Spectrophotometric Determination of Gold (III) using Tolterodine Tartrate (TLD) (R)-N, N-Diisopropyl-3-(2-Hydroxy-5-Ethylphenyl)-3-Phenylpropanamine L-Hydrogen Tartrate Reagent

SK. Rafi[1*], D. Venugopal Rao[2] and T. Sreenivasulu Reddy[3]

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

Authors' contributions

This work was carried out in collaboration between all authors. Author SKR designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Authors DVR and TSR managed the analyses of the study. Author TSR managed the literature searches and supervised the overall work and rendered valuable suggestions. All three of us read and approved the final manuscript.

Research Article

ABSTRACT

A Tolterodine tartrate (TLD) (R)-N, N-diisopropyl-3-(2-hydroxy-5-ethylphenyl)-3-phenylpropanamine L-hydrogen tartrate reagent. Its molecular formula and molecular weight are $C_{26}H_{37}NO_7$ and 475.6 respectively, was employed for the sensitive spectrophotometric determination of gold(III). The gold(III) ion forms a violet-colored complex with TLD in an aqueous solution at pH 4.0. The gold complex shows the absorption maximum at 540 nm, and Beer,s law obeyed in the range of 4.9 – 78.7 µg/ml. The molar absorptivity and sandell's sensitivity were found to be 2.41×10^3 mol^{-1} cm^{-1} and 0.0817 µg/cm^2 respectively. The complex shows 1:1 [Au (III): TLD] stochiometry with a stability constant of 9.98×10^4. The interference effect of various diverse ions has been

*Corresponding author: Email: tajche786@gmail.com;

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 were 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 $4ngg^{-1}$ in rocks, $1ngg^{-1}$ in soils, and $0.05\ ngmL^{-1}$ in sea water [1-2]. 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 non steroid anti-inflammatory drugs is failed to give relief. Gold is a soft metal and so is usually alloyed to give it more strength [3-4]. Alloy of gold with the other elements of I B group in international business and banking. So, simple, sensitive and selective methods for determination of trace gold [5-14] are always significant.

Among the several instrumental techniques spectrophotometric methods for the determination of metal ions [15-20] have an attractive attention due to their simplicity and low operating costs. A variety of spectrophotometric method for the determination of gold have been reported includes with [(R)-N, N-diisopropyl-3-(2-hydroxy-5-ethylphenyl)-3-phenylpropanamine L-hydrogen tartrate] Reagent.

 Tolterodine tartrate (TLD) [21] is one of the important classes of reagents widely employed for the spectrophotometric determination of metal ions. Tolterodine tartrate (TLD) contains good chelating agents [22] and form complexes with various metal ions by bonding

Stuctural formula of Tolterodine tartrate (TLD) is shown below
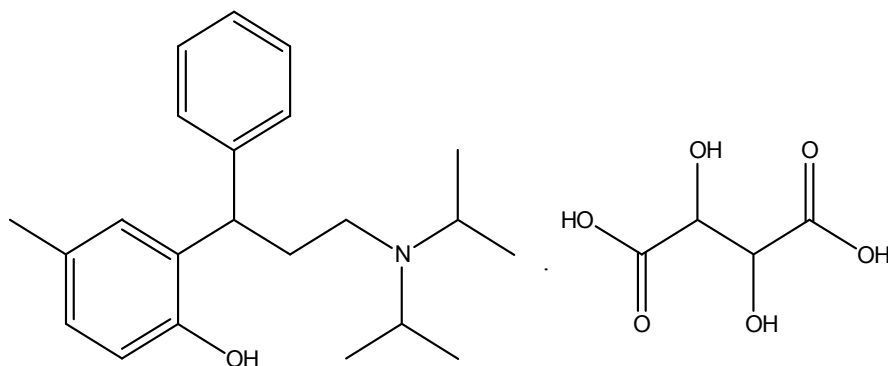
In the literature survey the spectophotometric methods for the determination of gold (III) using Tolterodine tartrate (TLD) are very less. The present work report the simple, sensitive,

selective and non extractive spectrophotometric determination of gold (III) using [(R)-N, N-diisopropyl-3-(2-hydroxy-5-ethylphenyl)-3-phenylpropanamine L-hydrogen tartrate] Reagent. The developed method has been used for the determination of gold (III) in various kinds of alloys.

