Available online at www.elixirpublishers.com (Elixir International Journal)

Applied Chemistry

ISSN: 2229-712X

Elixir Appl. Chem. 54 (2013) 12383-12386

Spectrophotometric Determination of gold (III) using Lamotrogine[6-(2-3-dichloro phenyl)-1,2,4 triazine 3,5 diamine] Reagent

SK.Rafi[1], Venu Gopal Rao[2] and T. Sreenivasulu Reddy[3]

[1]Department of Chemistry, Priyadarshini College of Engineering and Technology , Nellore 524004, India.
[2]Dr. Reddy's Labaratories. Hyderabad, India.
[3]Depatment of Chemistry, Sri Krishnadevaraya University. Anathapur-515003, India.

ARTICLE INFO

Article history:
Received: 8 November 2012;
Received in revised form:
27 December 2012;
Accepted: 3 January 2013;

Keywords
Spectrophotometric,
Lamotrigine,
LMG.

ABSTRACT

A Lamotrigine (LMG) reagent, 6-(2,3-dichlorophenyl)-1, 2,4-triazine-3,5-diamine. Its molecular formula and molecular weight are $C_9H_7N_5Cl_2$ and 256.09 respectively, was employed for the sensitive spectrophotometric determination of gold(III). The gold(III) ion forms a yellow-coloured complex with LMG in an aqueous solution at p^H 3.0. The gold complex shows the absorption maximum at 400 nm, and Beer's law obeyed in the range of 10-160 µg/ml. The molar absorptivity and sandell's sensitivity were found to be 1.38 X 10^3 mol $^{-1}$ cm^{-1} and 0.0184 µg cm^{-2} respectively. The complex shows 1:1 [Au(III) : LMG] stochiometry with a stability constant of 4.77X10^4. The interference effect of various diverse ions has been studied. In addition to zero- order, first derivative spectrophotometric methods was also developed for the determination of gold(III) in trace amount which was more sensitive than the zero-order method. The developed method has been used for the determination of gold(III) in various kinds of alloys. The results was in excellent agreement with certified values.

1.Introduction

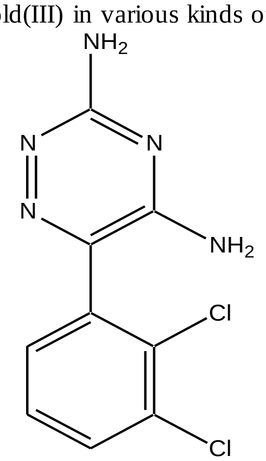
Gold is considered to be one of the most significant noble metals due to its wide application in industry and economic activity. It is the most interesting micro amount elements due to its significant role on biology. Gold occurs at very low natural contents, about 4ng g^{-1} In rocks, 1ngg^{-1} in soils, and 0.05 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 "chrysoteraphy [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. Alloy of gold with the other elements of I B group in the periodic table are most frequently used, and gold still has great significancein 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 veriety of spectrophotometric method for the determination of gold have been reported includes with [6-(2-3-dichloro phenyl)-1,2,4 triazine 3,5 diamine] Reagent.

Lamotrigine is one of the important classes of reagents widely employed for the spectrophotometric determination of metal ions. Lamotrigine contain good chelating agents and form complexes with various metal ions by bonding

Stuctural formula of Lamotrigine is shown below

In the literature survey the spectophotometric methods for the determination of gold(III) using lamotrogine are very less. The present work report the simple, sensitive, selective and nonextracrive spectrophotometric determination of gold(III) using [6-(2-3- dichloro phenyl)-1,2,4 triazine 3,5 diamine] Reagent. The developed method has been used for the determination of gold(III) in various kinds of alloys.



2.Experimental

2.1 Apparatus

The absorbance and pH measurements were made on a shimadzu UV – visible spectrophotometer (model UV – 160) 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 with in ± 0.01pH

2.2 Reagents and Chemicals

The [6-(2-3- dichloro phenyl)-1,2,4 triazine 3,5 diamine (LMG) was purchased from SD fine chemicals, India. The gold(III) chloride trihydrate ($HAuCl_4.3H_2O$) 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.

Tele:
E-mail addresses: rafiche786@yahoo.com

100mg of lamotrigine is weighed accurately and transferred in to a 100ml standard flask dissolved made up to the mark with methanol this solution is diluted as required.

