

## Research Article

# Spectrophotometric Determination of Gold(III) Using 2-Hydroxy-3-Methoxy Benzaldehyde Thiosemicarbazone as a Chromophoric Reagent

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A chromophoric reagent, 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBATSC), was employed for the sensitive spectrophotometric determination of gold(III). The gold(III) ion forms a blue-coloured complex with HMBATSC in an aqueous dimethyl formamide at pH 6.0. The gold complex shows the absorption maximum at 385 nm, and Beer's law was obeyed in the range 0.49–8.37  $\mu\text{g mL}^{-1}$ . The molar absorptivity and Sandell's sensitivity were found to be  $1.28 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  and  $0.015 \mu\text{g cm}^{-2}$ , respectively. The complex shows 1 : 1 [Au(III) : HMBATSC] stoichiometry with a stability constant of  $1.32 \times 10^6$ . The interference effect of various diverse ions has been studied. In addition to zero-order, first- and second-order derivative spectrophotometric methods were also developed for the determination of gold(III) in microgram amounts which were more sensitive than the zero-order method. The developed method has been used for the determination of gold(III) in environmental water samples and certified reference materials. The results were in excellent agreement with the certified values.

## 1. Introduction

Gold is considered to be one of the most significant noble metals due to its wide applications in industry and economic activity. It is the most interesting microamount elements due to its significant role on biology. Gold occurs at very low natural contents, about  $4 \text{ ng g}^{-1}$  in rocks,  $1 \text{ ng g}^{-1}$  in soils, and  $0.05 \text{ ng mL}^{-1}$  in sea water. Gold particles are present in the bodies of fish, aquatic invertebrates, and humans. It has been used in medicine, for example, to cure rheumatoid arthritis under treatment called "chrysotherapy [sic]." It is prescribed when treatment with nonsteroid anti-inflammatory drugs is failed to give relief. Gold is a soft metal and so is usually alloyed to give it more strength. Alloys of gold with the other elements of I B group in the periodic table are most frequently used, and gold still has great significance in international business and banking. So, simple, sensitive and selective methods for determination of trace gold are always significant.

Among the several instrumental techniques spectrophotometric methods for the determination of metal ions have an attractive attention due to their simplicity and low operating costs. A variety of spectrophotometric methods for the determination of gold have, therefore, been reported which includes different chromophoric reagents, 2-[2-(4-dimethylamino-phenyl)-vinyl]-1,3,3-trimethyl-3H-indolium [1], bis(salicylaldehyde) orthophenylenediamine [2], 5-(4-carboxylphenyl-azo)-8-hydroxyquinoline [3], ethopropazine hydrochloride and isothipendyl hydrochloride [4], morin [5], and 2-carboxyl-1-naphthalthiorhodanine [6].

Thiosemicarbazones [7–10] are one of the important classes of reagents widely employed for the spectrophotometric determination of metal ions. A good number of thiosemicarbazone ligands have been derived by simply condensing aliphatic, aromatic or heterocyclic aldehydes, or ketones with thiosemicarbazide [11]. Thiosemicarbazones contain azomethine nitrogen atom and thioamide group.

TABLE 1: Tolerance limit of diverse ions in the determination of Au(III) ( $0.76 \mu\text{g mL}^{-1}$ ).

Diverse ion	Tolerance limit ( $\mu\text{g mL}^{-1}$ )
Chloride, Iodide, Thio sulphate, EDTA, Ascarbate, Tartrate, Pb(II), Th(IV), U(VI), W(VI), Sn(II)	1000–2000
Sulphate, phosphate, nitrate, Zr(IV), Ag(I), Y(III), Tl(III), Te(IV)	600–1000
Flouride, thiourea, Mo(II), Cd(II), Hg(II)	300–500
Citrate, thiocyanate, oxalate	200–250
Al(III), In(III), Ru(III)	200–250
Se(IV), Pd(II), Mn(II), Zn(II)	50–70
Fe(II), Cu(II)	25–30
Ga(III), Co(II), V(V), Ni(II)	11–15
Fe(III), V(IV), Cr(VI)	5–7

