

Second order Derivative Spectrophotometric determination of Aluminum (III) using 3,4-DihydroxyBenzaldehydeThiosemicarbazone(DHBTSC) in presence of micelle medium

M.Nagarjuna¹, V.Tejeswara Rao²,D. Nirmala Devi³,D.Aditya Deepthi⁴, M.Mogalali raju^{5*}

1.Department of Physics, Dhanekula institute of Engineering and Technology,Ganguru.

2. Department of Chemistry, MVR PG College, Visakhapatnam.

3. Dept of BS& H, Vignan's institute of Engineering for Women, Kapujaggarajupeta, Visakhapatnam, 530049

4.Department of Chemistry,St. JOSEPHS COLLEGE FOR WOMEN (A),Gnanapuram.

5. Deapartment of Chemistry, Vikas college of Engineering &Technology, Vijayawada.

ABSTRACT

A rapid and sensitive method has been developed for the determination of Aluminum(III) based on complexation reaction between the metal ion and 3,4,-dihydroxybenzaldehydethiosemicarbazone (DHBTSC) in the presence of non-ionic surfactant Tween-80. The important parameters affecting the analytical procedure were optimized. Absorption maximum for a ternary complex was noted at λ_{\max} 382 nm. The reaction was found to be rapid at room temperature and absorbance remained constant for more than 24hrs. The method obeys Beer's law in the range of 6.74 to 60.70ng/ml. The apparent molar absorptivity of $6.0 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ and Sandell's sensitivity 0.044ng/ml. The effect of foreign ions was tested by taking a constant concentration of metal ion and determining its concentration in the presence of ≥ 100 folds in excess of foreign ions. The method was successfully used in the determination of Aluminum(III) in Water samples and cement samples. Second order derivative spectrophotometric methods were developed at λ_{\max} 430nm for the determination of Aluminum, which was more sensitive than the zero order method.

Keywords: Spectrophotometric Determination, Aluminum, 3,4-DHBTSC, Surfactant Tween-80, cement sample, Water sample.

Introduction

Aluminum is recognized as an important toxic substance causing considerable morbidity and mortality, particularly in patients with chronic renal failure. Diseases that have been associated with aluminum include dialysis dementia. Renal osteodystrophy and Alzheimer's disease. Aluminum also has an effect on red blood cells, parathyroid glands and chromosomes. The main clinical manifestations of aluminum toxicity include progressive encephalopathy, osteomalacia, microcytic hypochromic anaemia and cholestasis. Many sources have been shown to be

contaminated with aluminum. These include the water used for dialysis, medicines containing aluminum, such as aluminum-containing phosphate binding gels, total parenteral nutrition solutions, processed human serum albumin, intravenous fluids in infants and other environmental and industrial sources [1-3]

Long-term total parenteral nutrition (TPN) patients can inadvertently receive significant amounts of aluminum present as contaminant in TPN. Many of the solutions for parenteral nutrition have an aluminum content which exceeds the suggested threshold concentration of $25 \mu\text{g l}^{-1}$ recommended by the American Society for Clinical Nutrition (ASCN) and the American Society for Parenteral and Enteral Nutrition (ASPEN) [4].

Aluminum is among the third most abundant metals in the earth's crust, with a mean concentration of 8.13% by weight [5]. Familiar uses of aluminum are in beverage cans, pots and pans, airplanes, and foil. Aluminum compounds are used in different products such as antacids, astringents, buffered aspirin, food additives, and antiperspirants. In most of the natural water, the concentration of aluminum is reported to be low due to limited solubility at the pH normally encountered in fresh water. As a result of human activities, a considerable mobilization of aluminum has occurred. It is very difficult to elucidate the complete distribution of aluminum compounds in natural waters because of the large number of compounds, that all participate in dynamic interaction; the total concentration of aluminum, ranging from a few $\mu\text{g l}^{-1}$ in transparent neutral waters to mg l^{-1} in brownish water of low pH and the presence of organic and other substances that might interfere with its determination [6,7].

Among bio applications, aluminum is considered as an essential element in the nutrition of animals and humans as it acts as cofactor in numerous enzymes and play an important role in protein synthesis and cell division [8]. It also plays important role in the maintenance of cell membrane stability and in the function of immune system, It also constitutes an active ingredient in medical products intended for tropical applications. Aluminum deficiency may effect severely therefore, it is important to monitor its concentration in both environmental water samples and pharmaceutical formulations.