2. EXPERIMENTALS

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 within ±0.01pH

2.2 Reagents and Chemicals

The [(R)-N, N-diisopropyl-3-(2-hydroxy-5-ethylphenyl)-3-phenylpropanamine L-hydrogen tartrate (TLD) 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.

A 100mg of Tolterodine tartrate (TLD) 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 $0.1 molL^{-1}$ gold (III) was prepared by dissolving precise amount of $HAuCl_4.3H_2O$ in $1 molL^{-1}$ hydrochloric acid and standardized using standard procedure.

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

The SDS surfactant was prepared by dissolving 2mg 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 4.0), varying volumes of $5.0 X 10^{-3} molL^{-1}$ Au(III) solution, and 2ml of TLD ($2.1 x 10^{-3} molL^{-1}$) solution are taken, then add 1.5ml 2% SDS is surfactant solution and the volume made up to the mark with doubly distilled water. This solution heated 60minutes at 65ºC for violet colure complex formation, after cooling it to room temperature, the absorbance was measured at 540 nm against the reagent blank. The calibration curve is constructed by plotting the absorbance

against the amount of Au(III). The calibration graph follows the straight line equation, the concentration of solution, was measured from the absorbance or peak height.

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 Tolterodine tartrate (TLD) forming a violet – colored soluble complex in the acidic buffer solution in the presence of 1.5ml 2% SDS surfactant. The absorbance spectra of the TLD and its gold(III) complex under optimum conditions were presented in Fig-1. The gold (III) complex has an absorption maximum at 540nm, and at this wavelength the reagent has very small absorbance, Hence, further analytical studies were carried out at 540 nm.
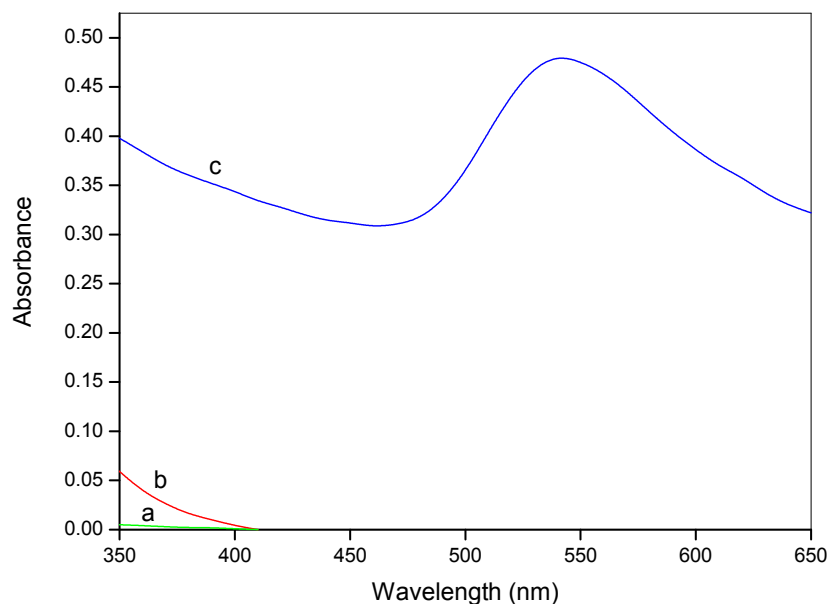

Fig. 1. (a) TLD Vs buffer blank. (b). Au(III) Vs buffer blank. (c). TLD – Au(III) Vs buffer blank
[Au(III)] = 5 x 10^{-3} molL^{-1}; [TLD]= 2.1 x 10^{-3} molL^{-1}

Preliminary studies have indicated that TLD reacts with Au(III) in aqueous acidic medium to form violet colour species after heating the experimental solution at 65ºC for 60 minutes and cooling it to room temperature. The absorbance of the complex was found to be constant fo r more than 85 hours.The effect of pH on the intensity of colour formation is studied to

optimize the pH of the gold complex. The results indicate that absorbance is maximum and constant in the pH range of 3.5 – 4.5. Hence pH 4.0 is chosen for further studies.