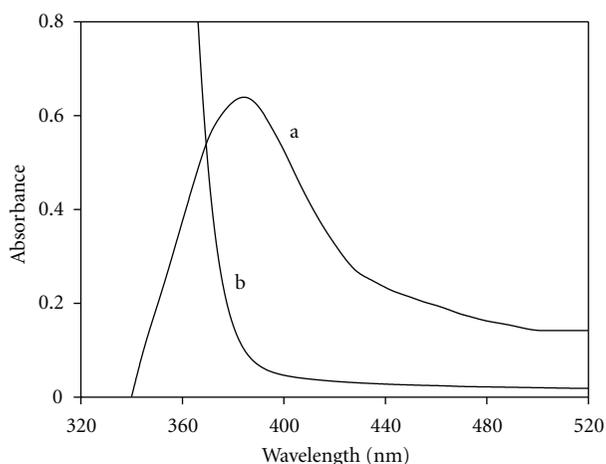


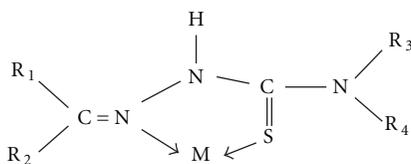
FIGURE 1: Absorption spectra of (a) HMBATSC; (b) [Au(III)-HMBATSC] versus reagent blank;  $[\text{Au(III)}] = 5 \times 10^{-4} \text{ M}$ ;  $[\text{HMBATSC}] = 5 \times 10^{-3} \text{ M}$ ;  $\text{pH} = 6.0$ .

TABLE 2: Determination of Au(III) in environmental water samples.

Sample	Amount of Au(III) ( $\mu\text{g mL}^{-1}$ )		Recovery (%)
	Added	Found*	
Tap water 1	0.490	0.482	98.36
Tap water 2	0.735	0.744	101.23
Rain water 1	0.735	0.739	100.54
Rain water 2	0.985	0.976	99.08
Well water 1	0.985	0.996	101.12
Well water 2	1.230	1.221	99.27
Lake water 1	1.230	1.246	101.31
Lake water 2	1.480	1.471	99.39

\* Average of five determinations.

So, these reagents act as good chelating agents and form complexes with various metal ions by bonding (as shown below) through thioketo sulphur and hydrazine-nitrogen atom.



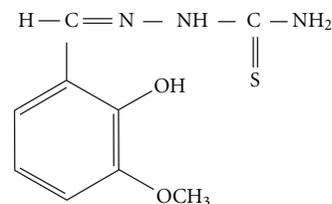
In the literature survey the spectrophotometric methods for the determination of gold(III) using thiosemicarbazones are very less. The anisaldehyde-4-phenyl-3-thiosemicarbazone is one of the thiosemicarbazones used for the extractive spectrophotometric determination of gold [12]. The present work reports the simple, sensitive, selective and nonextractive spectrometric determination of gold(III) using 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBATC) as a chromophoric reagent. The developed method has been used for the determination of gold(III) in environmental water samples and reference materials.

## 2. Experimental

**2.1. Apparatus.** The absorbance and pH measurements were made on a Shimadzu UV-visible spectrophotometer (model UV-160A) fitted with 1-cm quartz cells and Philips digital pH meter (model L1 613), respectively. The pH meter has temperature compensation arrangement and has reproducibility of measurements within  $\pm 0.01$  pH.

**2.2. Reagents and Chemicals.** The 2-hydroxy-3-methoxy benzaldehyde and thiosemicarbazide were purchased from SD Fine Chemicals, India. The gold(III) chloride trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ) was obtained from Alchemy Laboratories, India. All chemicals and solvents used were of analytical reagent grade. Doubly distilled water was used for the preparation of all solutions and experiments.

The reagent, HMBATSC, was prepared and characterized (IR and NMR spectral data) using reported procedure [13]. The structural formula of HMBATSC was given below.



A 0.01 M solution of the reagent was prepared by dissolving 0.2250 g of HMBATSC in dimethyl formamide (DMF) and diluting to 100 mL with DMF. Lower concentrations were prepared by diluting an appropriate volume of 0.01 M reagent solution.