A stock solution of 0.1 gold(III) was prepared by dissolving precise amount of $HAuCl_4.3H_2O$ in 1M hydrochloric acid and standardized using standard procedure.

The buffer solution were prepared by mixing in 0.2M sodium acetate + 1M hydrochloric acid (pH 2.5 – 3.5) and 0.2M sodium acetate + 0.2M acetic acid (pH 3.0 -6.0). The of these solutions was checked with above mentioned pH meter.

The SDS surfactant was prepared by dissolving 2gm of sodium dodecyl sulphate (SRL Chemicals) in 100ml of double distilled water.

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 10ml standard flasks, 5ml buffer solution (pH 3.0), varying volumes of 5.0 X 10^{-3} M Au(III) solution, and 2ml of LMG(3.85 X 10^{-3}M) solution were taken, then add 2% SDS surfactant solution and the volume made up to the mark with doubly distilled water this solution heated 60minutes at 65^0C for yellow colure complex formation, after cooling it to room temperature. The absorbance was measured at 400nm 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 ,where was the concentration of solution, was measured absorbance or peak height, and " " and " " were constants.

2.3.2 Derivative methods

For the above solutions, first derivative spectra were recorded with a scan speed of fast (nearly 2400nm min^{-1}), slit width of 1nm 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.

3. Results and discussion

3.1. Zero-order method

The gold(III) reacts with LMG (lamotrigine) forming a yellow – colored soluble complex in the acidic buffer solution in the presence of 2% SDS surfactant. The absorbance spectra of the LMG and its gold(III) complex under optimum conditions were presented in Figure 1.The gold (III) complex has an absorption maximum at 400nm, and at this wavelength the reagent has very small absorbance, Hence, further analytical studies were carried out at 400m.

Preliminary syudies have indicated that LMG reacts with Au(III) in aqueous acidic medium to form yellow colour species after heating the experimental solution at 65^0C for 60 minutes and cooling it to room temperature. The absorbance of the complex was found to be constant for more than 85 hours.The effect of pH on the intensity of colour 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 2.5 – 3.5. Hence pH 3.0 was chosen for further studies.

A 10-fold molar excess of LMG was necessary for comlex and constant colour 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)-LMG] 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 (Figure 2). The correlation coeffcient (γ) of the calibration curve for experimental data was 0.9996. From the calibration plot, it is observed that Beer's law was obeyed in the range of 4.92-78.76 µg/ml. The molar absorptivity and Sandall's sensitivity were 2.03 X 10^3 mol^{-1} cm^{-1} and 0.0969 µg cm^{-2}, respectively. The relative standard deviation at a concentration level of 19.69 µg/ml of Au(III) was found to be 0.004% (10 determinations).

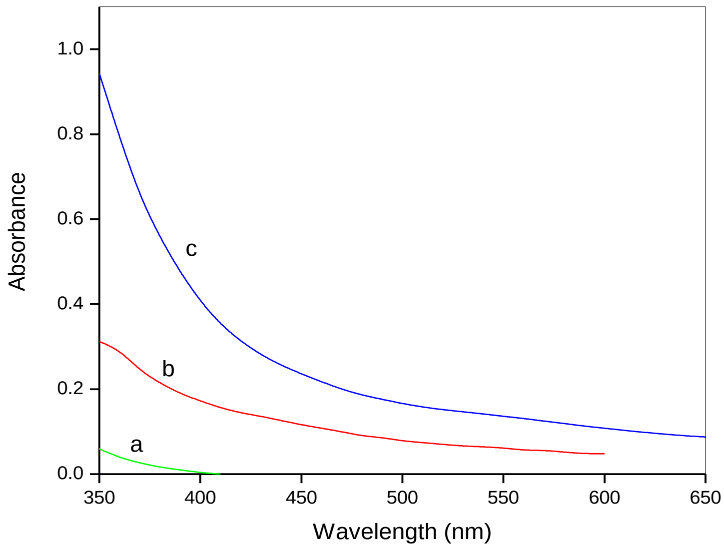


Figure 1: Absorption spectra of LMG – Au(III) system
a. Au(III) Vs buffer blank
b. LMG – Au(III) Vs buffer blank (Au(III) excess)
c. LMG – Au(III) Vs buffer blank (LMG excess)
[Au(III)] = 5.0 x 10^{-3}M; [LMG] = 3.85 x 10^{-3}M

