

Sensitive derivative spectrophotometric determination of gold(III) using 3,5-dimethoxy-4-hydroxybenzaldehyde isonicotinoyl hydrazone (DMHBIH) in presence of micellar medium

G.V.S. VALLINATH^{1*}, K.B. CHANDRASEKHAR¹, N. DEVANNA¹

¹ Department of Chemistry, JNTU, Anantapur, Anantapur-515002, Andhra Pradesh, India

* Corresponding author. Tel.: +91-98495-15835; e-mail: vallinath999@gmail.com

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A simple and sensitive spectrophotometric method has been developed for the determination of gold(III) using the newly synthesized reagent 3,5-dimethoxy-4-hydroxybenzaldehyde isonicotinoyl hydrazone (DMHBIH) in a neutral surfactant of Triton X-100 (5 %) (micellar medium). Gold(III) forms an orange coloured water soluble complex with the reagent in acidic medium pH 4.0. The molar absorptivity and Sandell's sensitivity of the coloured species are $1.14 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $0.004587 \mu\text{g/cm}^2$, respectively. Beer's law is obeyed in the range 0.197-1.97 $\mu\text{g/ml}$ of Au(III) at λ_{max} at 386 nm. The developed derivative spectrophotometric method was satisfactorily applied for the determination of gold(III) in synthetic mixtures, certified reference materials, water samples and pharmaceutical samples.

Gold(III) / 3,5-dimethoxy-4-hydroxybenzaldehyde isonicotinoylhydrazone (DMHBIH) / Micellar medium / Derivative spectrophotometry

1. 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. Gold is a good conductor of heat and electricity, and is unaffected by air, nitric, hydrochloric, or sulphuric acid and most other reagents.

The most common gold compounds are auric chloride (AuCl_3) and chlorauric acid (HAuCl_4). Gold has eighteen isotopes. It is chiefly used for coinage, ornaments, jewellery *etc.*

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, in electronic tubes, as gold-plated grid wire. Gold powder and gold sheet are used for soldering semiconductors and as a plating material. Gold alloys have a number of applications, *e.g.* gold-gallium and gold-antimony alloys are used in electronic industry,

gold-silver or gold-platinum alloys have dental applications, are 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 an important class of known analytical reagents [2-11]. 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 complexes and has been utilized as a medium for the spectrophotometric determination of metal chelates [12-15].

The present paper describes a new, very simple, rapid, sensitive and derivative spectrophotometric determination of gold(III) in micellar medium. The method consists of the formation of an orange coloured metal complex using 3,5-dimethoxy-4-hydroxybenzaldehyde isonicotinoyl hydrazone (DMHBIH) with gold(III) and the stability of the complex in presence of a micellar solution of Triton X-100 (5 %) is presented.

2. Experimental

A Shimadzu 160A microcomputer based UV-VIS spectrophotometer equipped with 1.0 cm quartz cells was used for all spectral measurements. The instrumental parameters were optimized and the best results were obtained with scan speed 2400 nm/min, slit width 1 nm and $\Delta\lambda = 2$ nm for first order derivative mode in the wavelength range 350-650 nm. An 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 5 ml of Triton X-100 (A.R. Merck) to 100 ml with doubly distilled water. Buffer solutions were prepared by using 0.1M HCl, 0.1 M NaOH, 0.1M disodium hydrogen phosphate and 0.1 M potassium dihydrogen phosphate. Solutions of various ions of suitable concentrations were prepared using A.R. grade chemicals.

The reagent 3,5-dimethoxy-4-hydroxy-benzaldehydeisonicotinoylhydrazone (DMHBIH) was

synthesized by refluxing equimolar amounts of 3,5-dimethoxy-4-hydroxybenzaldehyde and isonicotinoyl hydrazone. In a 250 ml round bottomed flask a hot ethanolic solution of 3,5-dimethoxy-4-hydroxybenzaldehyde (1.8212 g, 0.01 mole) and a hot ethanolic solution of isonicotinoylhydrazone (1.3714 g, 0.01 mole) were mixed and refluxed using a water condenser for 3 hours. On cooling the reaction mixture, a greenish 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 %, m.p. 221°C). The structure of DMHBIH was confirmed based on the IR, NMR and mass spectral data (see Table 1) and is given in Fig. 1.