A 10-fold molar excess of TLD was necessary for complex and constant colure 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) - TLD] 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 (Fig. 2). The correlation coefficient (γ) 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 4.9 – 78.7 µg/ml. The molar absorptivity and Sandall's sensitivity were 2.41×10^3 mol^{-1} cm^{-1} and 0.0817 µg/cm^2 respectively. The relative standard deviation at a concentration level of 19.69 µg/ml of Au (III) is found to be 6.56×10^{-4} (10 determinations).
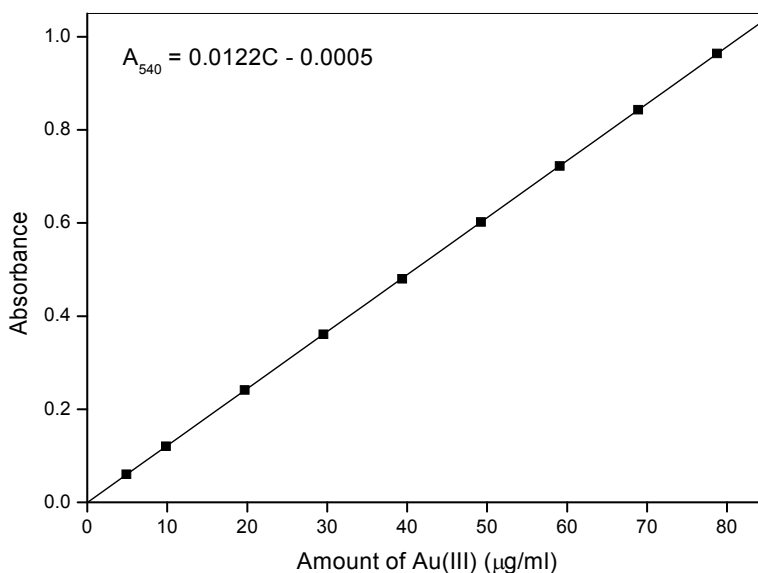
$$A_{540} = 0.0122C - 0.0005$$

Fig. 2. Absorbance Vs amount of Au (III) (µg/ml) [TLD] = 2.1 X 10^{-3} moIL^{-1}; pH = 4.0; λ = 540 nm

The composition of complex was determined by job's (Fig. 3(a)) and molar ratio methods (Fig. 3(b)). Both methods showed that a molar ratio of Au(III) to TLD was 1:1. The stability constant was determined by job's method as 9.98×10^4.

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 μg 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).
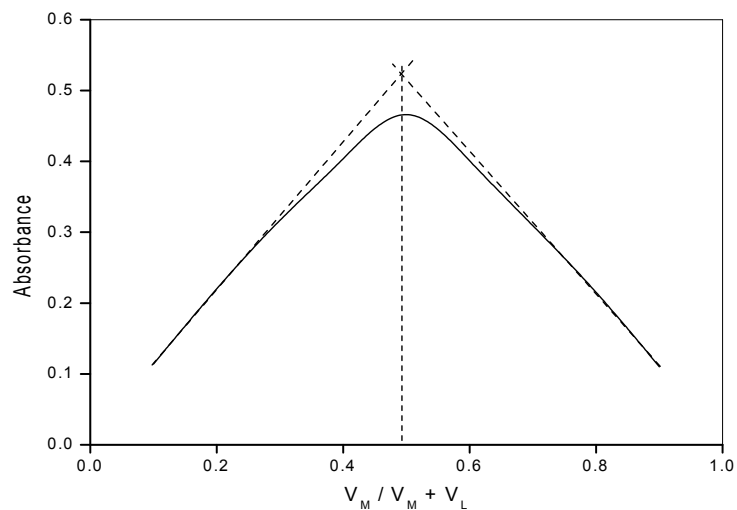
Fig. 3(a) Job's curve [Au(III)] = [TLD] = 5.0 x 10^{-3} moIL^{-1}; pH 4.0 ; λ = 540 nm