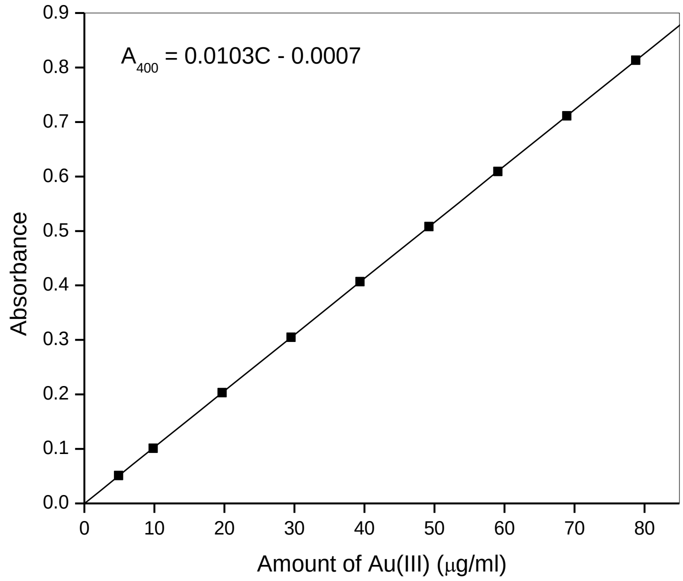


Figure 2: Absorbance Vs Amount of Au(III) (µg/ml)
[LMG] = 3.85 x 10^{-3}M ; pH = 3.0; λ = 400 nm

The composition of complex was determined by job's (Figure 3(a)) and molar ratio methods (Figure 3(b)). Both methods showed that a molar ratio of Au(III) to LMG was 1:1. The stability constant was determined by job's method as 4.77 X 10^4.

Table - 1
Tolerance limit of foreign ions [gold(III)] = 20µg/ml ; pH = 3.0

Ion	Tolerance limit (µg/ml)	Ion	Tolerance limit (µg/ml)
Iodide	21	Mo(VI)	136
Bromide	74	Ir(III)	273
Chloride	506	Co(II)	85
Fluoride	361	Ba(II)	196
Carbonate	571	Zn(II)	124
Sulphate	1371	Ce(IV)	199
Nitrate	1177	W(VI)	218
Phosphate	1353	Mn(II)	79
Oxalate	1002	V(V)	49
Thiocyanate	275	Ag(I)	104
EDTA	2093	U(VI)	341
Tartrate	1294	Zr(VI)	131
Citrate	408	Se(IV)	151
Acetate	702	Th(IV)	331
Ascarbate	427	Te(IV)	121
Na(I)	269	Pb(II)	198
K(I)	743	Ga(III)	133
Mg(II)	428	In(III)	219
Ca(II)	762	Y(III)	253
Ru(III)	144	La(III)	531
Cr(VI)	74	Ti(IV)	183
Fe(III)	79	Ni(II)	223
Cu(II)	91	Al(III)	104
Cd(II)	164	NH4(I)	342
Hg(II)	285	Pd(II)	103

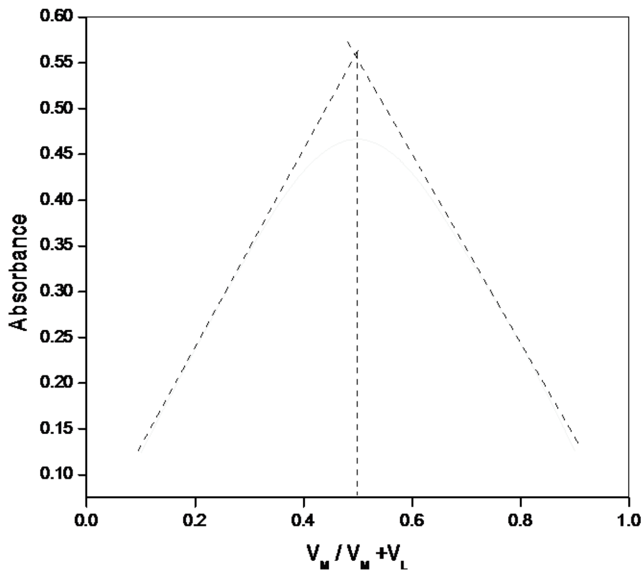


Figure 3(a) : Job's curve
[Au(III)] = [LMG] = 5.0 x 10^{-3}M ; pH 3.0 ; λ = 380 nm

The effect of various foreign ions that were generally associated with gold ion on its determination under optimum conditions was investigated by the determination 20 µ 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 ± 4%. The effect of various cations and anions invesigated. It was found that all the ions did not interfer in the zero-order determination of Au(III).