The organic reagents for the spectrophotometric determination of aluminum include pyrocatechol violet, Ferron, Oxine (8-Hydroxyquinoline), Eriochrome cyanine R and chromazurol S. Among many spectrophotometric determination methods of aluminum chromeazurol-S, pyrocatechol-violet, 8-hydroxyquinoline, ferron and eriochrome cyanine-S were commonly used [9-14]. However most of these methods were reported less sensitive. Various other reports have indicated some new hydrazones, semicarbazones and their applications to the spectrophotometric determination of aluminum were published [15-18]. The organic reagent 8-hydroxyquinoline is extracted into organic solvent such as chloroform and carbon tetrachloride. These are time consuming, tedious and involve the use of chlorinated solvents that cause contamination in the atmosphere. They offer however, no significant progress with respect to either sensitivity or selectivity in comparison with the method reported herein. Aluminon is a triammonium salt of 5-

[(3-carboxy-4-hydroxyphenyl)(3-carboxy-4-oxocyclohexa-2,5-dien-1-ylidene) methyl] -2-hydroxybenzoic acid and it forms a water soluble complex with aluminum which aluminum which absorbs light in the visible range of 515-530nm. It has been extensively used as a classical organic reagent for the spectrophotometric determination of aluminum in different matrices[19-24]. The complexing properties of aluminon have been used for the spectrophotometric determination of aluminum in micellar medium.

In the recent years, surfactants have become of great interest because of providing a reaction medium in which the sensitivity and selectivity of numerous reaction were improved [25-31]. The presence of surfactants especially cationic surfactants such as cetyltrimethylammonium chloride (CTAC), cetylpyridinium chloride (CPC), xephiramine (Zp) have been studied for the colour reaction between various dyes and metal ions. Usually, the metal chelate complexes formed in the micellar systems are more stable than those formed in the absence of surfactants. The most remarkable advantage of surfactants includes; a) formation of the ternary complexes with the higher molar absorption I.e, increasing sensitivity, b) expansion of color reaction area or determination range, c) large bathochromic shift i.e sharp contract, d) resistance to the interfering ions or increase in selectivity and stability of complexes, etc.. These effects show the advantage of such surfactant systems in the development of new spectrophotometric methods for determining micro amount of metals ions anions, biological compounds, drugs and pesticides.

In present communication, a spectrophotometric method is reported that can be used for the quantitative determination of aluminum directly based on the complexation reaction between aluminum ion and aluminon in the presence of cationic surfactant CPC. Different factors affecting the reaction of aluminum in micellar media were optimized. The proposed method has been successfully applied to the determination of aluminum in water samples from different origin and pharmaceutical products. The results were compared with those obtained by employing FAAS technique and a good agreement is observed.

Recently enhanced sensitivity in spectrophotometer was achieved by utilizing the ability of certain surfactants to sensitize the binary complexes of the metal ion with chromogenic ligands[21,22] sensitization are result of the replacement of acidic protons of the liganded dye molecule by surfactant[23] (or) adsorption of the metal reagent complex on the micelles of the surfactant [24] cationic, anionic and nonionic surfactants are often used to sensitize the metallochromic indicators. In this context, updated surfactant – sensitized reaction have recently been developed in spectrophotometry[25-29].

The present study was hence planned to suggest a very simple and reasonably good method for determination of mercury ions at low concentration, using the reported reagent, DHBTSC as binary complex and sensitizing the reagent with Tween 80 as ternary complex using spectrophotometer which is still frequently used because of its low cost and simplicity.

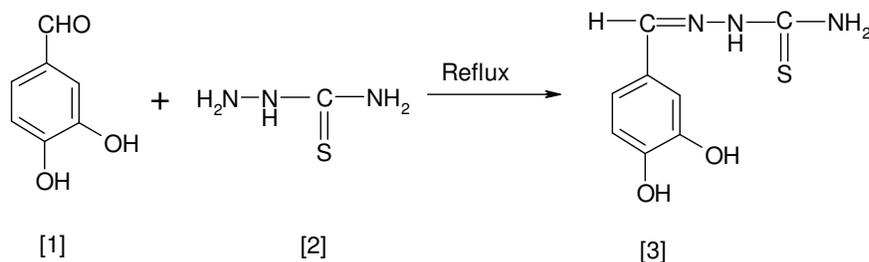
Experimental

Apparatus

The Absorbance and pH measurements were made on a Shimadzu UV-visible spectrophotometer (Model UV -160A) fitted with 1cm Quartz cells and Philips digital pH meter (model L1 613 respectively.)

Reagents and solutions

Preparation of 3,4-di hydroxybenzaldehethiosemicarbazone(DHBTS):The Reagent (DHBTS) is prepared by the sah and Daniels procedure. 7 g of 3,4-dihydroxybenzaldehyde(1) was dissolved in 100 mL of methanol and 4.6 g of thiosemicarbazide(2) were dissolved in hot water. The two solutions were taken in 250 mL Erlenmeyer flask and refluxed for 3 hrs. pale yellow colored crystals were separated out on cooling. These crystals were collected by filtration and washed several times with hot water and 50 percent methanol. The product(3,4-dihydroxybenzaldehydethiosemicarbazone)(3) (m.p 221-223⁰c) was recrystallised twice from boiling methanol and dried in vacuum.



