Spectrophotometric Determination of Silver(I) and Chromium(VI) by Using 2 – [(6 – Nitro – 2 – Benzothiazolyl) azo] – 4 , 5 –diphenyl imidazole As Analytical Reagent

Azhar A. Ghali
Department of Chemistry, College of Education, University of Al – Qadisiya , Iraq

Abstract

A simple , rapid and sensitive spectrophotometric method for the determination of silver(I) and chromium(VI) ions by using 2 – [(6 – Nitro – 2 – Benzothiazolyl) azo] – 4 , 5 – diphenyl imidazole **(**6 – NO_2 BTADI**)** as complexing reagent. The **(**6 – NO_2 BTADI**)** reagent gives intense pink colour when react with these in acetate buffer solution. The maximum absorbance observed at 566 nm and 570 nm for Ag(I) and Cr(VI) respectively. The molar absorptivity and sandell's sensitivity for silver(I) and chromium(VI) complexes are 0.4898×10^4, 0.1182×10^4 $L.mol^{-1}.cm^{-1}$ and 0.0220, 0.0440 $\mu g/cm^2$ respectively. The stability constant of 1:1 [M:L] complexes of Ag(I) and Cr(VI) are 0.3456×10^6 and 0.0796×10^6 $L.mol^{-1}$ respectively. The linear range of 0.2-12.5 µg mL^{-1}, 0.8-30 µg mL^{-1} along with limit of detection 0.11 µg mL^{-1}, 0.77 µg mL^{-1} , relative standard deviation for seven replication measurements (4 µg Ag mL^{-1} and 15 µg Cr mL^{-1}) of (1.30%) and (1.62%) ,and the recovery range of (99) and (97.54) were obtained for Ag(I) and Cr(VI) ions respectively. The developed method was applied for the determination of Ag(I) and Cr(VI) in spiked water samples.

Introduction

Heterocyclic azo compounds represent an interesting class of highly sensitive complexing reagents and play an important role in analytical chemistry as chromogenic agents. Thiazolyazo reagents are popular as metal complexing ligands in spectrophotometry, High Performance Liquid Chromatography (HPLC) and Capillary Electrophoresis (CE) due to the advantages that they can form highly sensitive metal complexes, and are very easily synthesize and purified(1,2) .The use of thiazolylazo derivatives in spectrophotometry is based on the coloured compounds resulting from their reaction with most of the transition metals. They can form different types of coordination compounds particularly with transition metals due to the several electron rich donor centers with unusual structural and chemical properties. Because of the importance of thiazolylazo derivatives and their ability to act as polyfunctional ligand many studies on their metal complexes have been carried out (3,4).

Silver and chromium are highly useful elements and used in various industrial processes and products(5,6), have resulted in an increased these elements content of environmental samples. However, silver complexes are dominant in effluent and other sources of contamination . The toxicity of silver is characterized by a severe pulmonary edema, hemorrhage, and necrosis of bone marrow, liver, and kidney . Long-term human exposure to silver salts or colloidal silver may cause argria . Repeated exposure of animals to silver may produce anemia, cardiac enlargement, growth retardation, and degenerative changes in the liver . Extremely low concentrations of Ag(I) are present in various complex samples like drinking water (51 g cm^{-3}), soil, rock, coal fly ash, cigarette smoke, alloys, plants, sea water, etc (7-10).

Chromium occurs in several chemical species and it is not biodegradable in the environment . Its species exist mainly in two different oxidation states in water, Cr(III) and Cr(VI), which have different effects on environmental poisoning, biological effects and human health. Chromium(III) is considered an essential element controlling glucose lipid and protein metabolism in mammals, while chromium(VI) is definitely highly toxic for biological systems, with mutagenic and potential carcinogenic properties (11). The toxicity of Cr(VI) compounds derives from its ability to diffuse through cell membrane and oxidise biological molecules (12).

So, they are receiving increasing attention in pollution and nutritional studies. Various analytical techniques of great importance in environmental trace determination of metals and non-metals, such as on-line Atomic Absorption Spectrometry (AAS) , Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), ICP-Mass Spectrometry (ICP-MS) and Ion Chromatography (IC), etc. applied to determine (13-17). Some of these are very sensitive, but require costly instrumentation. But, spectrophotometric methods for determination of metals have a lot of merits such as simplicity, economical, little contamination and convenient to use. For this reason, a wide variety of spectrophotometric methods for the determination of silver and chromium have been reported(18-21).

This paper reports, 2–(6 –nitro – 2 – benzothiazolyl) azo] – 4 , 5 – diphenyl imidazole , which was prepared by Al – adilee (22) ,as an analytical reagent for the micro determination of Ag(I) and Cr(VI). The method has been found to be simple, rapid and sensitive for the determination these metal ions.

EXPERIMENTAL

Apparatus

Absorption spectra in absolute ethanol were recorded using UV-Visible Spectrophotometer T 80 , England using 1cm quartz cells. Functional groups of reagent and its complexes were identificated with a FT-IR spectrometer shimadzu 8400, in range(4000-400) cm^{-1} using KBr disc. pH measurements were carried out using a Philips PW 9421 pH meter (pH± 0.001).

Reagents and Solutions

All the chemicals used were of analytical reagent grade, and were used without further purification. Ethanol were purchased from (GCC, England) . A 1.0×10^{-4} mol L^{-1} (6-NO_2BTADI) was prepared by dissolving (0.0106 g) of 2–(6 –nitro – 2 – benzothiazolyl) azo] – 4 , 5 – diphenyl imidazole in 250 mL absolute ethanol. Stock solutions of Ag(I) and Cr (VI) ions (1000 mg L^{-1}) were prepared by dissolving (0.1574 g) of $AgNO_3$(BDH) and (0.3734 g) of K_2CrO_4 (Merck) in 100 mL deionized water, respectively. Working standard solutions of each metal ion were freshly prepared by appropriate dilutions of the stock standard solutions. The pH of the medium (3-9) were adjusted with ammonium acetate (0.01 mol L^{-1}) –ammonia – glacial acetic acid buffer solution .