The reagent solution (0.01M) was prepared by dissolving 0.3022 g of DMHBIH in 100 ml of dimethylformamide (DMF). The reagent solution is stable for 48 hours.

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

Table 1 Spectral data of of the DMHBIH reagent: a) IR spectral bands (cm^{-1}), b) ^1H NMR (200 MHz) spectrum recorded in DMSO- d_6 solvent. The mass spectrum showed that a molecular ion peak at m/z 302.2 (M+1) corresponding to molecular weight.

a)	
Bands (cm^{-1})	Assignments
3429.03 (s, br)	v NH stretching
2924.16 (m)	v OH stretching
1658.62 (s)	v > C=O stretching
1578.92 (s)	v C=N stretching
1514.12 (m)	v C=N stretching (pyridine ring)
1372.71 (w)	v N-H stretching (primary amide)
1123.66 (m)	
836.12 (m)	v C-H bending
749.239 (m)	
689.53 (s)	v C-C bending

b)	
δ value	Assignments
11.9 (S, 1H)	NH
8.97 (S, 1H)	OH (phenolic)
8.78 (d, 2H)	ArH (pyridine ring)
8.34 (S, 1H)	N=C-H
7.8 (d, 2H)	ArH (pyridine ring)
7.01 (S, 2H)	ArH (aldehydic)
3.8 (S, 6H)	-OCH ₃ (2 methoxy)
3.3 (S, 2H)	water in solvent
2.5 (S, 6H)	DMSO (solvent)

Table 2 Analytical characteristics of 3,5-dimethoxy-4-hydroxybenzaldehyde isonicotinoylhydrazone.

Metal ion	pH	λ_{\max} (nm)	Molar absorptivity ϵ ($l\ mol^{-1}\ cm^{-1}$)
Ru(III)	4.25	390	1.7×10^4
Fe(III)	4.0	386	1.875×10^4
Au(III)	4.0	386	1.14×10^5 ^a

^a present work**Fig. 1** Structure of 3,5-Dimethoxy-4-hydroxybenzaldehyde isonicotinoylhydrazone (DMHBIH).

For the spectrophotometric determination of gold(III), an aliquot of the solution containing 0.197 to 1.97 $\mu\text{g/ml}$ of gold(III), 3.0 ml of buffer solution (pH 4.0), 0.5 ml of 5 % Triton X-100 and 0.5 ml of $5 \times 10^{-3}\text{M}$ DMHBIH reagent solution were taken in a 10 ml volumetric flask and the solution was diluted up to the mark with doubly distilled water. The absorbance was read at 386 nm in a 1.0 cm cell against a 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 350-650 nm. The derivative peak height was measured by the peak-zero method at 450 nm. The peak height was plotted against the amount of gold(III) to obtain the calibration curve. The second order derivative spectrum of the Au(III)–DMHBIH system was recorded with reference to the reagent blank in the wave length range 350-650 nm. In the second order derivative spectrum the peak height at 470 nm was measured from the zero line of spectrum. The calibration plot was constructed by plotting the derivative amplitude against the amount of gold(III).

3. Results and discussion

The reagent 3,5-dimethoxy-4-hydroxybenzaldehydeisonicotinoylhydrazone (DMHBIH) was easily synthesized as any other Schiff base reagent. The new chromogenic reagent DMHBIH was not used for the spectrophotometric determination of gold(III).

The colour reactions of some important metal ions with DMHBIH are summarized in Table 2. The colour reactions are mainly due to complex formation of DMHBIH with divalent, trivalent, tetravalent metal ions such as Cu(II), Fe(III), Pt(IV), and Au(III) in acid medium / alkaline medium to give intense coloured complexes. In acidic medium, the ligand presumably co-ordinates the metal ion as di-anion to give neutral complexes.

The absorption spectra of DMHBIH and its gold(III) complex under the optimum conditions are shown in Figs. 2,3. The Au(III)-DMHBIH complex shows the maximum absorbance at 386 nm, where the reagent blank does not absorb appreciably.