All chemicals used were of analytical reagents grade or the highest purity available. Double distilled deionized water, which is non-absorbant under ultraviolet radiation, was used throughout. Glass vassals were cleaned by soaking in acidified solutions of KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$, followed by washing with concentrated HNO_3 and rised several times with deionized water.

Tween-80 solution 1%. . A 100 mL of Tween-80 solution was prepared by dissolving 1 mL of pure tween-80 in 100 mL if doubly distilled deionized water, sonicated for 15 min and diluted with deionized water when it became transparent.

3,4-Dihydroxybenzaldehydethiosemicarbazone (DHBTS) ($1 \times 10^{-4} \text{mol/dm}^3$)

A 25 mL solution was prepared by dissolving 0.0528 g of recrystallised sample in dimethylformamide and it was suitably diluted to get the required concentration.

Aluminum (III) standard solution ($1.0 \times 10^3 \mu\text{g/mL}$)

Aluminum standard solution was prepared by dissolving 0.4941 g of (Aldrich) in distilled water and diluted to 100 mL with distilled water. Working standard solutions were standardized by a potentiometric method.²⁷

Procedure

Direct spectrophotometry

In each of set of different 10 mL volumetric flasks, 5 ml of buffer solution (pH 6.0), 1 mL of DHBTC ($1 \times 10^{-3} \text{mol/dm}^3$) and various volumes of $1 \times 10^{-6} \text{mol/dm}^3$ Aluminum(III) finally added 1 mL of 1% Tween-80 and f solution were taken and made up to the mark with double distilled water. The absorbance was measured at 382nm against the reagent blank. The calibration plot was prepared by plotting the absorbance against the amount of Aluminum(III).

Second order derivative spectrophotometry

For the above solutions, second order derivative spectra were recorded with a scan speed of fast (nearly 2400 nm min^{-1}); slit width of 1 nm with nine degrees freedom, in the wavelength range 390-510 nm. The derivative amplitude measured at wavelength 430 nm and plotted against amount of Aluminum(III) to obtain the calibration.

The calibration graph follows the straight line equation $Y = aC + b$; where C is the concentration of the solution, Y is measured absorbance or peak or valley height and a and b are constants. By substituting the corresponding experimental data substituted in the above equation, the calibration equations were calculated as $A_{382} = 0.3706C - 0.099$ for zero order method, $A_{430} = 0.022C + 0.0034$ for second order derivative method.

Results and Discussion

Factors affecting the absorbance

Absorption spectra

The absorption spectra of the Aluminum (III)-3,4-DHBTC system in a micellar medium were recording using a spectrophotometer. The absorption spectra of the Al(III)-3,4-DHBTC is a symmetric curve with the maximum absorbance at 382nm and an average molar absorption coefficient of $6.0 \times 10^5 \text{L mol}^{-1} \text{cm}^{-1}$ (Fig. 1). The reagent blank exhibited negligible absorbance, despite having a wavelength in the same region. In all instances, measurements were made at 382 nm against a reagent blank.

Effect of surfactant: of the various surfactants [nonionic {poly oxyethylenedodecylether (Brij - 35), Polyoxyethylenesorbitanmonoplamate (Tween-40), Polyoxyethylenesorbitanmonioleate (Tween-80), Triton-X-100} ; cationic [cetyltrimethylammoniumbromide (CTAB)] : and

anionic { cetlpridinium chloride (CPC) , sodium dedecy sulfate SDS } studied. Tween-80 was found to be the best surfactant for the system. In a 1%(V/L) Tween-80 medium however, the maximum absorbance was observed hence, a 1%(V/L) Tween-80 solution was used in the determination procedure.

Different volumes of 1%(V/L)Tween-80 were added to a fixed metal ion concentration, and the absorbance was measured according to the standard procedure. It was observed that at 26.98ng/ml Hg-chelate methal.0.25-1.75 mL of 1%(V/V) Tween-80 produced a contestant absorbance of the A(III)l-chelate(*Fig. 2*). A greater Excess of Tween-80 were not studied. For all subsequent measurements, 1mL 1%(V/V) Tween-80 was added.

Effect of Acidity

The absorbance of the complex reaches a maximum over a pH range of 5.0 to 7.0. The higher pH values may lead to hydrolysis of Al(III) -3,4-DHBTSC system. The absorbance was at a maximum and constant when a 10 ml of solution (1mgL^{-1} ; path length ,1) contained 1-7 mL (pH6.0) of acidic buffer at room temperature (25 ± 5 c) . Outside this range of acidity , the absorbance decreased (*Fig. 3*) . For all subsequent measurements 5.0 ml (pH 6.0)acidic buffer was added.

Effect of time

The reaction is very fast. Constant maximum absorbance was obtained just after dilution to volume, and remained strictly unaltered 24h.

