Spectrophotometric Determination of Chromium(III) and Iron(III)by Used of 2-((E)-(1H-benzo[d]imidazol2-yl) diazenyl)-5-((E)-benzylideneimino)phenol;(BIADPI)as Organic Reagent

KHALID J. AL-ADILEE*, SHAIMAA .M.EASSA and HAITHAM .K. DAKHIL

Department of Chemistry, College of Education, University of Al – Qadisiya, Iraq.
*Correspondence author E-mail:khalid.jawad@qu.edu.iq

ABSTRACT

The azo reagent 2-((E)-(1H-benzo[d]imidazol2-yl)diazenyl)-5-((E)-benzyl ideneimino) phenol (BIADPI) was prepared and examined by using element analysis (C.H.N.), UV-Vis., Mass spectrum, ^{1}H-NMR spectrum and infrared spectra. A sensitive and selective spectrophotometric method is proposed for the rapid determination of iron (III) and chromium(III) using (BIADPI), as spectrophotometer reagent. The reaction between this reagent with chromium (III) and iron (III) is instantaneous at (586,536) nm (λ_{max}) and pH=(7.5,4) to form perpul complexes having a mole ratio 1 : 2 (metal : ligand) for Cr(III) and Fe(III) the absorbance remains stable for over 24 hours. Beer's law is obeyed in the rang of (1-14) µg.ml^{-1} and (1-21) µg.ml^{-1} with molar absorptivity (€) = (7.768x10^5 , 9.3575x10^5) L.mol^{-1}.cm^{-1} and a detection limit of (0.275-0.14) µg.ml^{-1} obtained respectively. The precision and accuracy were obtained to be R.S.D%=(0.9-0.467)%,Re%=(99.1-98.2-)% and E$_{rel}$%= (-1.8 - 0.9)%.The method is successfully employed for the determination of iron(III) in Pharmaceutical preparations (Anemia drugs). The most important interferences were due to Ni(II), Zn(II), Co(II), Cd(II), Cu(II) and Hg(II) and suitable masking agents were used.

Keywords: (BIADPI),Determination ,Chromium, Iron, Spectrophotometry, Schiff base.

INTRODUCTION

Azo Schiff base compounds are very important well known and generally used substances in cosmetics industries and textile paper and coloring agents for foods[1]. Azo Schiff bases essential intermediates for the production of some applications for example biological activity[2-4], analytical[5,6], Anticancer[7,8], clinical[9,10], and catalystical[11]. Azo

schiff bases compounds derivative from the reaction between the Schiff derived from the reaction of aromatic aldehydes and aliphatic or aromatic amines represented important series of widely studied organic reagent[12]. Azo schiff base and their complexes with transition metal ions are also of importance due to their complexing, catalystical, biological properties[13]. and corrosion inhabitation in acid media[14,15].This class of azo compounds posses

active (π- acidic) azo imine (-N= N-C=N-) function, for this reason a number of these azoimidazoles were prepared and their abilities as chelating ligands was investigated[16-18].

Chromium exist in natural water in two stable oxidation states, Cr(III) and Cr(III). Among these two predominant forms, Cr(III) is considered to be essential to mammals for the maintenance of glucose, lipid and protein metabolism, where as Cr(III) is a toxic and S460 SUVARAPU et al. carcinogenic form[17-19]. Because of the above reasons the determination of chromium in environmental and biological samples is of great interest. Determination of Cr(III) in micro quantities is of interest to analytical chemists. Although AAS is the most common method of chromium detection. Besides AAS, a number of other methods has been reported for Cr(III) determination such as NAA, ICP-MS, ICP-AES[21-23]. Moreover, such techniques are usually not available in most laboratories. Because of expensive cost of the above instruments most of the researchers are still interested in colorimetric and spectrophotometric methods[24]. Iron is an essential nutrient. World Health Organization(WHO) estimation for iron minimal daily requirements depends on age, sex and man physiological status, and they range from 10 to 50 mg/d. The average lethal dose for iron is 200-250 mg/kg body weight. However, literature presents data for death cases resulting from swelling of 40 mg/kg body weight doses[25]. In this paper we report, 2-((E)-(1H-benzo[d]imidazol2-yl)diazenyl)-5-((E)-benzyl ideneimino)phenol(BIADPI) , which was prepared by Al – adilee[26], as an analytical reagent for the micro determination of Fe(III) and Cr(III). The method has been found to be simple, rapid and sensitive for the determination of these metal ions.

EXPERIMENTAL

All chemical which are of analar grade are purchased from Aldrich ,BDH, Merck, GCC, England and Sigma. All the solvents used Ethanol, methanol, dimethyl sulfoxide and Teterahydrofuranare of Analar grade. The solvents were purified by distillation and double distilled water was used throughout the experiment. The infrared spectra of the ligand (BIADPI) and their metal complexes were run as KBr discs in range (4000-400) cm^{-1} on a shimadzu 8400 FTIR spectrophotometer. Element analysis (C.H.N) were performed by using a Euro EA elemental analyzes.^{1}HNMR spectrum of ligand were determined in CDCl$_3$ (internal standared TMS) on Bruker spectrophotometer (Tarbiat modarres univesity, Iran), Mass spectrum of ligand was obtained using Agilent Technologies 5975C at 70e and MSD energy using a direct insertion probe (Acqmethod low energy) at temperature 90-110°C(Tarbiat Modarres universtry, Iran). absorption spectra were measured on aT80 UV-Vis spectrophotometer and absorbance were measured on Apel PD -303UV- visible spectrophotometer using 1 cm quartz cells, The metal contents of the complexes were measured by using atomicabsorption by aPg AA-6300 Atomic absorption spectrophotometer , A model WTW multi 720, pH – meter was used to adjust and measure the pH of the solution , melting point was measured using SMP30 Stuart, UK. Experiments and preperation of solutions and washing all glasses , distilled water is used twice doubly distilled water.