Gold(III) reacts with DMHBIH in acidic buffer to give orange coloured water soluble species. The colour reaction between gold(III) and DMHBIH was instantaneous even at room temperature in pH range 3.0-5.0, the maximum colour intensity was observed at pH 4.0 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)–DMHBIH remains constant for more than 6 hours.

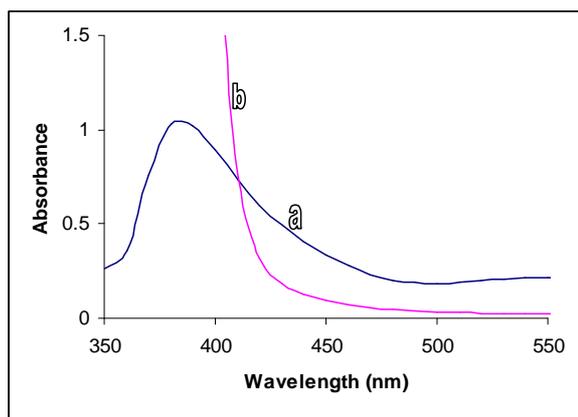
The effect of surfactants such as Triton X-100, sodium dodecyl benzene sulphonate (SDBS) and cetyl trimethyl ammonium bromide(CTAB) on the absorption profiles of the system has been investigated and presented in Table 3. In presence of Triton X-100 (5 %) the complex is more stable and exhibited maximum absorbance. Hence Triton X-100 (5 %) has been selected for further studies.

Table 3 Influence of different surfactants on the Au(III)-DMHBIH complex.

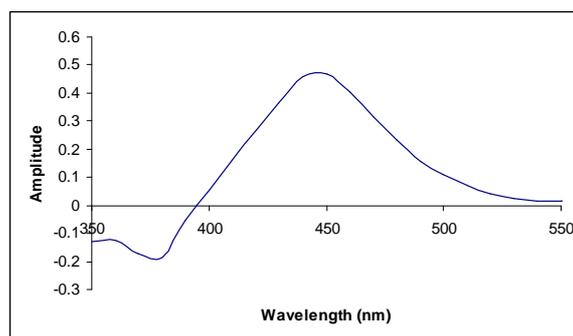
Surfactant	Type	Absorbance at 386 nm
None		0.793
Triton X-100 (5 %)	Neutral	1.65
CTAB(5 %)	Cationic	0.717
SDBS(5 %)	Anionic	0.888

Table 4 Physico-chemical and analytical characteristics of Au(III)-DMHBIH.

Characteristics	Results
Colour	orange
λ_{\max} (nm)	386
pH range (optimum)	3.0-5.0
Mole of reagent required per mole of metal ion for full colour development	10 folds
Molar absorptivity ($1 \text{ mol}^{-1} \text{ cm}^{-1}$) (ϵ)	1.14×10^5
Sandell's sensitivity ($\mu\text{g}/\text{cm}^2$)	0.004587
Beer's law validity range ($\mu\text{g}/\text{ml}$)	0.197-1.97
Optimum concentration range ($\mu\text{g}/\text{ml}$)	0.482-2.642
Composition of complex ($M:L$) obtained by the Job and mole ratio methods	1:1
Stability constant of the complex	29.40×10^7
Standard deviation	0.00011
Relative standard deviation (%)	0.03

**Fig. 2** Zero order absorption spectra: (a) (III)-DMHBIH complex of 0.197 $\mu\text{g}/\text{ml}$ Au(III); (b) reagent (DMHBIH) vs. DMF blank.

When varying the amounts of 5 % Triton X-100 solution from 0.5 ml to 4.0 ml, constant absorbance was obtained from 0.5 ml. The absorbance remains constant up to 4.0 ml of 5 % Triton X-100. Hence 0.5 ml 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 DMHBIH ($5 \times 10^{-3} \text{M}$) from 0.5 ml to 4.0 ml, constant absorbance was obtained from 0.5 ml, therefore a 10-fold molar excess of reagent is adequate for full colour development.