Effect of reagent concentration:

Different molar excess of 3,4 –DHBTSC were added to a fixed metal –ion concentration, and the absorbance's were measured according to the standard procedure. It was observed that at 26.98 ng/ml Aluminum metal(optical path length , 1 cm) reagent molar ratios 1:10 and 1:100 produced a constant absorbance of the Al(III)-Chelate(*Fig. 4*) . A greater excess of the reagent was not studied. For all subsequent measurement 1mL of $1\times 10^{-3}\text{mol/dm}^3$ 3,4 –DHBTSC reagent was added.

Calibration graph (Beers Law and sensitivity)

The Calibration curve for the determination of mercury has been constructed (*Fig. 5*) using the optimum experimental conditions. The straight line calibration curve indicates that Beers' law is obeyed at least over a range of 6.74 to 60.70 ng of Aluminum(III) per10 mL.Linear regression analysis of the calibration curve gives a correlation coefficient of 0.9945. The apparent molar absorptivity(ϵ_{382}) calculated from the slop of regression line is $6.0 \times 10^5\text{L mol}^{-1}\text{cm}^{-1}$ The Sandell's sensitivity(concentration for 0.001 absorbance unit) was found to be 0.044ng cm^{-2} .

Effect of foreign ions :

To study the selectivity of the proposed method, the effect of diverse ions on the determination of Al(III) was investigated by adding a known quantity of the desired ion to a solution containing 26.98 ng/mL of Al(III) which was determined as described in the given procedure. The tolerance limit was defined as the concentration at which the species caused an error of less than $\pm 5\%$. The results obtained are summarized in *Table 1*. Based on the results, most cations and anions did not interfere with the Al(III) determination even in their presence in the amounts 1000-fold greater than Al(III). In the absence of a masking agent, Fe(III) did not interfere with the Al(III) determination up to 50-fold concentration of this ion. Interferences caused by Cr^{3+} , Hg^{2+} , and Fe^{3+} could be masked with EDTA ($100 \mu\text{g mL}^{-1}$) up to 100-, 30-, and 80-fold respectively. An advantage of this method is low interference effect of Fe(III) on the determination of Al(III). The results clearly confirm selectivity of the method.

Composition of the Metal – Reagent complex

Jobs method of continuous variation (*Fig .6*) and the molar – ratio method were applied to ascertain the stoichiometric composition of the complex. Al(III) -3,4-DHBTSC(1:1) complex was indicated by both methods. The stability constant was determined by Jobs Method as 0.52×10^7 .

Applications:

The Present method was successfully applied to the determination of Aluminum in water and cement samples.

Determination of Aluminum in water samples

The proposed method was applied for the determination of Aluminum in water samples collected in different parts in Visakhapatnam city and River Krishna, River Godavari. The samples were stored at $\sim 5^\circ\text{C}$ in metal free polyethylene bottles. The water samples were filtered through a Whatman filter paper No 41 in a Pyrex glass beakers. The contents were evaporated to nearly dryness and re-dissolved with 10 mL of double distilled water. Then the solution was transferred into a 25 mL measuring flask and made up to the volume with double distilled de-ionized water. To determine the accuracy of the method, a known amount of aluminum was determined. 2.0 mL of pre-concentrated water sample was taken into a 10 mL measuring flask and spiked with known amount of aluminum and contents were determined following the general determination procedure. Absorbance was measured after 10 minutes at 382 nm, relative to a blank prepared in the same way except the addition of aluminum. The results show a good recovery of aluminum from water samples (*Table 2*).

Determination of Aluminum in cement sample

The developed method was applied for the determination of Aluminum in cement sample. Required amount of cement is taken, dissolved in concentrated hydrochloric acid and digested for half an hour by heating on a hot plate. The solution is cooled and filtered and filtrate is collected quantitatively in 50 mL standard flask and made upto the mark with double distilled water. To determined accuracy of the method , a known amount of aluminum was determined. A known aliquot of sample is taken in 10 mL volumetric flask containing 5 mL of buffer of pH(6.0), 0.5 mL of 0.1 mol dm⁻³ citrate solution (to mask iron), 0.5 mL of 0.1 mol dm⁻³ thiourea solution (to mask copper) and 1.0 mL of the reagent solution were added to the flask and the contents are made up to the mark with distilled water. The absorbance of the solution was measured at 382 nm against reagent blank. The amount of aluminum present in the sample was determined from the pre-determined calibration plot. The results are presented in the *Table 3*.

Second order derivative method

The second order derivative curve recorded (*Fig. 7*) for experimental solution showed the derivative amplitude were measured at 430 nm (peak) for different concentrations of Aluminum(III) and plots were made between the amount of Al(III) and the derivative amplitude. The plots were linear and obeyed Beer's law in the range 5.396-21.584 ng/mL at 430 nm respectively.

Comparison of results

The analytical characteristics of the zero and second order derivative methods in the present investigations for Aluminum(III) were compared and present in *Table 4*. The results in this table reveal that second order derivative method is more sensitive and selective than the zero order method.