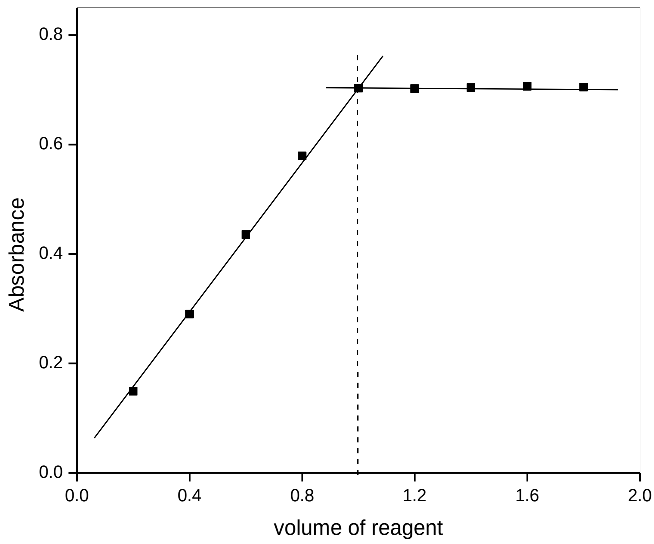


Figure 3(b) : Mole ratio plot
[Au(III)] = [LMG] = 5.0 x 10^{-3}M ; pH = 3.0 ; λ = 380 nm

3.2 derivative methods

The fist derivative spectra of experimental solutions containing different amounts of Au(III) were recorded in the wavelength region. The first derivative spectra (Figure 4) showed maximum amplitude at 420nm. The derivitive amlitudes at at420nm were found to be propotional to the concentrations of Au(III).

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.

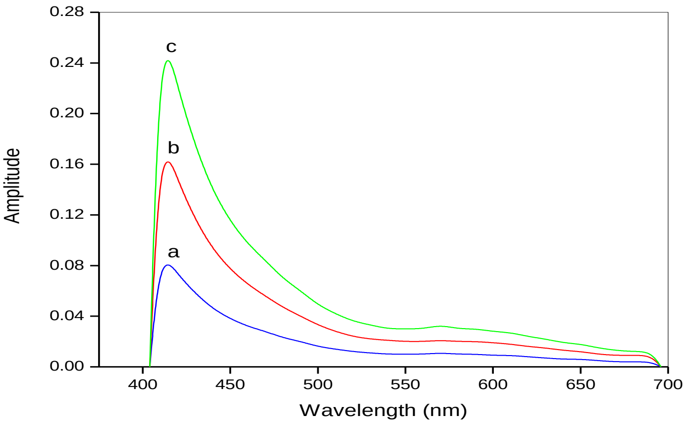


Figure 4: First derivative spectra of LMG – Au(III) Vs LMG blank [Au(III)] = a. 1.0 x 10^{-4}M; b. 2.0 x 10^{-4}M; c. 3.0 x 10^{-4}M

Applications

The proposed method was applied for the determination of gold(III) in Egyptian gold alloy samples and certified reference materials. the results of the determinations are given in Table 2.

Determination of gold(III) in Egyptian Gold Alloy samples

Egyptian Gold Alloy (sample Nos)	Certified Composition (%)	Amount of gold(III) (μg/ml)		Error (%)
		Taken	Found *	
1.	Au (87.66); Cu (6.81); Ag (6.12)	87.66	88.09	0.49
2.	Au (74.92); Cu (12.53); Ag (12.48)	74.92	74.55	-0.49
3.	Au (55.15); Cu (20.82); Ag (20.82)	55.15	55.87	1.31

* Average of Seven determinations

4. Conclusions

The present work gives a rapid, simple, sensitive, and selective method for the nonextractive spectrophotometric determination of gold(III). The developed method require the use of a surfactant. Further, derivative spectrophotometric methods also developed and are more sensitive than zero-order method. The most foreign ions do not interfere with the determination. The developed method was used for the determination of gold(III) in Egyptian gold alloy samples and certified reference materials.