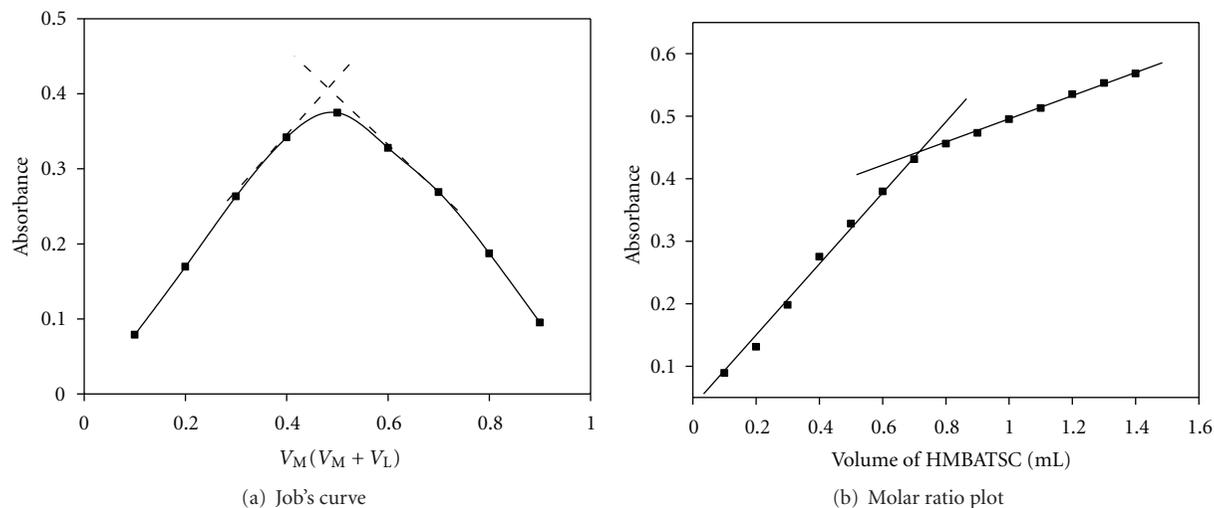


FIGURE 2:  $[\text{Au(III)}] = [\text{HMBATSC}] = 5 \times 10^{-3} \text{ M}$ ; other conditions as in standard procedure.

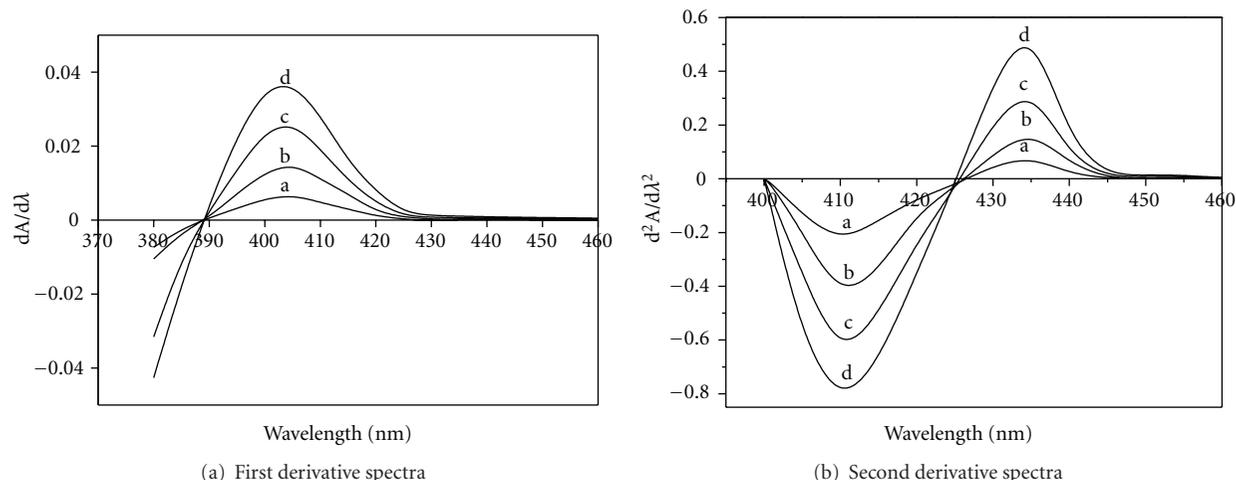


FIGURE 3: Ni(II)–HMBATSC versus reagent blank; Ni(II) ( $\mu\text{g mL}^{-1}$ ) = (1) 0.245; (2) 0.490; (3) 0.735; (4) 0.980; other conditions as in standard procedure.

A stock solution of 0.1 M gold(III) was prepared by dissolving precise amount of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  in 1 M hydrochloric acid and standardized using standard procedure.

The buffer solutions were prepared by mixing 0.2 M acetic acid + 0.2 M sodium acetate (pH 3.0–7.0) and 2.0 M ammonia + 2.0 M ammonium chloride (pH 8.0–10.0). The pH of these solutions was checked with the above-mentioned pH meter.