The sensitivity of the zero method in the present investigations was compared with those of some reported methods and presented in *Table 5*

Conclusion

This method offers several interesting features such as simplicity, rapidity, and low cost besides sensitivity. The number of associated elements does not interfere in the determination. The selectivity of the reagent is also improved by the use of suitable masking agents to suppress the interference of metal ions like Fe(III), Hg(II), and Cr(III). Hence the proposed method is recommended for the determination of Aluminum (III) with DHBTS in presence of micelles by spectrophotometric method, at minor and trace levels, besides its use for analysis of real samples such as water and cement samples.

References

1. K.Popiska, J.Kierku, M.Lyszkowska, J.Socha, E.Pietraszek, W.Kmiotek and J.Ksiazyk, *Nutrition*, **1999**,9,.683.
2. M.Blanua, L.Prester, M.crnogorac, Z.Pureti, L.Bubi-Filipi and Z.Dadi, *Arh. Hig.RadaToksikol.*, **1997**,48, 197.
3. B.Gammelgaard and E.Sandberg, *J.Trace Elem, Electrolytes Health Dis.*,**1989**, 3 , 39
4. M. Marta Luconi, A. Roberto, *Analyst*,**2001**,126, 1172-1176
5. .B.Mason in: *The Earth Sciences (A.N.Strahler)(Harper &Row, New ork, 2nd , Eds.(1971).*
6. C.F.BacsJr and R.E.Mesmer: *The Hydrolysis of Cation, John Wiley & Sons, New York, (1976).*
7. J.urgess, *Analyst*,**1992**, 117, 605.
8. I.A1- Saleh and N.Shinwari, *Biometals*,**1996**, 9, 385.
9. C.Exley and J.D.Birchall, *Polyhedron*, **1992**, 11, 1901.
10. N.W.Menzies,L.C.Bell and D.G Edwards, *J.Soil Sci.*,**1991**,42, 585.
11. G.M.Morrison, *Analyst*, **1990**, 115, 1371.
12. R.W.Gensemer,*J.Phycol*, **1990**, 126, 250.
13. B.Fairman andA.Sanz-Medel, *IntJ. Environ. Anal.chem.***1993**, 50, 161.
14. J.R.Kramer,J.Gleed and K.Gracey, *Anal.ChimActa.*,**1994**, 284, 599.
15. D.Chakravarti, Y.Lu, J.Cheng,M.H.Back and W.H.Schroeder,*Anal. Chim.Acta.* **1993**, 284, 47.
16. G.Zhang andH.Q.Yang, *Fenxi Huaxue*,**1990**, 18, 933.
17. X.Z.Fan,B.C.WuH.C.Liu, C.Wu,Huadong,XuebaoZirankexueban.**1993**, 3, 69.
18. S.Kamino.T.Yamaguchi, I.Mori, T.Miyamoto, M.Kusumi and Y.Fikota. *Anal. Sci.*,**2005**, 21, 549.
19. A.K.Alva and D.G.Edwards, C.J.Asher and F.P.C.Blamey, *Soil Sci,Soc,Am,J.***1986**, 50, 133.
20. A.K.Alva and D.G.Edwards, C.J.Asher and F.P.C.Blamey, *Soil Sci,Soc,Am,J.***1986**, 50, 959.
21. A.D.Noble, M.E. Sumner and A.K.Alva, *Soil Sci.Soc.Am.J.***1988**, 52, 1398.
22. A.D.Noble, M.E. Sumner and A.K.Alva, *Soil Sci.Soc.Am.J.***1988**, 52, 1059.
23. A.K.Alva and M.E.Sumner, *Soil,Sci.***1989**, 147, 278.
24. D.F.Evans, J.Parr and E.N.Coker,*Polyhedron*, **1990**,9, 813.
25. S.Liu,*Analyst*,**1982**, 107, 428.
26. A.S.Amine and Y.M.Issa,*JPharmaceut,Biomed.Anal.*, **2003**, 31, 491.
27. M.Benamor,K.Belhamel and M.T.Draa,*J.Pharmaceut,Biomed. Anal.*,**2000**, 23,1033.
28. C.D.Stalikas and T.Trend, *Anal Chem.*,**2002**, 21, 343.
29. M.Soylak and O.T.Glu,*Talanta*,**2000**, 53, 125.
30. X.ZhuL.Bao,R.Guo and J.Wu,*Anal.Chim. Acta*, **2004**,43, 523..
31. A.Safavi, M.Mizae and H.Abdollahi, *Anal, Lett*,**2003**, 36, 699