References

1. R. Serbin, y. r. Bazel, M. Torok et al., "Investigation of the reaction of gold(III) with 2-[2-(4-Dimethylamino-pheyl)-vinyl]-1,3,3-trimethyl-3H-indolium. Application for determination of gold," journal of the Chinese chemical society, vol. 56, no. 6, pp. 1168-1174,2009. View at Scopus

2. R.Soomoro, M. J. ahmed, N. Memon, and H. Khan, "A simple and selective Spectrophotometric method for the determination of trace gold in real, environmental, biological, geological and soil samples using bis(salicylaldehyde) orthophenylnediamine," Analytical Chemistry Insights, vol. 3, pp. 75-90, 2008. View at Scopus

3. M. Balcerzak, A. Kosiorek, and E. Swiecicka, "Morin as a spectrophotometric reagent for gold," Journal ofAnalytical Chemistry, vol. 61, no. 2, pp. 119-123, 2006. View at Publisher. View at Google Scholar. View at Scopus

4. D.prem kumar, A. Praveen Kumar, T.Veera reddy and P.Raveendra reddy, "Spectrophotometric Determination of Gold(III) using 2-Hydroxy-3 Methoxy Benzaldehyde Thiosemicarbazone as a chromophoric Reagent," Journal of the ISRN Analytical chemistry, vol 2012 (2012),Article ID 705142,5 pages

5. M. B. Melwank, S. P. Masti, and J. Seetharamappa, "Dtermination of trace amounts of gold(III) using ethopropazine hydrochloride nd isothipendyl hydrochloride: a spectrophotometric study," Turkish journal of chemistry, vol. 26, no.1, pp.17-22, 2002. View atScopus

6. Z. Huang, F.Huang, X. Yang, Q. Wei, and C. Jing, "Solid phase extraction and spectrophotometric determination of trace gold using 5-(4-carboxylphenylazo)-8-hydroxyquinoline," Chemia Analityczna, Vol.52, no. 1, pp. 93-101, 2007. View at Scopus

7. Z. chen, Z. Huang, J. Chen, J. Yin, Q. Su, and G. Yang, "Spectrophotometric determination of gold in water and ore with 2-carboxyl-1-naphthalthiorhodanine," Analitical Letters, Vol. 39, 39, no. 3, pp. 579-587,2006. View at publisher. View at Google Sholar. View at Scopus

8. G Ramanjaneyulu, P. Raveendra Reddy, V. Krishna Reddy, and T. Sreenivasulureddy, "Direct and derivative spectrophotometric determination of Copper(II) with 5-bromosalicylaldehyde thiosemicarbazone," The Open Analytical Chemistry Journal, Vol. 2, pp. 78-82, 2008.

9. G Ramanjaneyulu, P. Raveendra Reddy, V. Krishna Reddy, and T. Sreenivasulureddy, "Direct and derivative spectrophotometric determination of Cobalt with 5-bromosalicylaldehyde thiosemicarbazone," Journal of the Indian Chemical society, Vol. 80,no. 8, pp. 773-776, 2003. View at scopus

10. G Ramanjaneyulu, P. Raveendra Reddy, V. Krishna Reddy, and T. Sreenivasulureddy, "Direct and derivative spectrophotometric determination of Iron in trace amount using 5-bromosalicylaldehyde thiosemicarbazone," Indian Journal of Chemistry A, Vol. 41, no. 7, pp. 1436-1437 .2002. View at scopus

11. A. I. Vogel, Practical Organic Chemistry, Longman, Londin, UK, 1973.

12. F. D. Snell, Photometric and Fluorometric Metod of analysis, John Wieley and Sons, New York, NY, USA, 1978

13. Ramesh SL, Anjaiah K V, Mathur R, RaoTG, Dasaram B, Charan SN, Rao DVS, sarma DS, Mohan MR, Balaram V, Raju PVS (2001) A Spectrosc 22:263-269

14. Malhotra RK, Ramanaiah GV , Satyanarayana K (1999) At Spectrosc 20:92-102

15. Anjali p (1998) Talanta 46:583-587

16. Balaram v, Ramesh SL (1999) J Indian Chem Soc 76:491-494

17. K.M.M.S.Prakash, L.D.Prabhakar, D.V.Reddy, Analyst 1986, 111,1301.

18. H.Ssanke Gowda, K.N.Thimmaiah, Indian J.Chem, Sect. A, 1976, 14,632.