($\mu\text{g/ml}$) shows a good linear fit. The various important analytical characteristics of [Au(III)-DMBBH] complex are summarized in Table-3.

Table-3: Physico-Chemical and Analytical Characteristics of [Au (III)-DMBBH]

Characteristics	Results
Colour	Wine red
λ_{max} (nm)	380
p ^H range (optimum)	3.0-6.0
Mole of reagent required per mole of metal ion for full colour development	10 folds
Molar absorptivity(L.mol ⁻¹ cm ⁻¹) (ϵ)	2.32 x10 ⁴
Sandell's sensitivity($\mu\text{g/cm}^2$)	0.00862
Beer's law validity range($\mu\text{g/ml}$)	0.4924-5.91
Optimum concentration range($\mu\text{g/ml}$)	0.985-5.4166
Composition of complex(M:L) obtained in Job's and mole ratio methods	1:2
Stability constant of the complex	6.66x10 ¹¹
Standard deviation	0.0002
Relative standard deviation(%)	0.07

The first order derivative spectral graph was shown in Figure-3. This shows that the derivative amplitudes measured at 439 nm for first order were found to be proportional to the amount of gold (III). The stoichiometry of the complex was found to be 1:2 investigated by Job's continuous variation method and molar ratio method, with a stability constant 6.66×10^{11} .

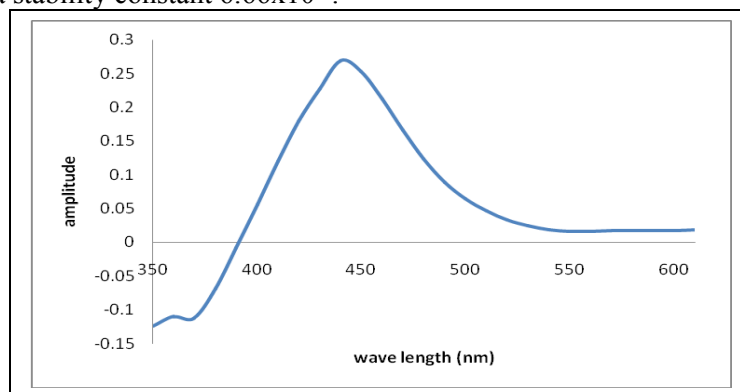


Fig.3. First order derivative spectra of [Au(III)-DMBBH] complex

The effect of various diverse ions in the determination of $2.4625 \mu\text{g/ml}$ Au(III) and tolerance limit of foreign ions was studied in the present method. The tolerance limit of a foreign ion was taken as the amount of foreign ion required to cause an error of $\pm 2\%$ in the absorbance. The results are given in Table-4. The data obtained in the derivative method is also incorporated. The data suggest that several associated anions and cations do not interfere when they are present in large excess. The interference of associated metal ion such as Copper (II) is decreased by adding masking agent thiourea and Cobalt (II) is decreased by adding masking agent triethanol amine.

Table 4. Tolerance limit of foreign ions in the determination of $2.4625 \mu\text{g/ml}$ Gold(III)

Ion added	Tolerance limit $\mu\text{g/mL}$	Ion added	Tolerance limit $\mu\text{g/mL}$
Tartarate	3303	Sn^{2+}	356
Ascorbic acid	1761	Os^{8+}	190
Bromide	1200	Mn^{2+}	82
Citrate	1125	Zn^{2+}	65
Chloride	1067	Sb^{2+}	60
Urea	900	Ni^{2+}	29
Sodium Tetraborate	670	Mo^{6+}	14
Nitrate	620	W^{6+}	9
Acetate	565	Co^{2+}	8.8**
Fluoride	190	NH_4^+	3.5
Sulphate	96	Cu^{2+}	3.2*
Phosphate	20	Ce^{4+}	2
Hg^{2+}	602	Pb^{2+}	2

