



Simultaneous Second Derivative Spectrophotometric Determination of Gold and Cobalt

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Abstract

A simple, sensitive, and selective second order derivative spectrophotometric method has been developed for the simultaneous determination of gold(III) and cobalt(II) using 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBATSC) as a chromophoric reagent. The reagent (HMBATSC) reacts with Au(III) and Co(II) at pH 6.0, forming soluble blue and brown species, respectively. The second order derivative spectrum of [Au(III)-HMBATSC] exhibits reasonably sufficient amplitude at 435 nm and zero amplitude at 455 nm, and [Co(II)-HMBATSC] shows maximum amplitude at 455 nm and zero amplitude at 435 nm. This difference in amplitudes was utilized to develop a second order derivative spectrophotometric method for the simultaneous determination of Au(III) and Co(II) in a mixture without solving the simultaneous equations by measuring the second derivative amplitudes at 435 nm and 455 nm, respectively. Further, the Beer's law was obeyed in the range 0.1178–3.7712 ml⁻¹ of Au(III) and 0.1225–3.7400 µg ml⁻¹ of Co(II). A large number of foreign ions do not interfere in the present method. The method is applied to the simultaneous determination of Au(III) in Rheumartho gold and Co(II) in Vitamin B₁₂ samples.

Key words: Derivative Spectrophotometry, Determination of Au(III) and Co(II), HMBATSC.

Introduction

Gold (Au) is one of most important noble metals due to its wide application in industry and economic activity. It has been used in medicine for quite some time. Gold belongs to the group of elements (noble metals) which occur on the earth in very low natural contents and used extensively in fields of chemical industry, agriculture, and medicine. 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. Due to the low level of gold in the environmental and pharmaceutical samples and its great importance, sensitive methods are required to determine the trace amounts of gold in different matrices.

Cobalt (Co), a micronutrient for biological organisms, plays an important role in the nitrogen fixation by bacteria and is also an internal part of vitamin B₁₂. Plants and different food materials contain extremely low concentrations of the metal. Its deficiency leads to diseases like stunted growth. At high concentration, it inhibits heme biosynthesis and enzyme activities. Cobalt-60 is used as an efficient radioactive tracer and an anti-cancer treatment agent in medicine. Some cobalt compounds, such as vitamin B₁₂ (cyanocobalamin), are imported for biological activities. Therefore, the determination of cobalt is valuable for the quality control of artificial and biologically samples in a simple selective and sensitive manner.

Therefore, simple, sensitive and selective methods for determination of trace gold are always significant.

A literary survey reveals that there are several techniques and methods have been reported for the determination of gold¹⁻³ and cobalt⁴⁻⁶ in different samples individually. However, there were no methods available for the simultaneous determination of gold(III) and cobalt(II). In the present work, it was aimed to develop a simple, sensitive and selective determination of gold(III) and cobalt(II) by second order derivative spectrophotometry using 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone (HMBATSC) as a chromophoric reagent which was developed for the determination of transition metal ions individually⁷⁻¹⁵ and also simultaneously¹⁶⁻¹⁹. The simplicity and low operating costs of spectrophotometric methods make them attractive as an alternative technique the determination of metal ions in different matrices.

Material and Methods

Experimental 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 ±0.01 pH. Second-order-derivative spectra were recorded with a scan speed of fast (nearly 2,400 nm min⁻¹) and a slit width of 1 nm, with nine degrees of freedom, in the required wavelength range (nm). The derivative amplitudes measured at required wavelengths were

plotted against amounts of gold(III) or cobalt(II) to obtain the calibration plot.

Reagents and Chemicals: The reagent, 2-hydroxy-3-methoxy benzaldehyde and thiosemicarbazide was 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. The cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was obtained from Alpha Chemika, Mumbai, India. All other 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 procedure¹⁶.

Preparation of solutions: 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. A stock solution of 0.1M 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. Stock solution of Co(II) (1×10^{-2} M) is prepared by dissolving appropriate amount of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in doubly distilled water containing a few drops of conc. HNO_3 in a 100 ml volumetric flask and standardized 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.

Results and Discussion

Derivative spectra: The metal ions, gold and cobalt react with the reagent, HMBATSC forming blue and brown-colored complexes, respectively, pH 6.0. The second order derivative spectra were recorded for the solution containing the metal ions, Au(III) or Co(II), 5 ml of buffer solution (pH 6.0) and HMBATSC in a total volume of 10 ml. The second order derivative spectra of [Au(III)-HMBATSC] and [Co(II)-HMBATSC] were recorded in the wavelength region 390 to 500 nm at pH 6.0 (figure-1). It was found that the second order derivative spectrum of Au(III) complex shows zero amplitudes at 425 and 455 nm and considerably large amplitude at 435 nm. On the other hand, Co(II) complex with HMBATSC shows sufficient amplitude at 455 nm and zero amplitude at 435 nm. The experimental results indicate the derivative amplitudes obey Beer's law at 435 and 455 nm for Au(III) and Co(II), respectively. Therefore, Au(III) and Co(II) can be determined simultaneously in a mixture without separation by measuring the second order derivative amplitudes at 435 nm and 455 nm,

respectively.