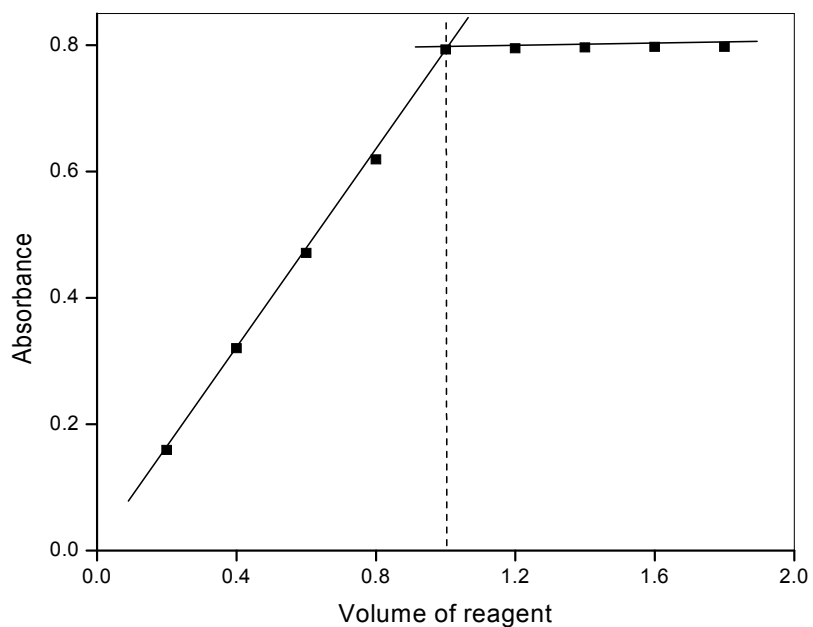**Fig. 3(b). Mole ratio plot [Au(III)] = [TLD] = 5.0 x 10^{-3} moIL^{-1} ; pH = 4.0 ; λ = 540 nm**

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 (Fig. 4) showed maximum amplitude at 585nm. The derivitive amlitudes at 585nm were found to be propotional to the concentrations of Au(III).