32. M. Buratti, C. Valla, O. Pellegrino, FM Rubino and Colombi, *Anal Biochem*, **2006**, 63, 353.
33. MJ. Ahmed and J. Hossan *Talanta*, **1995**, 42, 1135
34. AM. Diaz, JMH. Mariscal, MIP. Reguera and LFC Vallvey, *Talanta*, **1993**, 40, 1059
35. NK. Agnihotri, HB. Singh, RL. Sharma and VK. Singh, *Talanta*, **1993**, 40, 415
36. H. Ying-Ping, Y. Ke-mei and Z. Hua-shan, *J. Natural Sci*, **1999**, 4, 219
37. JH. Mendez, RC. Martinez, BM Cordero and LG. Davila, *Analytica Chimica Acta*. **1983**, 149:379.
38. M. Jamaluddin Ahmed, M. Reazul Hoque, A.S.M. Shahed Hossain Khan, *Eurasian J. Anal. Chem*, **2010**, 5, 1-15.

Table 1: Tolerance limit of interfering ions in the determination of 26.98 ng mL⁻¹ of Al(III).

Ion	Interferent –to –analyte ratio (w/w)
Na ⁺ , K ⁺ , Ba ²⁺ , Ca ²⁺ , Mg ²⁺ , Ni ²⁺ , Mn ²⁺ , Li ⁺ , Co ²⁺ , Pt ²⁺	
Au ³⁺ , So ₄ ²⁻ , Cu ²⁺ ,	1000 ^a
Sr ²⁺	400
CN ⁻	300
EDTA	100
Fe ³⁺	50
I ⁻ , Cr ³⁺ , Hg ²⁺	2

^a Maximum ratio tested

Table 2. Determination of Aluminum in water

Matrices	Added(μg)	Found(μg)	Recovery (%)
Tap water(Visakhapatnam city)	4.0	3.86	96.50
	8.0	7.54	94.25
River water, Krishna	4.0	3.86	96.50
	5.5	5.18	94.18
	7.0	6.56	93.71
River Godavari	5.5	5.24	95.27
	7.0	6.75	96.42
	8.5	8.12	95.52

Table 3. Determination of Aluminum in cement sample

Sample and composition (%)	Amount of Aluminum		Relative error (%)
	Taken(μg)	Found(μg)	
Portland cement *	0.400	0.403	+1.5
	0.800	0.805	+1.25
	1.200	1.203	+1.5

*CaO = 50.60, SiO₂ = 20.25, Al₂O₃ = 5.10, MgO = 2.3, Fe₂O₃ = 1.2, SO₃ = 1.2, NaO₂ = 1, K₂O = 1.

Table 4. Comparison of results of Aluminum(III)

Parameter	Zero order	Second derivative
Analytical wave length(nm)	382	430
Beer's law range(ng/mL)	6.74-60.70	5.396-21.584
Angular coefficient(m)	0.3706	0.0022
Y-ntercept(b)	0.0099	0.0034
Correlation coefficient(r)	0.9945	0.9987
Standared deviation(s)	0.0126	0.019
Molar absorptivity(ϵ)(L mol ⁻¹ cm ⁻¹)	6.0 x 10 ⁵	8.7 x 10 ⁵

Table 5. Comparison with other methods

Reagent	Medium	pH	Molar absorption co-efficient(L mol ⁻¹ cm ⁻¹)	Beer's law	Remarks
Methylthymolblue[32]	Extraction	1.5-4.7	1.32 x 10 ⁵	0.15-1($\mu\text{g}/\text{mL}$)	Solvent extractive, Less selective, Less sensitive.
Morin[33]	Ethanollic medium	0.01-0.05(mol L ⁻¹) H ₂ SO ₄	5.3 x 10 ³	0.05-5($\mu\text{g}/\text{mL}$)	Less selective, Less sensitive, Lengthy.
Chrome azurol S [34]	Extraction	5.5	2.4 x 10 ³	0.6-4($\mu\text{g}/\text{mL}$)	Less selective, Less sensitive, Lengthy, time consuming.

5,8-dihydroxy-1,4-naphthoquinone[35]	Non-ionic surfactant	4.7	1.04×10^4	0.01-1.08($\mu\text{g/mL}$)	Less selective, Less sensitive.
2,3,7-trihydroxy-9-[4-(2,4-dihydroxy)phenylazol]phenylfluorone[36]	Aqueous	6.5	1.1×10^4	0-2.2($\mu\text{g/mL}$)	Less selective due to much interference, Less sensitive.
Alizarin red S [37]	Acetate buffer	4.75	1.7×10^3	0.1-10($\mu\text{g/ml}$)	Less selective due to much interference, Less sensitive.
2-hydroxynaphthaldehyde-benzoylhydrazone[38]	Aqueous	1.25×10^{-4} mol/L H_2SO_4	2.21×10^4	0.01-2($\mu\text{g/ml}$)	Less selective, Less sensitive, Lengthy
3,4-dihydroxybenzaldehyde-thiosemicarbazone(DHBTSC) C) (Present method)	Aqueous	6.0	6.0×10^5	6.74-60-70(ng/ml)	Ultrasensitive, Highly selective, Aqueous reaction medium. Very simple & rapid, Non-extractive.