Prepartion of Novel Azo-schiff Baes Ligand (BIADPI)

The novel azo-schiff base ligand (BIADPI) was prepared by condensation of benzaldehyde (3.41 g; 0.01 mole) with 3-amino phenol (1.09 gm; 0.01 mole) in 30 ml ethanol in the presences 5 drops of glacial acitic acid as a catalyst and the mixture was refluxed for 5 h. at 60°C.The resltant solution was cooled at room temperature .The dark yellow solid of 3-(benzylidene amino)phenol was formed was filtered and recrystallized in absolute ethanol.Yield 87% ;m.p=149°C. Azo compound was prepared by the diazotization coupling reaction using procedure described for arylazo -imidazole dyes[26] with some modification Scheme(1).2-Amino benzimidazole(1.33 gm, 0.01 mole) was dissolved in mixture 25 ml distilled water and 5 ml of concentrated hydrochloric acid and cooled to 0-5°C.The solution was diazotized at 0-5°C with (0.75 gm;0.01 mole) sodium nitrate was disolved in 25 ml distilled water was added drop wise to solution of 2-amino benzimidazole and stirring continuously at 0-5°C and left to stand 30 min .This diazonium solution was added to (1.97 gm; 0.01 mole) of 3-(benzylidene amino) phenol was dissolved in 100 ml ethanole and 30 ml of 6% sodiume hydroxide. The mixture was stirred continuously for 2 h. at 0-5°C in ice-bath and allowed to stand over- night. The precipitate was filtered and washed with distilled water and

ethanol solution to remove the excess of unreacted substances and recrystallized from ethanol and dried in oven at 50°C for several hours. The purity was confirmed by the elemntal analysis and TLC techniques.Yield;79%:m.p; 160°C.

Reagent and Solutions

All the chemicals used were of analytical reagent grade, and were used without further purification. Ethanol were purchased.

- 1x10^{-3}M (BIADPI) standard solution was prepared by dissolving (0.0342)g in 100 ml of absolute ethanol.

- Stock Cr(III) solution; A solution of Cr(III) (1000 µg.ml-1) was prepared by dissolving (0.5210 g) of CrCl$_2$.6H$_2$O in 100 mL deionized water. Other standard solutions of Cr(III) were prepared by dilution of stock solution with distilled water .

- Stock Fe(III) solution ;A solution of Fe(III) (1000 µg.ml-1) was prepared by dissolving (0.3025)g of FeCl$_3$ in (1 ml) in (HCl) and full the flask to (100 ml) by deionized water. Other standard solutions of Fe(III) were prepared by dilution of stock solution with distilled water.

- The pH of the medium (2-9) was adjusted with ammonium acetate (0.01 mol L^{-1}) –ammonia – glacial acetic acid buffer solution .

General Procedure

Into a 10 mL calibrated flask , transfer 1 mL of sample solution containing less than 100 µg.ml^{-1} of Cr(III) and adjust the pH to 7.5 with ammonium acetate buffer, add 1 ml 1.0×10^{-3}M ethanolic (BIADPI) solution and diluted to the mark with deionized water. The absorbance of the resultant solution was measured after 10 min. at 586 nm at 25 °C against the corresponding reagent blank prepared under identical conditions but without Chromium ion.

Transfer 1.5 mL of sample solution containing less than100 µg.ml^{-1} of Fe(III) and adjust the pH to 4 with ammonium acetate buffer, add 1 ml 1.0×10^{-3}M ethanolic (BIADPI) solution and diluted to the mark with deionized water. The absorbance of the resultant solution was measured after 10 min. at 536 nm at 25°C against the corresponding reagent blank prepared under identical conditions but without Iron ion.

RESULTS AND DISCUSSION

Mass Spectrum of the Novel Azo-Schiff Bases Ligand (BIADPI)

The mass spectral fragmentations of azo-schiff bases ligand (BIADPI) shown in scheme-1 and figure 1.The base peak of azo-schiff base ligand at m/e$^+$=342.30 is attributed to the original molecular weight of the ligand (341.37) under investigation. The peak at m/e$^+$=239 is analougs to the loss of phenyl and azo methine (NCH) group.The loss of two nitrogen atoms (azo group) give a peak at m/e$^+$=211.The peak at m/e$^+$=159 due to loss of C$_4$H$_4$. The same spectrum show a peak at m/e$^+$=139 corresponding to loss of hydroxyl group and three hydrogen atoms from imidazole ring[27,28]

^{1}H-NMR Spectrum of Azo-Schiff Bases Ligand (BIADPI)

The ^{1}H-NMR spectrum of the azo schiff base ligand figure (2) was measured using in CDCl$_3$ as a solvent. The azo schiff base spectral results show a dblate peaks at δ=6.51-6.54 ppm attributed to phenol ring. The triblate peaks at δ =7.27-7.28 ppm attributed to the phenyl ring .The single peaks at δ =6.77 ppm and 6.78 ppm due to the NH and OH groups in ligand respectively. Also the same spectrum display signal at δ=7.58 ppm which are assigned to the phenyl ring of benzimidazole. The azo schiff base ligand shows single peak at δ=8.57 ppm which is assigned to the presence of protons of azo methine group[29,30].The singal peak at 1.26 ppm is due to the existence of CDCl$_3$ solvent.