Table 1. Tolerance limit of foreign ions gold (III) = 20µg/ml; pH = 4.0

Ion	Tolerance limit (µg/ml)	Ion	Tolerance limit (µg/ml)
Iodide	29	Mo(VI)	151
Bromide	86	Ir(III)	302
Chloride	558	Co(II)	92
Fluoride	399	Ba(II)	216
Carbonate	629	Zn(II)	134
Sulphate	1515	Ce(IV)	221
Nitrate	1302	W(VI)	242
Phosphate	1495	Mn(II)	88
Oxalate	1105	V(V)	53
Thiocyanate	304	Ag(I)	112
EDTA	2313	U(VI)	374
Tartrate	1429	Zr(VI)	144
Citrate	452	Se(IV)	166
Acetate	774	Th(IV)	365
Ascarbate	472	Te(IV)	133
Na(I)	297	Pb(II)	216
K(I)	817	Ga(III)	146
Mg(II)	503	In(III)	241
Ca(II)	839	Y(III)	281
Ru(III)	159	La(III)	582
Cr(VI)	82	Ti(IV)	201
Fe(III)	89	Ni(II)	246
Cu(II)	98	Al(III)	117
Cd(II)	177	NH4(I)	378
Hg(II)	317	Pd(II)	112
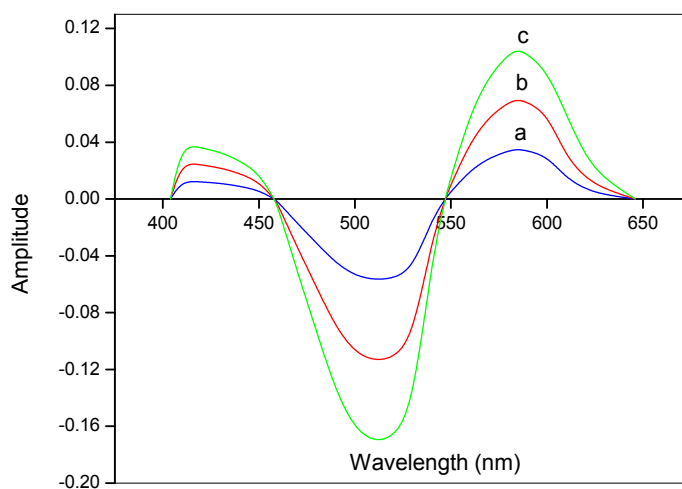
Fig. 4. First derivative spectra of TLD – Au(III) Vs TLD blank [Au (III)] = a. 1.0 x 10^{-4} molL^{-1}; b. 2.0 x 10^{-4} molL^{-1}; c. 3.0 x 10^{-4} molL^{-1}

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.

3.3 APPLICATION

The proposed method was applied for the determination of gold(III) in various Egyptian gold alloy samples by using Direct Spectrophotometric and Derivative Spectrophotometric methods. The results of the determinations are given in Table 2 and Table 3 respectively.

Table 2. Determination of gold(III) in Egyptian gold alloy samples

Egyptian gold alloy (sample no's)	Certified composition (%)	Amount of gold(III) (µg/ml)		Error (%)
		Taken	Found *	
1.	Au (87.66); Cu (6.81); Ag (6.12)	87.66	87.98	0.37
2.	Au (74.92); Cu (12.53); Ag (12.48)	74.92	73.99	-1.24
3.	Au (55.15); Cu (20.82); Ag (20.82)	55.15	55.86	1.29

Average of Seven determinations

Table 3. Determination of gold (III) in Egyptian Gold Alloy samples

Egyptian gold alloy (sample no's)	Certified composition (%)	Amount of gold(III) (µg/ml)		Error (%)
		Taken	Found *	
1.	Au (87.66); Cu (6.81); Ag (6.12)	87.66	86.88	-0.89
2.	Au (74.92); Cu (12.53); Ag (12.48)	74.92	75.55	0.84
3.	Au (55.15); Cu (20.82); Ag (20.82)	55.15	54.39	-1.38