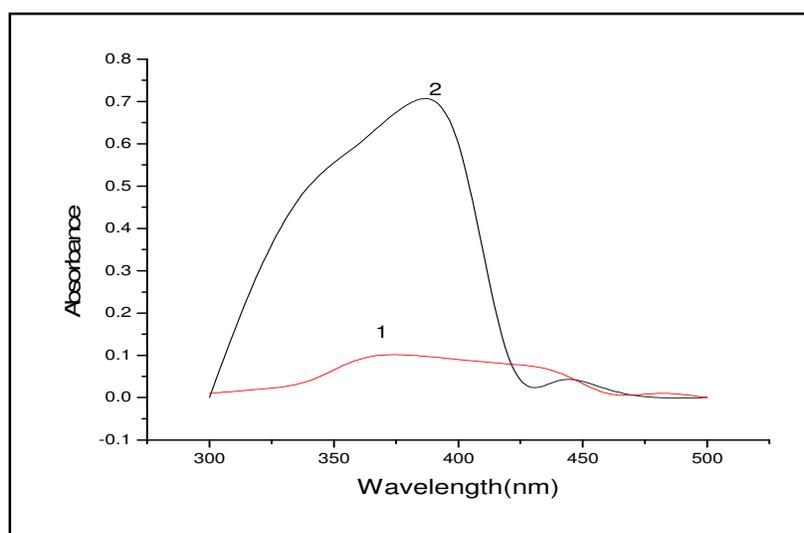


Fig. 11 and 2 absorption spectra of reagent blank and Al(III)-DHBTSC system ($\lambda_{\text{max}} = 382\text{nm}$) in nonionic micellar medium

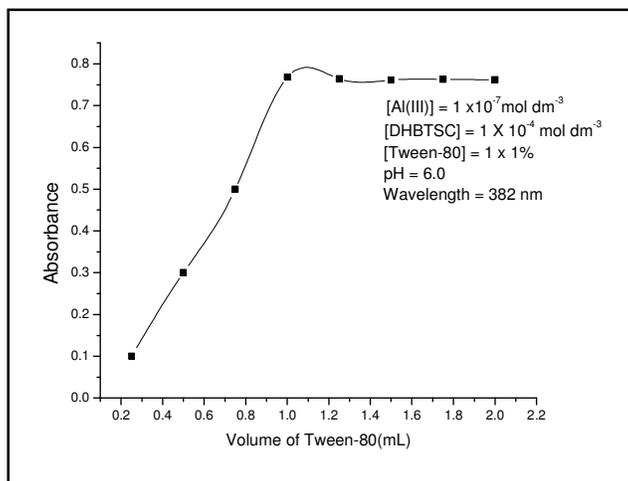


Fig. 2 Effect of surfactant on the absorbance of the Aluminum(III)-DHBTS system

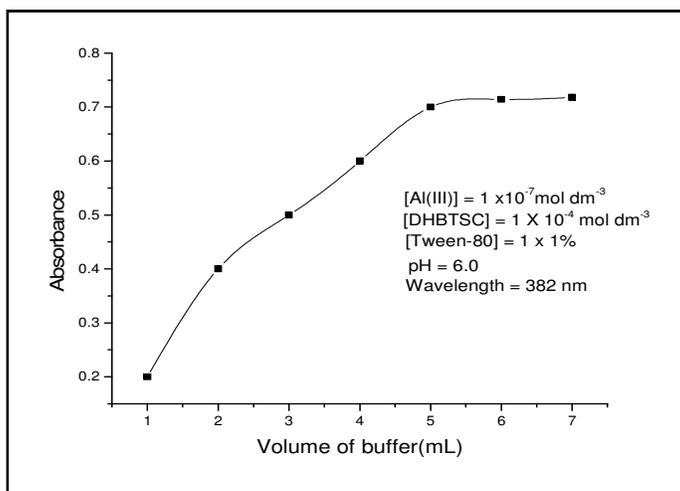


Fig. 3 Effect of Buffer solution on the absorbance of the Aluminum(III)-DHBTS system

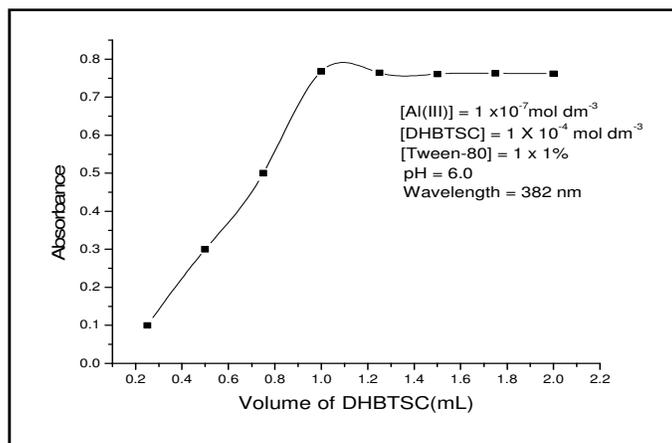


Fig. 4 Effect of reagent(DHBTS) on the absorbance of the Aluminum(III)-DHBTS system.