Infrared Spectra

The infrared spectroscopic data of reagent and their complex with Fe(III), and Cr(III) spectra are complicated owing to the extensive overlap of number of bands arising due to υ(O%H), υ(CP%N), υ(NP%N) and other bands originate due to phenyl and benzimidazol rings appeared in the region below 1650 cm^{-1}, the comparison between spectra of the reagent with those of two coordination complexes have revealed certain characteristics :-

1. The IR spectrum of reagent (BIADPI) gives characteristic broad band at 3601 cm^{-1} assigned to the phenolic υ(O%H). This suggests a strong intermolecular hydrogen bonding[31]. The spectra of Cr(III) and Fe(III)

complexes show broad and weak bands around (3194-3480)cm^{-1} which indicate the presence of water molecule in these complexes[32.]

2. The free reagent shows medium band around 3323 cm^{-1}which can be attributed to υ(N-H) stretching vibration of benzimidazol moiety[26]. The band appears at (3257-3318) cm^{-1} in solid chelate complexes of Cr(III) and Fe(III) spectra. Thus the remaining of the hydrogen of (N-H) group indicates non involvement in coordination of the reagent to the metal ions[26].

3. The spectrum of reagent shows absorption band at 1620 cm^{-1} which is considered to be υ(CP=N) of benzimidazol ring[31].This band shifts to lower frequency (1511-1497) cm^{-1} with a little change in shape in the metal complexesc spectra. These differences suggest the linkage of metal ion with nitrogen of hetrocyclic ring[32].

4. The azo group intens bands at 1481 cm^{-1} are due to asymmetric and symmetri stretching vibrations of the -N=N- group ,respectively33. The band appears at (1452-1434) cm^{-1} respectively with some decrease in intensity of metal complexes spectra. Both bands shifted and reduced in intensity this may indicate that azo group is coordinated to the metal ions to the formation complexes[34].

5. The appearance of weak intensity bands in spectra of metal complexes in the region of (560-460) cm^{-1}assignable due to υ(M-O) and υ(M-N) vibration, also indicated the metal oxygen binding to formation of the chelat complexes[35]. IR spectra data lead to suggest that the novel azo schiff base behaves as tridentate chelating agent coordination through the nitrogen atom (N$_3$) of azo group nearest to phenol ring, phenolic oxygen and nitrogen (N$_3$) atom of benzimidazole ring to give two-five membered chelate ring. Representaive examples for these spectra are given in figures 3,4 and 5 .

Absorption spectra

The UV- Vis spectrum of an ethanolic solution of the reagent (BIADPI) (1x10^{-3} M) showed peak (λ_{max}) was observed at the (249-326 nm) due to the (π-π*) from aromatic ring through the azo group (charge transfer) and (450 nm) was referred to the n- π* transition of intermolecular charge- transfer taken place from benzene through the azo group (-N=N) these spectra are given in figure 6.

Characteristics of the Complexes

Interaction of the metal ions Cr(III) and Fe(III) with the reagent has been studied in aqueous ethanolic solution. A bathchromic shift of Cr(III) and Fe(III) complexes show the absorption maxima of 586 and 536 nm with molar absorptivities (ε) of(7.768x10^5 and 9.3575x10^5) L.mol^{-1}.cm^{-1} obtained respectively while the reagent gave the absorption maxima of 450 nm. The wave length difference

Table 1: Analytical data and some analytical parameters of the proposed method for determination of Chromium(III) and Iron(III)

Analytical Parameter	Fe (III) / ppm	Cr (III) / ppm
λ_{max} (nm)	536	586
Regression equation	Y=0.0207X+0.0106	Y=0.0198X+0.0076
Molar absorptivity(L.mol^{-1}.cm^{-1})	9.3575x10^5	7.768x10^5
Sandell sensitivity(μg.cm^{-2})	0.0483	0.0505
Correlation coefficient(r)	0.9994	0.9995
Detection limit(D.L)	0.14	0.275
Lineardynamic range	1-21	1-14
Standerd deviation	0.0015	0.00187
Relative Standard deviation %	0.467 (N=7)	0. 9 (N=7)
Percent relative error	0.9	-1.8
Percent recovery	99.1	98.2
Composition of complex [M: L]	1:2	1:2

($\Delta \lambda_{max}$) is (136-86 nm) ,a great bathochromic shift in the visible region has been detected in the complex solutions spectra with respect to that of the free reagent. The high shift in the (λ_{max}) gave a good indication for complex formation.