**Fig. 3** First order derivative spectra of Au(III)-DMHBIH complex.

The order of addition of buffer solution, metal ion, Triton X-100 and reagent has no adverse effect on the absorbance of the Au(III)-DMHBIH complex. Beer's law is obeyed in the range 0.197 to 1.97 $\mu\text{g}/\text{ml}$. The molar absorptivity and Sandell's sensitivity of the Au(III)-DMHBIH complex was obtained from Beer's law. The linear regression analysis of the absorbance at λ_{\max} of the complex against metal ion ($\mu\text{g}/\text{ml}$) shows a good linear fit (Fig. 4). The various important analytical characteristics of the gold(III) DMHBIH complex are summarized in Table 4.

The first order derivative spectral graph is shown in Fig. 5. It shows that the derivative amplitudes measured at 450 nm for first order were found to be proportional to the amount of gold(III).

Table 5 Tolerance limit of foreign ions on the determination of 2.4625 µg/ml gold(III).

Ion added	Tolerance limit (µg/ml)	Ion added	Tolerance limit (µg/ml)
Bromide	3196.16	Pb ²⁺	104
Iodide	2538	Hg ²⁺	99
Urea	1500	Ca ²⁺	80
Chloride	1064	Zn ²⁺	65
Tetraborate	970	Sb ³⁺	61
Sulphate	940	Cd ²⁺	56
Oxalate	880	U ⁶⁺	12.0
Nitrate	620	Ag ⁺	11.0
Acetate	590	Co ²⁺	6.0
Thiocyanide	581	Sn ²⁺	6.0
Phosphate	475	Mo ⁶⁺	5.0
Ascorbic acid	176	As ³⁺	4.0
Tartarate	148	Ni ²⁺	3.0
Thiourea	115	Cr ³⁺	2.59
Fluoride	95	V ⁵⁺	2.54
W ⁶⁺	184	Al ³⁺	1.4
Sr ²⁺	175	Zr ⁴⁺	1.0
Ba ²⁺	137	Pd ²⁺	1.0
Mn ²⁺	110	Ru ³⁺	1.0
Bi ³⁺	105	Cu ²⁺ *	0.63, 1.27 ^a

^a masked by thiourea 245 µg/ml**Table 6** Determination of gold(III) in synthetic mixtures.

Sample No.	Composition of the mixture (µg/ml)	Gold(III) (µg/ml)		Recovery (%)
		Added	Found ^a	
1	Au(III)	0.5	0.48	96
2	As in 1 + Na (25) + Be(II) (25)	0.5	0.49	98
3	As in 2 + Zn (25) + Co (25)	0.5	0.495	99
4	As in 3 + Ca (25) + Cr(III) (25)	0.5	0.5	100
5	As in 4 + Mn(II) (25) + Ag(I) (10)	0.5	0.51	102
6	As in 5 + Ni(II) (25) + Hg(II) (25)	0.5	0.53	106

^a average of best three determinations among five determinations

The stoichiometry of the complex was found to be 1:1 (metal:ligand) investigated by Job's continuous variation method and the molar ratio method, with a stability constant 29.4×10^7 .

The effect of various diverse ions on the determination of 2.4625 µg/ml Au(III) and tolerance limit of foreign ions was studied. 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 or amplitude. The results are given in **Table 5**. The data obtained in the derivative method is also incorporated. The data suggest that several associated anions and cations, such as iodide, nitrate, thiosulphate, thiocyanide, bromide, sodium(I), calcium(II), bismuth(III), tungsten(VI), do not interfere when they are present in large excess. The tolerance limit values for many anions and cations are higher in the derivative method. The interference of associated metal ion such as copper(II) is decreased by adding the masking agent thiourea.

4. Applications

The proposed method was applied for the determination of gold(III) in synthetic mixtures, certified reference materials, water samples and pharmaceutical samples.

4.1. Determination of gold(III) in synthetic mixtures

Several synthetic mixtures of varying compositions containing gold(III) and diverse ions of known concentrations were determined by the present method; and the results were found to be highly reproducible. The results are presented in **Table 6**. Accurate recoveries were achieved in all solutions.

4.2. Determination of gold(III) in certified reference materials

A 0.5 g sample was accurately weighed and placed in a 50 ml Erlenmeyer flask. To this, 10 ml of concentrated nitric acid and 5 ml of concentrated

Table 7 Determination of gold(III) in certified reference materials.