Average of Seven determinations

4. CONCLUSIONS

The present work gives a rapid, simple, sensitive, and selective method for the non extractive spectrophotometric determination of gold (III). The developed method requires 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. The results was excellent agreement with egyptian certified reference materials.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Macy JM, Nunan K, Hagen KD. Chrysiogenes arsenatis gen. nov., sp. nov., a New Arsenate-Respiring Bacterium Isolated from Gold Mine Wastewater. International Journal of Systematic Bacteriology. 1996;46(4):1153–1157.
2. Monser L, Adhoum N. Modified activated carbon for the removal of copper, zinc, chromium and cyanide from wastewater. Separation and Purification Technology. 2002;26(2-3):137–146.
3. El-Sayed H, Huang X, El-Sayed MA. Surface Plasmon Resonance Scattering and Absorption of anti-EGFR Antibody Conjugated Gold Nanoparticles in Cancer Diagnostics: Applications in Oral Cancer. Nano Letters. 2005;5(5):829–834.
4. Su ZX, Pu QS, Luo XY, Chang XJ, Zhan GY, Ren FZ. Application of a macroporous resin containing imidazoline groups to preconcentration and separation of gold, platinum and palladium prior to ICP-AES determination. Talanta. 1995;42(8):1127–1133.
5. Serbin R, Bazel YR, Torok M, et al. Investigation of the Reaction of Gold(III) with 2-[2-(4-Dimethylamino-phenyl)-vinyl]-1,3,3-trimethyl-3H-indolium. Application for Determination of Gold. Journal of the Chinese chemical society. 2009;56(6):1168-1174.
6. Soomro R, Ahmed MJ, Memon N, Khan H. A Simple and Selective Spectrophotometric Method for the Determination of Trace Gold in Real, Environmental, Biological, Geological and Soil Samples Using Bis (Salicylaldehyde) Orthophenylenediamine. Analytical Chemistry Insights. 2008;3:75-90.
7. Balcerzak M, Kosiorek A, Swiecicka E. Comparison of x-ray fluorescent analysis and cupellation method for determination of gold in gold jewellery alloy. Journal of Analytical Chemistry. 2006;61(2):119-123.
8. Prem Kumar D, Praveen Kumar A, Veera reddy T, Raveendra Reddy P. Spectrophotometric Determination of Gold(III) Using 2-Hydroxy-3-Methoxy Benzaldehyde Thiosemicarbazone as a Chromophoric Reagent. Journal of the ISRN Analytical chemistry, 2012;volume 2012(2012),Article ID 705142:1-5.
9. Melwank MB, Masti SP, Seetharamappa J. Turkish Journal of chemistry. 2002;26(1):17-22.
10. Huang F, Huang Z, Yang X, Wei Q, Jing C. Chemia Analytica. 2007;52(1):93-101.
11. Z. Chen, Z. Huang, J. Chen, J. Yin, Q. Su, G. Yang. Spectrophotometric Determination of Gold in Water and Ore with 2-Carboxyl-1-Naphthalthiorhodanine Spectrophotometric Determination of Gold in Water and Ore with 2-Carboxyl-1-Naphthalthiorhodanine. Analytical Letters. 2006;39(3):579-587.
12. Rafi SK, Venugopal Rao D, Sreenivasulu Reddy T. Elixir Appl. Chem. 2013;54(2013):12383-12386.
13. Rafi SK, Veera reddy T, Sreenuvasulu Reddy T. International Journal of Recent Scientific Research. January 2013;4(1):84–87.
14. Rafi SK, Sreenivasulu Reddy T. Journal of Peagia Research Library, Der Chemica Sinica Sinica. 2013; 4(2):11 – 18.
15. Ramanjaneyulu G, Raveendra Reddy P, Krishna Reddy V, Sreenivasulureddy T, The Open Analytical Chemistry Journal. 2008;2:78-82.
16. Ramanjaneyulu G, Raveendra Reddy P, Krishna Reddy V, Sreenivasulureddy T, Journal of the Indian Chemical society. 2003;80(8):773-776.
17. Ramanjaneyulu G, Raveendra Reddy P, Krishna Reddy V, Sreenivasulu Reddy T, Indian Journal of Chemistry. 2002;41(7):1436-1437.
18. Mustafa Tuzen, Kadri, O. Saygi, Mustafa Soylak. Journal of Hazardous Material. 2008;56((1–3):591-595.

19.   Mustafa Soylak, Mustafa Tuzen. Coprecipitation of gold(III), palladium(II) and lead(II) for their flame atomic absorption spectrometric determinations. Journal of Hazardous Materials. 2008;152(2):656-661.
20.   Ali Duran, Mustafa Tuzen, Mustafa Soylak. Phase extraction adsorbent. Journal of Hazardous Materials. 2009;169(1-3):466-471.
21.   The Merk Index, Fourteenth edition, Whitehouse Station, NJ: Merk & co., Inc. 2005; Electronic version.
22.   Ravindra Kumar Y, Ramulu G, Vevakanand V, Vaidyanathan G, Keesari S, Kishore KM, Mukkanti K, Satyanarayana RM, Venkatraman S, Suryanarayana MV. J Pharm Biomed Anal. 2004;35:1279-1285.