Method Validation

　　　Under the optimized conditions, the calibration graphs were constructed by plotting the absorbance signal against the concentrations of each analyte subjected according to the general procedure. The solutions were transferred into the optical cell of 10-mm for the measurement of each metal ion spectrophotometrically at the respective absorption maxima against a reagent blank prepared under similar conditions .The calibration data and some analytical parameters are summarized in Table(1).
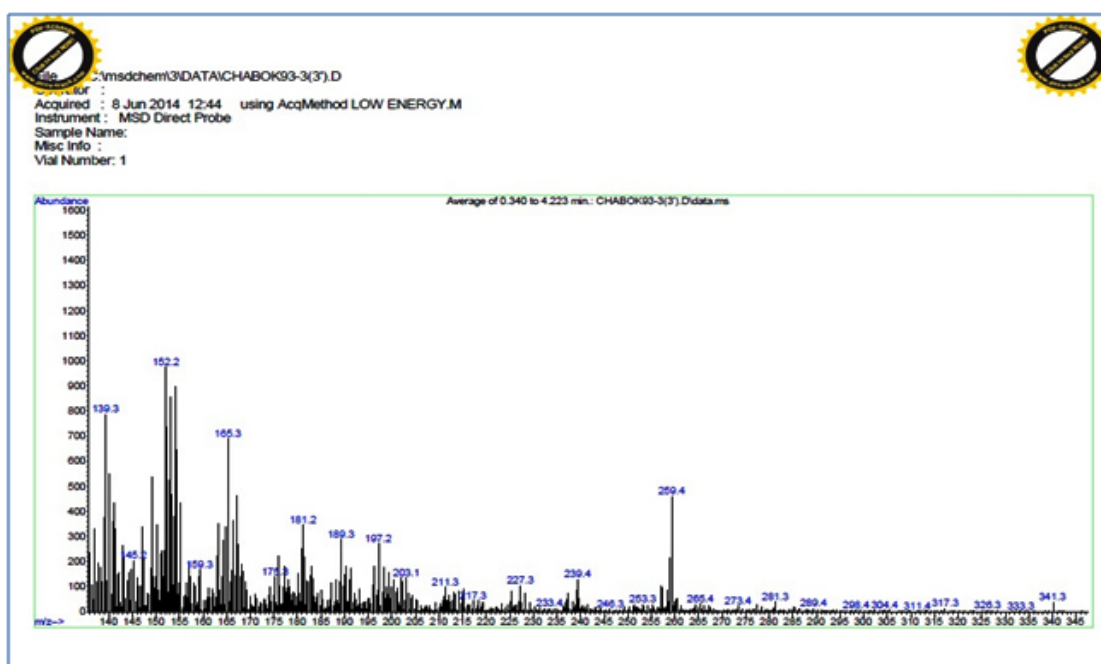
Fig. 1: Mass spectrum of azo-schiff base ligand(BIADPI)
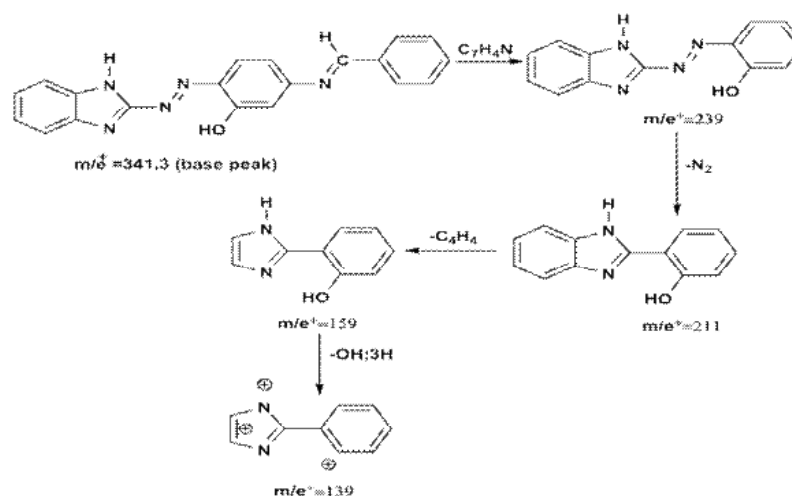
Scheme 1: Mass spectrum fragmentaino of azo-Schiff base ligand(BIADPI)

Optimization of Procedure

Effect of pH

The effect of pH on formation of the (Cr(VI) and Fe(III))- (BIADPI) complexes was determined by recording their absorbance signals at λ_{max}, over the range of 2-9, using different pH buffer solution ($NH_3+ CH_3COOH$). The results are shown in Figure 7.