Sample No.	Certified reference material (composition)	Gold(III) ($\mu\text{g/ml}$)		Error (%)
		Certified value	Found ^a	
1	OXG 60 (SiO_2 , Al_2O_3 , Na_2O , K_2O , CaO , MgO , TiO_2 , MnO , P_2O_5 , $\text{Fe}_2\text{O}_3^{\text{b}}$, LOI)	1.025	1.019	0.59
2	OXG 56 (SiO_2 , Al_2O_3 , Na_2O , K_2O , CaO , MgO , TiO_2 , MnO , P_2O_5 , $\text{Fe}_2\text{O}_3^{\text{b}}$, LOI)	0.611	0.607	0.65
3	SH 24 (SiO_2 , Al_2O_3 , Na_2O , K_2O , CaO , MgO , TiO_2 , MnO , P_2O_5 , Fe^{b} , S)	1.326	1.318	0.60

^a average of best three determinations among five determinations^b iron is masked by using fluoride**Table 8** Determination of gold(III) in water samples.

Sample No.	Sample	Gold(III) ($\mu\text{g/l}$)		Recovery (%)
		Added	Found ^a	
1	Jewels waste water ^b	0	124	100
		100	224	
2	Drain water ^c	0	28.0	101
		100	129	

^a average of best three determinations among five determinations^b Jewellers shops from Anantapur^c Jewellers shops area, Anantapur

hydrochloric acid were added carefully, covering the flask with a watch glass until the brisk reaction subsided. The solution was heated and simmered gently after the addition of 5 ml of concentrated nitric acid, until all carbides were decomposed. The solution was evaporated carefully to dense white fumes to drive off the oxides of nitrogen and then cooled to room temperature. After suitable dilution with distilled water, the contents of the flask were warmed to dissolve the soluble salts. The solution was then cooled and neutralized with a dilute ammonium hydroxide solution. The resulting solution was filtered, if necessary, through a Whatman No. 42 filter paper into a 50 ml calibrated flask. The residue was washed with a small volume of hot water and the volume was made up to the mark with distilled water.

A suitable aliquot of the above solution was taken in a 10 ml flask and used for the determination of gold(III) by the general procedure. The results are presented in **Table 7**.

4.3. 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 Fifield *et al.* [10]. The solution was cooled and neutralized with a 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 8**.

4.4. Determination of gold(III) in pharmaceutical samples

About 3 g of sample (Vasanta kusumakar ras, swarna guggul) was heated after treating it with 10 ml of 1N HNO_3 . Then, 10 ml 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 5 ml of 1M HCl were added. The solution was filtered and diluted to 50 ml with doubly distilled water.

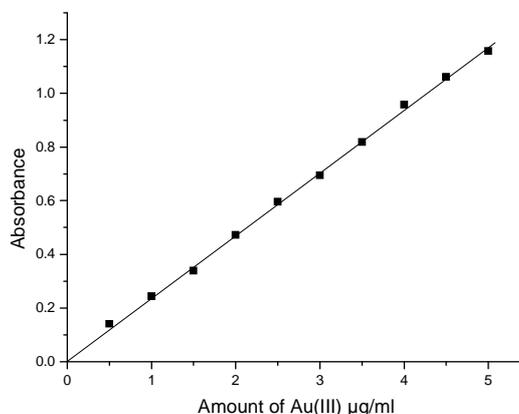
**Fig. 4** Zero order Beer's law plot of [Au(III)-DMHBIH] complex.

Table 9 Determination of gold(III) in pharmaceutical samples.

Sample	Gold(III) ($\mu\text{g}/\text{mg}$)		Error (%)
	Present	Found ^a	
Swarna Guggulu ^b	0.016	0.0158	-0.02
Vasanta Kusumakar Ras ^c	0.07	0.071	+1.43

^a average of best three determinations among five determinations

^b Swarna guggulu: each 125 mg tablet contains

Swarna bhasma – 2.0 mg Kumkuma – 3.0 mg
Ashwagandha – 20.0 mg Maha yogaraj guggulu – 100.0 mg

^c Vasanta Kusumakar Ras: each 125 mg tablet contains

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

Table 10 Determination of gold(III).