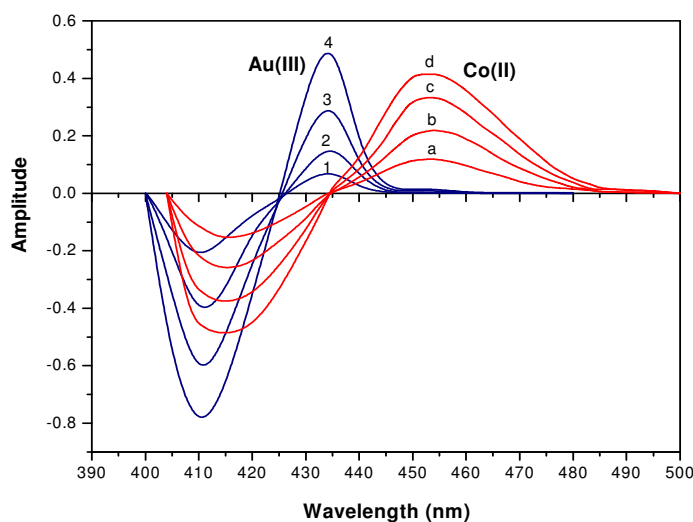


Figure-1
Second derivative spectra of [Au(III) - HMBATSC] and [Co(II) - HMBATSC] (red lines) at different concentrations [Au(III)] ($\mu\text{g mL}^{-1}$) - 1) 0.2450; 2) 0.4900; 3) 0.7350; 4) 0.9800, [Co(II)] ($\mu\text{g mL}^{-1}$) - a) 0.2357; b) 0.4714; c) 0.7071; d) 0.9428

Verification of Beer's law validity: Individual calibration plots were constructed by plotting the second derivative amplitudes measured at 435 nm against the amount of Au(III) and those measured at 455 nm against the amount of Co(II). The plots reveal that Beer's law was obeyed in the range 0.1178 – 3.7712 $\mu\text{g mL}^{-1}$ of Au(III) and 0.1225 – 3.7400 $\mu\text{g mL}^{-1}$ of Co(II).

Simultaneous determination of Au(III) and Co(II): Variable amounts of gold (0.1767 to 1.4136 $\mu\text{g mL}^{-1}$) and cobalt (0.1225 to 1.470 $\mu\text{g mL}^{-1}$) were treated with the required volume of the reagent at pH 6.0 in total volume of 10 ml and the second derivative spectra were recorded in the range 390 to 500 nm. The second order derivative amplitudes were measured at 435 nm and 455 nm and the amounts of Au(III) and Co(II) present in the mixture were computed from their respective calibration plots. The results are presented in table-1.

Applications: The developed simultaneous method was employed for the determination of amounts of Au(III) in *Rheumartho gold* and Co(II) in *Vitamin B₁₂* samples. The sample solutions were prepared as follows: A known quantity of sample was taken in a beaker. It was dissolved in minimum volume of alcohol, then added 3 ml of 0.01 M nitric acid and evaporated to dryness. The dried mass was again dissolved in alcohol. This was filtered through what man filter paper and the filtrate was diluted to 100 ml with distilled water. The lower concentrations were prepared by the appropriate dilution of the stock solution.

Table-1
Simultaneous second order derivative determination of Au(III) and Co(II)

Amount taken ($\mu\text{g mL}^{-1}$)		Amount found ($\mu\text{g mL}^{-1}$)		Recovery (%)	
Co(II)	Au(III)	Co(III)	Au(III)	Co(II)	Au(III)
0.1225	0.1767	0.1229	0.1772	100.33	100.28
0.1225	0.3534	0.1220	0.3525	99.59	99.74
0.1225	0.5301	0.1222	0.5292	99.76	99.83
0.1225	0.8835	0.1231	0.8851	100.48	100.18
0.1225	1.4136	0.1229	1.4155	100.32	100.13
0.1225	0.1767	0.1218	0.1759	99.43	99.54
0.2450	0.1767	0.2457	0.1776	100.28	100.51
0.4900	0.1767	0.4891	0.1771	99.82	100.23
0.9800	0.1767	0.9808	0.1761	100.08	99.66
1.470	0.1767	1.464	0.1763	99.59	99.77

*Average of five determinations.

Table-2
Determination of Au(III) and Co(II) in pharmaceutical samples

Sample and composition (mg/tablet)	Amount of metal ion found		
	Certified value	Earlier method ^{20,21}	Present method*
Vitamin B₁₂ (mg/tablet)	Co(II) ($\mu\text{g}/\text{tablet}$)		
Thiamino mononitrate(B ₁)	0.552	0.540	0.545
Riboflavine (B ₂)			
Pyridoxime hydrochloride			
Niacinamide			
Cyanocobalamine			
Folic acid			
Calcium pentathenate			
Sodium ascarbate			
<i>Rheumartho gold</i> Sri Baidyanath Ayurvedic Bhavan Ltd., India.	Au(III) (mg/capsule)		
	1.000	1.030	0.975

*Average of five determinations

A known aliquot of the sample was treated with 5 ml of buffer solution (pH 6.0), 0.5 ml of HMBATSC (1×10^{-3} M) and made up to the volume in a 10 ml volumetric flask with distilled water. The second derivative curve was recorded and the derivative amplitudes were measured at 435 nm and 455 nm. The amounts of Au(III) and Co(II) were computed from the measured amplitudes with the help of predetermined calibration plots. The results obtained are given in table-2.

Conclusion

The present method is simple, sensitive, and highly selective for the simultaneous determination of Au(III) and Co(II) in admixtures without separation and without solving simultaneous equations. The developed method was applied for determination of Au(III) and Co(II) in pharmaceutical samples.

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