As can be seen in Figure.(3), the absorbance first increased with increasing pH and
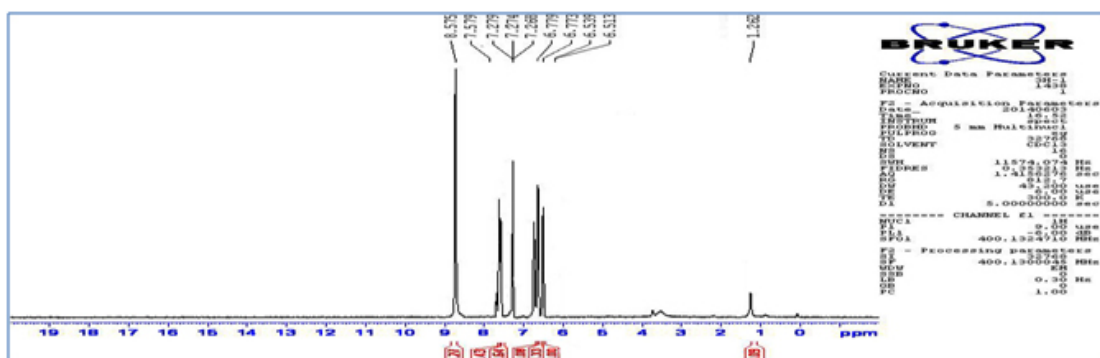
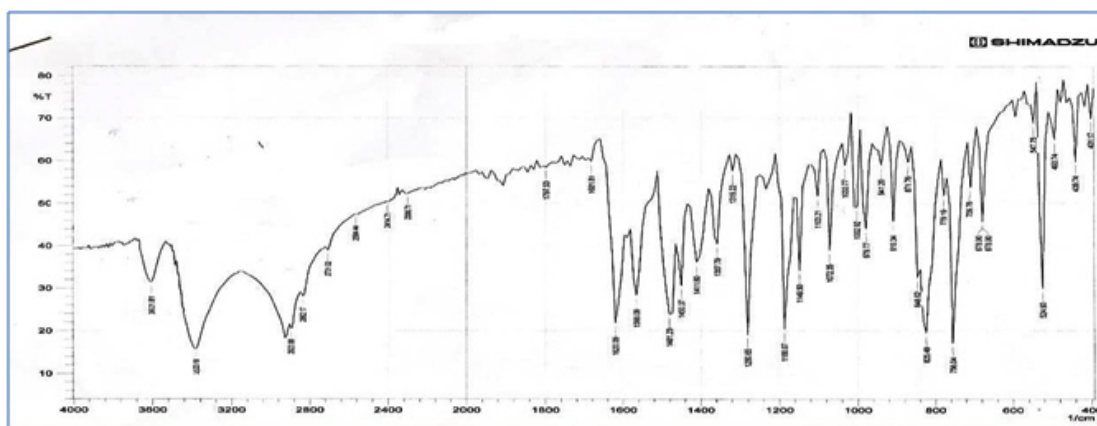Fig. 2: ¹H-NMR spectrum fragmentaino of azo-schiff base ligand (BIADPI)

Fig. 3: IR spectrum of the ligand (BIADPI)
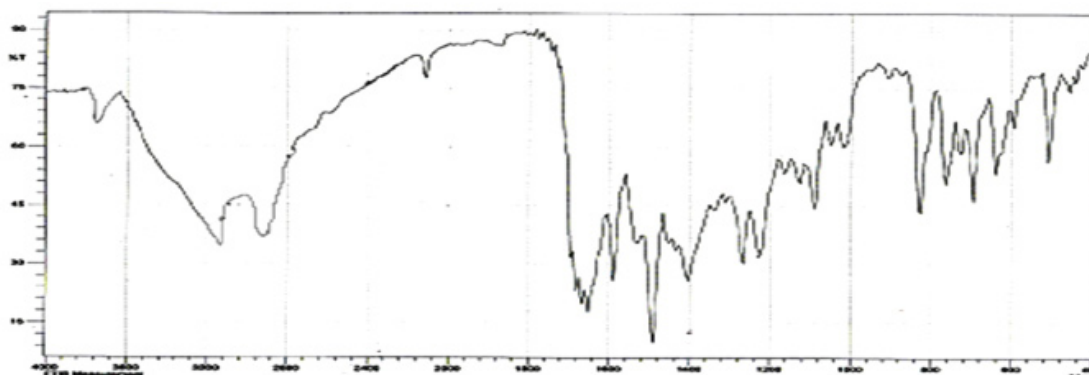
Fig. 4: FTIR Spectrum of the Fe(III) complex
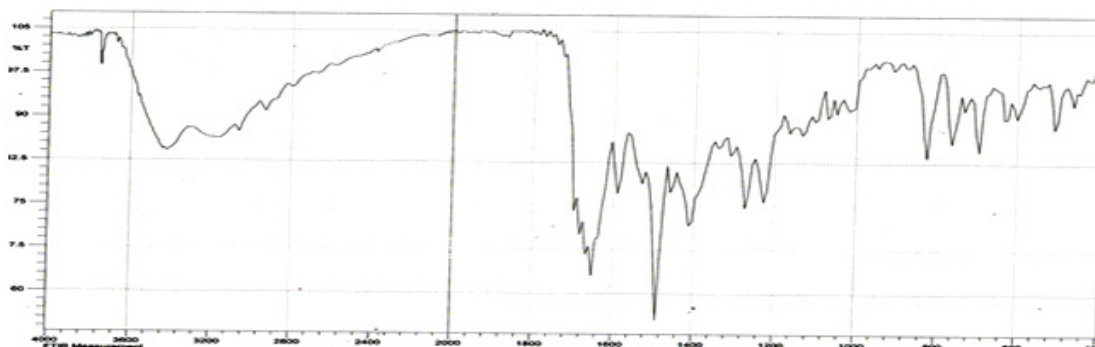
Fig. 5: FTIR Spectrum of the Cr(III) complex