Sample No.	Reagent	λ_{max} (nm)	Molar absorptivity	Reference
1	3,5-dimethoxy-4-hydroxy-2-amino acetophenone isonicotinoyl hydrazone	490	3.45×10^4	[20]
2	Mepazine hydrochloride	514	2.18×10^4	[21]
3	3,3-dimethyl-2-[4-(N-methyl-N-chloroethyl)amido phenylethylene]indole	555	7.29×10^4	[22]
4	Chrompyrazol	580	7.50×10^4	[23]
5	Ethyl violet	551	5.04×10^4	[24]
6	Rhodamine B	555	9.70×10^4	[25]
7	5-(2-pyridyl)methylene rhodamine	418	1.10×10^4	[26]
8	Morin	420	2.02×10^4	[27]
9	5(2,4Dihydroxybenzylidene) rhodamine(DHBR)	558	8.45×10^4	[28]
10	2'-Aminoacetophenone isonicotinoyl hydrazone(2'-AAINH)	440	3.50×10^4	[29]
11	Propericiazine	511	3.85×10^4	[30]
12	Ethopazine hydrochloride(EPI)	513	2.00×10^4	[31]
13	3,5-dimethoxy-4-hydroxybenzaldehydeisonicotinoyl hydrazone (DMHBIH)	386	1.14×10^5	Present work

The gold(III) in this solution was determined by the recommended derivative procedure from a predetermined calibration plot. Results are presented in [Table 9](#).

5. Conclusions

The present method using 3,5-dimethoxy-4-hydroxybenzaldehyde isonicotinoyl hydrazone (DMHBIH) as spectrophotometric reagent for the determination of gold(III) in aqueous medium in presence of Triton X-100 surfactant is sensitive and simple. Many of the methods involve either heating at a specific temperature [16,17] or extraction [18,19] 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 DMHBIH 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. Spectrophotometric determination of gold(III) with this method is compared with other reagents and presented in [Table 10](#) [20-31]. The present method is simple, rapid, selective and more precise for the determination of gold(III).

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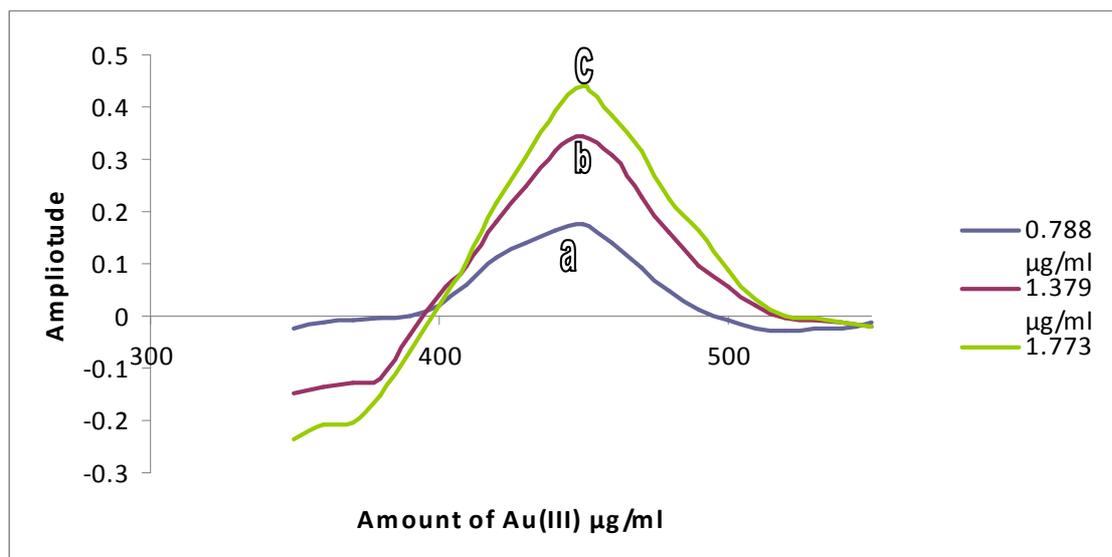


Fig. 5 First order Beer's law derivative spectra of Au(III)-DMHBIH complex: (a) 0.788 $\mu\text{g/ml}$ of Au(III); (b) 1.379 $\mu\text{g/ml}$ of Au(III); (c) 1.773 $\mu\text{g/ml}$ of Au(III).

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