The working solutions were prepared daily by diluting the stock solution to an appropriate volume. The solutions of the studied interfering ions of suitable concentrations were prepared using analytical grade reagents.

### 2.3. General Procedure

**2.3.1. Direct Spectrophotometry.** In each of a set of different 10 mL standard flasks, 5 mL buffer solution (pH 6.0), varying

volumes of  $5 \times 10^{-4} \text{ M}$  Au(III) solution, and 1 mL of HMBATSC ( $5 \times 10^{-3} \text{ M}$ ) were taken, and the volume was made up to the mark with doubly distilled water. The absorbance was measured at 385 nm against the reagent blank. The calibration curve was constructed by plotting the absorbance against the amount of Au(III). The calibration graph follows the straight line equation  $Y = ac + b$ , where  $c$  was the concentration of the solution,  $Y$  was measured absorbance or peak height, and “ $a$ ” and “ $b$ ” were constants.

**2.3.2. Derivative Methods.** For the above solutions, first- and second-order derivative spectra were recorded with a scan speed of fast (nearly  $2400 \text{ nm min}^{-1}$ ), slit width of 1 nm with one degree of freedom. The derivative peak height was measured by the peak-zero method at respective wavelengths. The peak height was plotted against the amount of Au(III) to obtain the calibration.

TABLE 3: Determination of Au(III) in environmental water samples.

Certified reference materials (Composition)	Gold ( $\mu\text{g mL}^{-1}$ )		Relative error (%)
	Certified value	Found ( $n = 5$ )*	
OXG 60 ( $\text{SiO}_2$ , $\text{Al}_2\text{O}_3$ , $\text{Na}_2\text{O}$ , $\text{K}_2\text{O}$ , $\text{CaO}$ , $\text{MgO}$ , $\text{TiO}_2$ , $\text{MnO}$ , $\text{P}_2\text{O}_5$ , $\text{Fe}_2\text{O}_3$ <sup>x</sup> )	1.025	1.012	1.3
SH 24 ( $\text{SiO}_2$ , $\text{Al}_2\text{O}_3$ , $\text{Na}_2\text{O}$ , $\text{K}_2\text{O}$ , $\text{CaO}$ , $\text{MgO}$ , $\text{TiO}_2$ , $\text{MnO}$ , $\text{P}_2\text{O}_5$ , $\text{Fe}^x$ , S)	1.326	1.312	1.4

\* Average of Five determinations.

<sup>x</sup>1410  $\mu\text{g mL}^{-1}$  of tartrate to mask "Fe."

### 3. Results and Discussion

**3.1. Zero-Order Method.** The gold(III) reacts with HMBATSC forming a blue-colored soluble complex in the acidic buffer medium. The absorption spectra of the HMBATSC and its gold(III) complex under optimum conditions were presented in Figure 1. The gold(III) complex has an absorption maximum at 385 nm, and at this wavelength the reagent has very small absorbance. Hence, further analytical studies were carried out at 385 nm.

Preliminary studies have indicated that HMBATSC reacts with Au(III) in aqueous acidic medium at room temperature to form blue-colored species. The color reaction between Au(III) and HMBATSC was instantaneous at room temperature. The absorbance of the complex was found to be constant for more than 72 hours. The effect of pH on the intensity of color formation was studied to optimize the pH of the gold complex. The results indicate that absorbance was maximum and constant in the pH range of 5.0–7.0. Hence pH 6.0 was chosen for further studies.

A 10-fold molar excess of HMBATSC was necessary for complex and constant color development. Excess of the reagent has no effect on the sensitivity and absorbance of the complex. To determine the amount of Au(III) at micro levels, Beer's law was verified for [Au(III)-HMBATSC] complex by measuring the absorbance of the solutions containing different amounts of Au(III). A linear plot between the absorbance and the amount of Au(III) gives the straight line which obeys the equation  $Y = 0.1170C + 0.0140$ . The correlation coefficient ( $r$ ) of the calibration curve for experimental data was 0.9995. From the calibration plot, it is observed that Beer's law was obeyed in the range of 0.49–8.37  $\mu\text{g mL}^{-1}$ . The molar absorptivity and Sandell's sensitivity were  $1.28 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  and  $0.015 \mu\text{g cm}^{-2}$ , respectively. The relative standard deviation at a concentration level of 0.49  $\mu\text{g mL}^{-1}$  of Au(III) was found to be 1.98% (10 determinations).