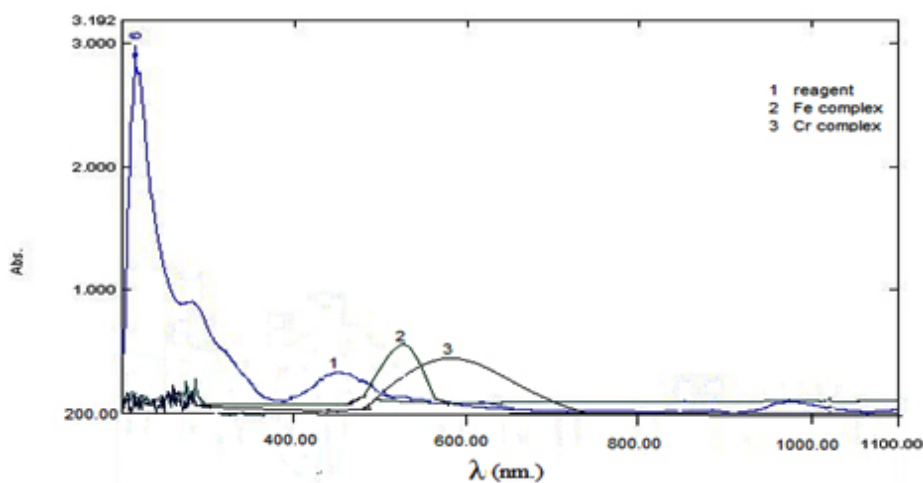

Fig. 6: Absorption spectra (1) Reagent (BIADPI) = 1.0 x 10^{-3} M (2) Fe(III)-(BIADPI) complex = 15 ìg mL^{-1} at pH= 4 . (3) Cr(III)- (BIADPI)complex = 10 ìg mL^{-1} at pH= 7.5
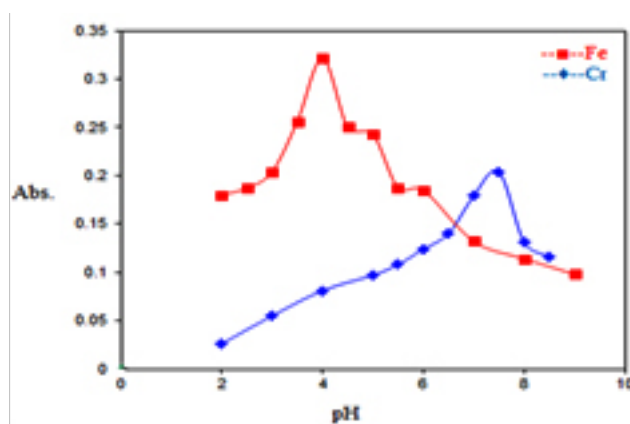

Fig. 7: Effect of pH on the formation of (BIADPI)-M^{+3} complexes with Cr(III) and Fe(III) ions

reached a maximum at pH 4 for Fe(III) and 7.5 for Cr(III) complexes, respectively. The absorbance gradually decreased may be due to formming another chromophoric formala of reagent at higher pH . Therefore, pH 4 and 7.5 were selected as the optimum pH for complete formation of Cr(III) and Fe(III) complexes, respectively.

Effect of Temperature and Time

The effects of temperature and time were examined due to their importance for the reaction completion. Consequently, a study was carried out to choose the range of temperature that enhances higher absorbance signals for Cr(III) and Fe(III) ions. The temperature was varied from 10°C to 80°C in a search of optimum value. It can be seen from Figures.
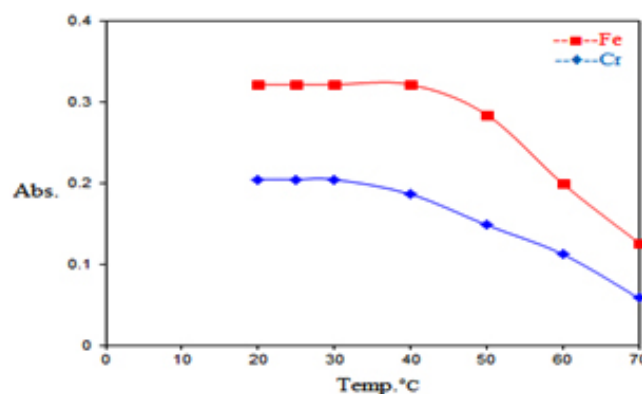

Fig. 8: Effect of the temperature on the absorbance for (BIADPI)-M^{+3} complexes with Cr(III) and Fe(III) ions
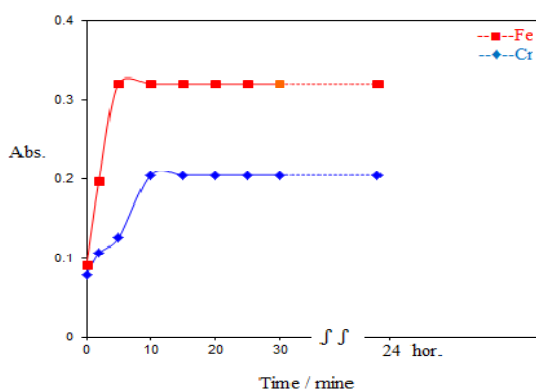

Fig. 9: Effect of time on the absorbance for (BIADPI)-M^{+3} complexes with Cr(III) and Fe(III) ions

8 that the highest absorbance signals were achieved when the temperature at approximatly (20-40)°C. It was also observed that the incubation time of 5 min for Fe(III) and 10 min are sufficient for the maximum absorbance of Cr(III) Figures. 9.

Composition of the Complex

The composition and the stability constant evaluated the mole ratio methods (figure 10,11). The method showed that the molar ratio of Fe(III) and Cr(III) are 1:2, (metal : ligand) to reagent (BIADPI). The stability constant is found to be(4.7×10^9) L.mol^{-1} and (9.4×10^8)L.mol^{-1} for Fe(III) and Cr(III) respectively.