**masked by triethanol amine $223 \mu\text{g/ml}$. *masked by thiourea $380 \mu\text{g/ml}$

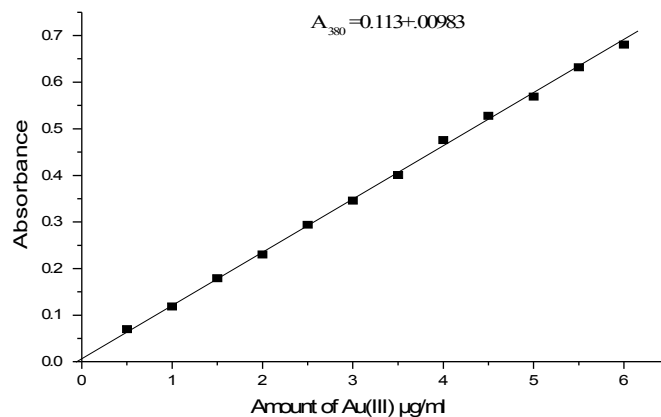


Fig.4. Zero order Beer's law plot of [Au(III)-DMBBH] complex

APPLICATIONS

The proposed method was applied for the determination of gold (III) in water samples and pharmaceutical samples.

Determination of Gold(III) in water samples: Each water sample(250 ml) filtered with Whatman No.40 was mixed with 10 ml of concentrated nitric acid in a 500 ml distillation flask. The sample was digested in the presence of an excess of KMnO_4 solution according to the method recommended by field et al.¹⁰. The solution was cooled and neutralized with dilute ammonium hydroxide solution. The digest was transferred into a 50 ml calibrated flask and diluted up to the mark with distilled water. Aliquots of these solutions were taken for analysis for the determination of Gold (III) and the results are presented in Table-5.

Table 5. Determination of Gold(III) in water samples.

S.No.	Sample	Gold (III) µg/L		Recovery (%)
		Added	Found	
1	Jewels waste water ^a	0	125	102
		100	227	
2	Drain water ^b	0	27.0	101
		100	128.0	

*average of best three determinations among five determinations

a Jewellers shops from Anantapur.

b Jewellers shops area, Anantapur.

Determination of Gold(III) in pharmaceutical samples: About 3g of sample (Vasanta kusumakar ras, swarna guggul) was heated after treating it with 10 ml of 1N HNO_3 . Then, 10ml 1:1 mixture of HNO_3 and HClO_4 were added and the solution was heated until dryness. The residue was dissolved in hot doubly distilled water and 5ml of 1M HCl were added. The solution was filtered and diluted to 50 ml with doubly distilled water. The gold (III) in this solution was determined by the recommended derivative procedure from a predetermined calibration plot. Results are presented in Table-6.

Table 6: Determination of Gold (III) in pharmaceutical samples.

Sample	Amount of Au(III) present($\mu\text{g/ml}$)	Amount of Au(III) found($\mu\text{g/ml}$)	Error %
Swarna Guggulu ¹	0.015	0.0157	+0.05
Vasanta Kusumakar Ras ²	0.06	0.070	+0.2

***average of best three determinations among five determinations**

1. Swarna guggulu: Each 125 mg tablet contains

Swarna bhasma - 2.0 mg Kumkuma - 3.0 mg
Ashwagandha - 20.0 mg Mahayogaraj guggulu -100mg

2. Vasanta Kusumakar Ras: Each 125 mg tablet contains

Swarna bhasma - 8.62 mg Rajat bhasma - 8.62mg
Vanga bhasma - 12.93 mg Naga bhasma - 12.93mg
Lauha bhasma - 17.24 mg Abhraka bhasma -17.24mg
Prarala bhasma - 17.24 mg Mukta bhasma -17.24mg
Rasa sindhur - 17.24mg

CONCLUSION

The present method using 3,5-dimethoxy-4-hydroxybenzaldehyde benzoylhydrazone(DMBBH) as spectrophotometric reagent for the determination of gold (III) in aqueous medium in presence of TritonX-100 surfactant is sensitive and simple. Many of the methods involve either heating at a specific temperature¹²⁻¹³ or extraction¹⁴⁻¹⁵ of the reaction mixture. However heating at a specific temperature for a long time is laborious and time consuming. The determination of gold (III) using DMBBH is not laborious and there is no need of heating or extraction of the components. Further the reagent is easy to synthesize using available chemicals. More over the present method is simple, rapid, selective and more precise for the determination of gold (III).

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