The composition of the complex was determined by Job's (Figure 2(a)) and molar ratio methods (Figure 2(b)). Both methods showed that a molar ratio of Au(III) to HMBATSC was 1:2. The stability constant was determined by Job's method as  $1.32 \times 10^6$ .

The effect of various foreign ions that were generally associated with gold ion on its determination under optimum conditions was investigated by the determination 5  $\mu\text{g mL}^{-1}$  of Au(III), and the results are presented in Table 1. The tolerance limit was set as the amount of foreign ion that

caused an error in the absorbance by  $\pm 2\%$ . The most of the anions, which, examined have tolerance limits of greater than 200-fold excess, indicated high tolerance levels. Many of the metal cations were tolerable more than 50-fold excess. The metal ions Fe(II), Ni(II), and Cu(II) were tolerable up to 25–30-fold excess. Ga(III), Co(II), V(V) and Ni(II) tolerable up to 11–15-fold excess, and the metal ions include Fe(III), V(IV), and Cr(VI) that interfere seriously. The masking agents like ascorbate, EDTA, and tartrate are not interfering in the recovery of gold. Therefore, these masking agents were used to obviate interferents such as Fe(III), V(IV), and Cr(VI), and up to a 25  $\mu\text{g}$  level in the determination of vanadium (IV).

**3.2. Derivative Methods.** The first- and second-order derivative spectra of experimental solutions containing different amounts of Au(III) were recorded in the wavelength region. The first derivative spectra (Figure 3(a)) showed maximum amplitude at 404 nm. The derivative amplitudes at 404 nm were found to be proportional to the concentrations of Au(III). The Beer's law was obeyed in the concentration range 0.25–10.46  $\mu\text{g mL}^{-1}$  of Au(III). The second-order derivative spectra were presented in Figure 3(b) and indicate a valley at 411 nm and a peak at 434 nm. At these wavelengths the derivative amplitudes were proportional to the amount of Au(III). The Beer's law was obeyed in the range 0.12–10.46  $\mu\text{g mL}^{-1}$  at 411 nm and 0.12–10.46  $\mu\text{g mL}^{-1}$  at 434 nm.

The effect of various cations and anions on the derivative methods was also investigated. It was noticed that all the ions that did not interfere in the zero-order determinations of Au(III) (cf. Table 1) also did not interfere in all the derivative spectrophotometric methods. In the zero-order method, Ga(III), Co(II), V(V), and Ni(II) tolerable up to 11–15-fold, but in all derivative spectroscopic methods, they were tolerable up to 25-fold excess. The metal ions Fe(III), V(IV), and Cr(VI) interfered in 10-fold excess in both of the derivative spectrophotometric methods.

**Applications.** The proposed method was applied for the determination of gold in environmental water samples and certified reference materials.

**Determination of Au(III) in Water Samples.** The water samples (1 L) collected in a clean 2 L beaker from Anantapur (Andhra Pradesh, India) were filtered through 0.45  $\mu\text{m}$  pore size membrane filters immediately after sampling. The water

samples were slowly evaporated to about 25 mL. 5 mL of H<sub>2</sub>O<sub>2</sub> was added and evaporated to dryness [14]. It was then dissolved in 2 mL of water and filtered to remove insoluble substance. The filtrate was collected in 100 mL volumetric flask quantitatively and diluted to the mark with distilled water. The filtered water samples were analyzed using the proposed to determine gold(III) using zero order method. A known amount of Au(III) was added to the water samples, and the recovery was evaluated as an average of five determinations. The results were presented in Table 2 and indicate that the recoveries were in the acceptable range Determination of Au(III) in certified reference materials.

*Determination of Au(III) in Certified Reference Materials.* The first-order derivative method was used to determine the gold(III) in certified reference materials. A required amount of sample was accurately weighed and treated as per the recommended procedure [14]. A suitable aliquot of the sample solution was taken in a 10 mL-calibrated flask, and the amount of gold(III) content was determined by recommended procedure as described in experimental section. The results obtained were in good agreement with certified values and are presented in Table 3.

#### 4. Conclusions

The present work gives a rapid, simple, sensitive, and selective method for the nonextractive spectrophotometric determination of gold(III). The developed method does not require the use of a surfactant. Further, derivative spectrophotometric methods also developed and are more sensitive than zero-order method. The molar absorptivity of the gold(III)-HMBATSC complex reaches  $1.51 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ , and most foreign ions do not interfere with the determination. The developed method was used for the determination of gold(III) in environmental water samples and certified reference materials.

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