Table 2: The percentage of iron in a manner and atomic absorption method under consideration

| Already exists in the form of the model(Ferbas syrups ample)	Calculated under way % Fe	flame atomic absorption method
30 mg	29.34	29.02

Table 3: Effect of foreign ions on the determination of Cr(III) in concentration (10) ppm and suitable masking agents

| Foreign ion 100 ppm	Masking agent (1.0)ml k[0.01]M	Error %
Cu²⁺	5-Sulfosalicylic(0.5)[0.01]	0.003
Ni²⁺	NaNO₂(0.2)[0.1]	-0.001
Zn²⁺	Sodium acetate (0.5) [0.01]	0.002
Hg²⁺	Sodium acetate (1.0)[0.01]	-0.004
Cd²⁺	5-Sulfosalicylic(0.75)[0.01]	0.004
Co²⁺	Oxalic acid (0.4) [0.2]	-0.002

Table 4: Effect of foreign ions on the determination of Fe(III) in concentration (15)ppm and suitable masking agents

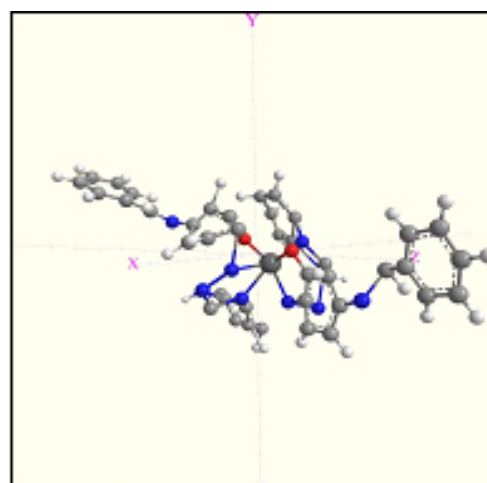| Foreign ion 100 ppm	Masking agent (1.0)ml k[0.01]M	Error %
Cu²⁺	Na₂S₂O₃ (1.0)[0.02]	0.002
Ni²⁺	Tartaric aid (2.0)[0.01]	0.004
Hg²⁺	Na₂S₂O₃(0.2)[0.1]	0.001
Zn²⁺	KCl (0.2) [0.01]	0.03
Cd²⁺	Na₂S₂O₃ (1.0)[0.01]	0.03
Co²⁺	KI(0.4)[0.1]	0.03
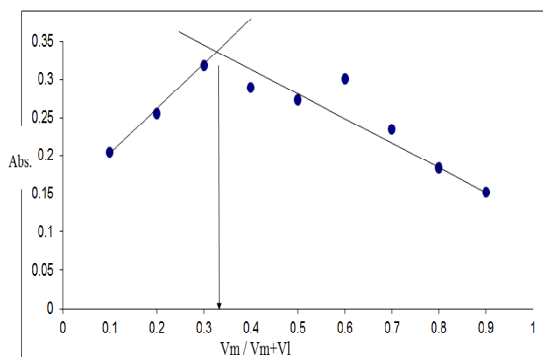
Fig. 10: Continuous variation method for Fe(III) complex with reagent (BIADPI)at pH=4
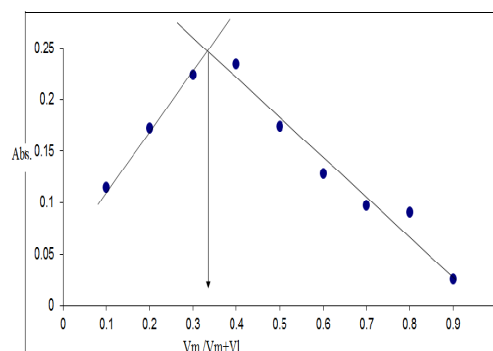
Fig. 11: Continuous variation method for Cr (III) complex with reagent at pH=7.5
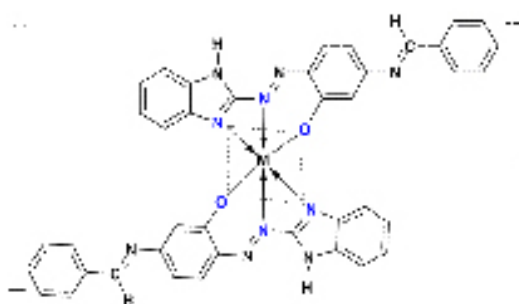
Whene M = Cr(III) and Fe(III) , n=1 ,m=1

Fig. 12 : The proposed structural formula of Cr(III) complex

According to their results and discussed through different techniques the proposed structural formula of chelate complexes prepared is suggested and shown in figure 12.

Analytical application

The proposed spectra photometric method will be of invaluable for the determination of iron (III) in Pharmaceutical preparations (Anemia drugs). The result obtained from the proposed method was compared with those given by atomic absorption spectroscopy(AAS),(standard additions method). The concentration of iron (III) analyzed by the proposed method show a good agreement of the results obtained by the two methods.

Interference Studies Chromium(III) and Iron(III) Complexes

The effect of the interference of ions which form complexes with the reagent (BIADPI) during its reaction with {(Chromium(III) 10 ppm and Iron 15 ppm} were studied. The selectivity of various

masking agents are examined for eliminating the effect of the interfering eight ions for each one. These are 5-Sulfosalicylic acid , $NaNO_2$, Sodium acetate, Oxalic acid, Tartaric acid, $Na_2S_2O_3$, KCl and KI. The results are shown in tables(3,4).