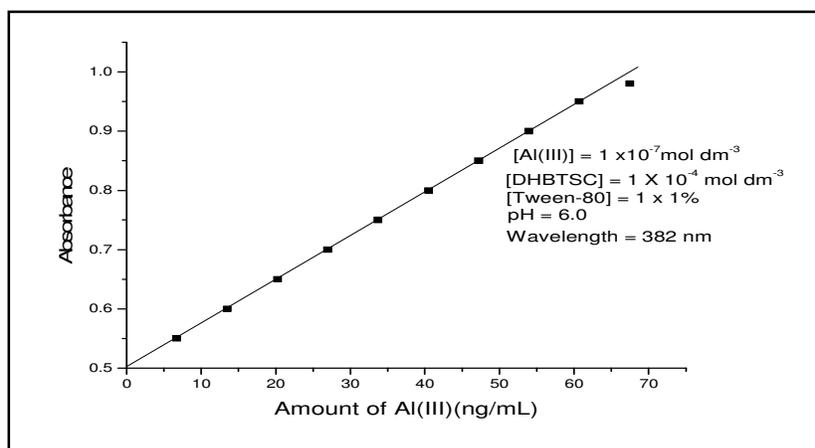


Fig. 5 Calibration graph

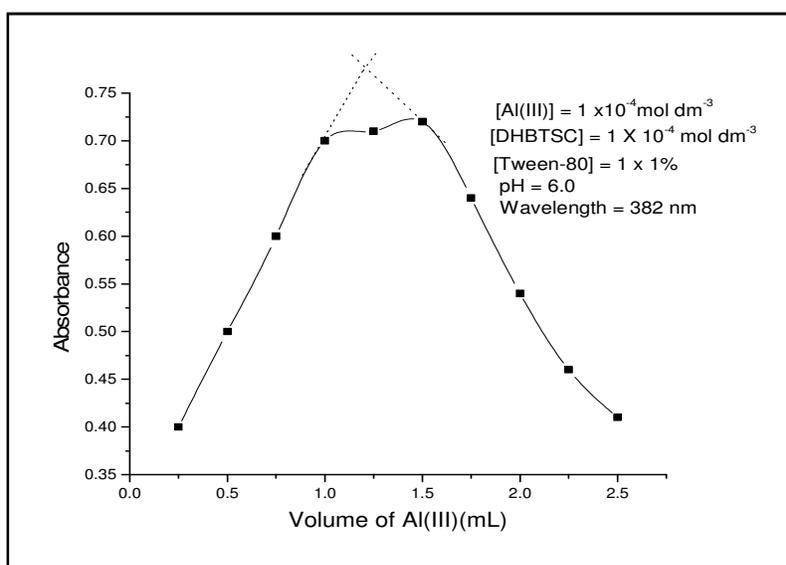


Fig. 6 Job's curve

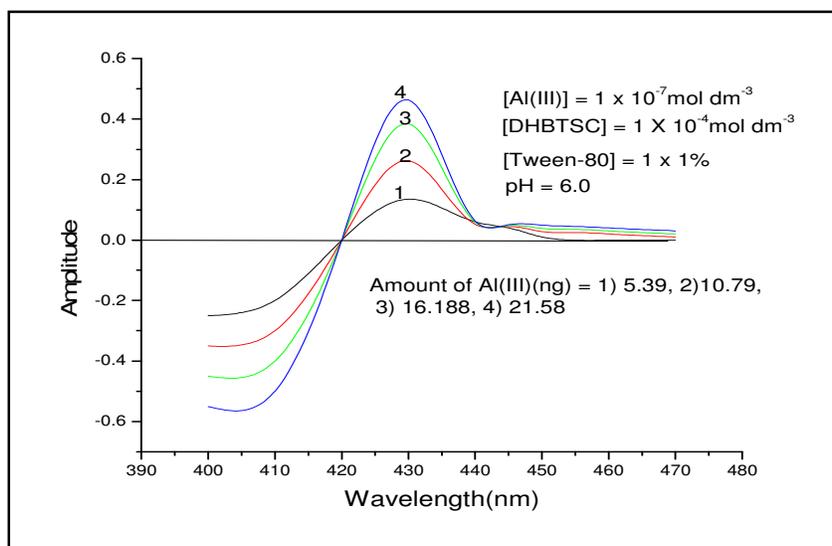


Fig. 7 Second derivative spectra of Aluminum(III)-DHBTS Vs reagent blank.