CONCLUSION

In this work 2-((E)-(1H-benzo[d]imidazol2-yl) diazenyl)-5-((E)-benzyl ideneimino) phenol (BIADPI) was used for determination of microamounts of Cr(III) and Fe(III). The molar absorpinity of this complaxes are 9357.53, 7768.7 l.mol.cm^{-1}respectirelly.Most foreign ions donot interfere with ions study when masked using different masking agents . Because the (BIADPI) can rapidly react with Cr(III) and Fe(III) at room temperature , this method can determine these ions spectrophotometrically without heating or extraction . It is sensitive , selective , rapid , easy and convenient method for determining the ions Cr(III) and Fe(III) .

REFRENCES

1. Eissa H. H. *J. Current Res. Sci .* **2013**,*12*, 96-103.
2. Jian,L.V.*JInorg.Biochem*.**2006**,*100*,888.
3. Balasurbramanian, K.p. *spectrochimica Acta part A:Mol Biomol.spect*. **2007**,6850.
4. Tumer,M.; Ekinci,D.;Tumer,F.A. *spectrochimica Acta part A:MolBiomol.spect*.**2007**,*67*,916.
5. Fakhari, A.R.; Khorrami, A.R. ; Naeimi, H. *Talanta*. **2005**, *66*, 161-162.
6. Gholivand, M.B. *Talanta* .**2007**, *73*,553.
7. Pathak, p.;Jolly, V.S; Sharma, K.p. *orient J.Chem*.**2000**, *16*,161-162.
8. Desai, S.B; Desai, P.B.; Desai, K.R. *Metrocycl. Commun*. **2000**, *7*,83-90.
9. Huong, Z. *Thermochimicacta A*.**1998**, 320-121.
10. Taguchi, T. *J.Am.Soc. Nephrol.* **2002** , *13*,2478.
11. Virginie, C. *Teterahedron lett* .**2007**, *48*,5561.
12. Asieh, Y. ; vahidAzimi. *Eur-chem. Bull*.**2013**, *2*(7), 453-455.
13. Salih, A. A. ; shaker ,sh. A. *oriental J. Chem.* **2011**, *27*(3), 835-845.
14. EL-ajaily ,M. M.; Abdulla ,F.I.; suliman, M.s. ; Akasha ,R.A. *Asian J. of Adv. Basic sci*. **2014**, *2*(2), 17-30.
15. EL-ajaily ,M. M.; Abdulla ,F.I.; Akasha ,R.A.; suliman, M.s .*J. Chem. pharm. Res*.**2013**, *5*(12), 1144-1161.
16. AL-adilee, K.J. ; Hessoon H.M. *Journal of Chemical and Pharmaceutical Research*.**2015**, *7*(8),89-103.
17. Turyan, I. ; Mandler, D. *Anal Chem*. **1997**, *69*, 894.
18. Krishna, M.V. B. ; Chandrasekaran, K. *Talanta* .**2005**,*65*, 135–143.
19. Nriagu J O and Nieboer E, Chromium in the Natural and Human Environment. John Wiley and Sons, New York, **1989**.
20. Ressalan ,S.; Chauhan, R. S.; Goswami, A. K .; Purohit, D. N. *Rev Anal Chem*. **1997**,*16(*2),69.
21. Takeda ,K.; Watanabe, S.; Naka, H; Okuzaki, J.; Fujimoto, T. *Anal Chim Acta*.**1998**, *377*,1, 47 .
22. Satyaveni S, Preconcentration and

Determination of Trace Metals by ICP-AES, Ph.D Thesis, S.V.University, India, **2007**.

23.   Ahmed, M. J.; Jahan, I. ; Banoo, S. *Anal Sci*. **2002**, *18*,805.

24.   Georgieva, N.; Dospatliev, L.; Yaneva, Z. *Trakia Journal of Sciences*. **2010**, *8*(2) ,511-516.

25.   AL-Adilee, K. J. *RJPBCS*. **2015**, *6*(5),1297-1308.

26.   Elajaily ,M.;Ramadan, A. *J. Chem. Pharm. Res*. **2013,***5*(12),1141-1151.

27.   AL-Adilee, K. J. ; Fanfon, D.Y. *J. Chem. Chem. Eng*. **2012,***6*,1016-1028.

28.   Habeeb ,H. A.; AL-Adilee, K. J. ; Jaber, S. A. *J. Chem. and Mater.Res.***2014**,*6*(8),69-80.

29.   Kumer N. ; Mishra, P. Sh. *Arch .Appl. Sci. Res*. **2001**,*5*(5),191-197.

30.   Mehdi ,R.T. ; Ali ,A.M. *IBN AL-Haitham, J. of pure and appl. Sci*. **2005**,*18*(2), 50-58.

31.   Ali, A.M. *Nat. J. of Chem*. **2006**,*23*.,335-343.

32.   Masoud, M. S. ; Mhamed, G. B. ; Abdul-Razek,Y. H. *J. Korean. Chem. Soc*. **2002**, *46*(2), 99-116.

33.   Ali,A.M.; Kadhum M.O. ; AlHamdany Z. .M.B. *J. Al-Qadisiya for pure science*. **2006**, *3*, (11),134-146.

34.   AL-Adilee, K. J.; Abass, A. K. ; Taher ,A. M. *Journal of Molecula Structure*. **2016**, *1108*, 378-39.