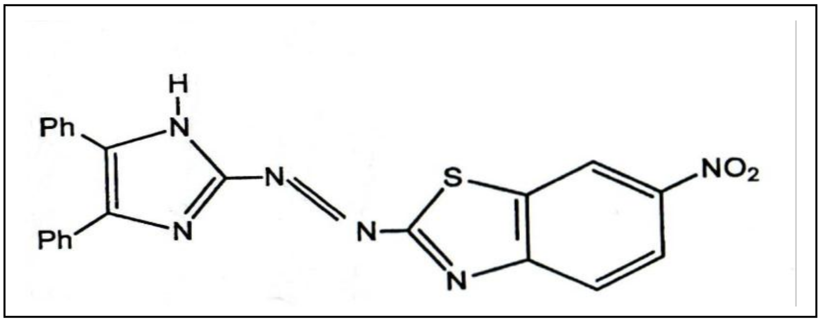


Fig.(1): Structure of the reagent (6 – NO_2BTADI)

General procedure

In to a 10 mL calibrated flask , transfer 1 mL of sample solution containing less than 100 µg.ml^{-1} of Ag(I) and adjust the pH to 6.5 with ammonium acetate buffer, add 3 ml 1.0×10^{-4}M ethanolic (6-NO_2BTADI) solution and diluted to the mark with deionized water. The absorbance of the resultant solution was measured after 10 min at 566 nm at 25 C° against the corresponding reagent blank prepared under identical conditions but without silver. The same procedure for chromium (VI) at pH 5.5 and the absorbance of the result solution after 15 min at 570 nm.

Results and Discussion:

Infrared spectra

The IR spectrum of the (6-NO_2BTADI) shows a strong band at (1580-1595) cm^{-1} due to υ(C = N) of imidazole ring. This bands shifts to lower wave number 1555– 1535 cm^{-1} in the metal complexes spectra, these shifts suggest the linkage of metal ion with nitrogen of imidazol ring(23) .

Two absorption bands are observed at 1500 cm^{-1} and 1430 cm^{-1} in the reagent spectrum which are due to the azo υ(N = N) (24) . The positions of these bands in the spectra of complexes are shifted to a lower frequencies (1435 – 1410) cm^{-1} with decreased in intensity . Both bands are shifted and reduced intensities this may indicate that azo group is coordinated to the metal ions . When on the other hand, the spectra bands of at 1095 and 1010 cm^{-1} in reagent was characterized for the υ(C-S) don't suffer from any shift in metal complexes. Thus, it is suggested that the S atom of the hetero cyclic thiazole ring is not coordinated to the metal ion (25).

The presence of new medium intensity bands in the 420–490 and 530–560 cm^{-1} regions, assignable to υ (M–N) and υ (M–Cl) in the spectra of all the complexes(26).

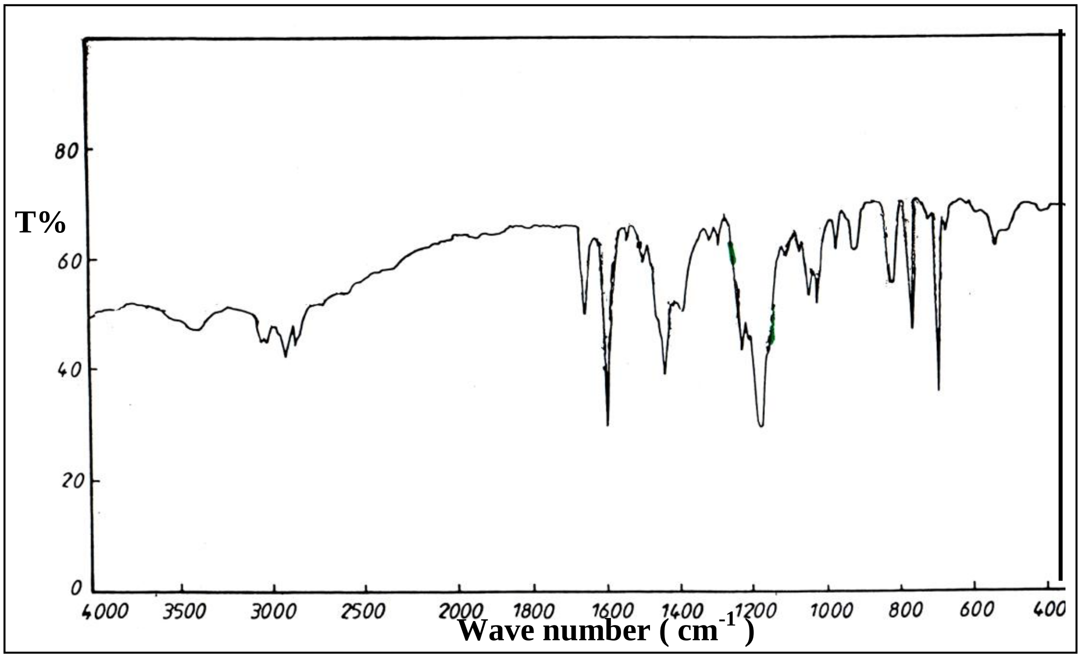


Fig.(2) : IR spectrum of the ligand (6 – NO_2 BTADI)

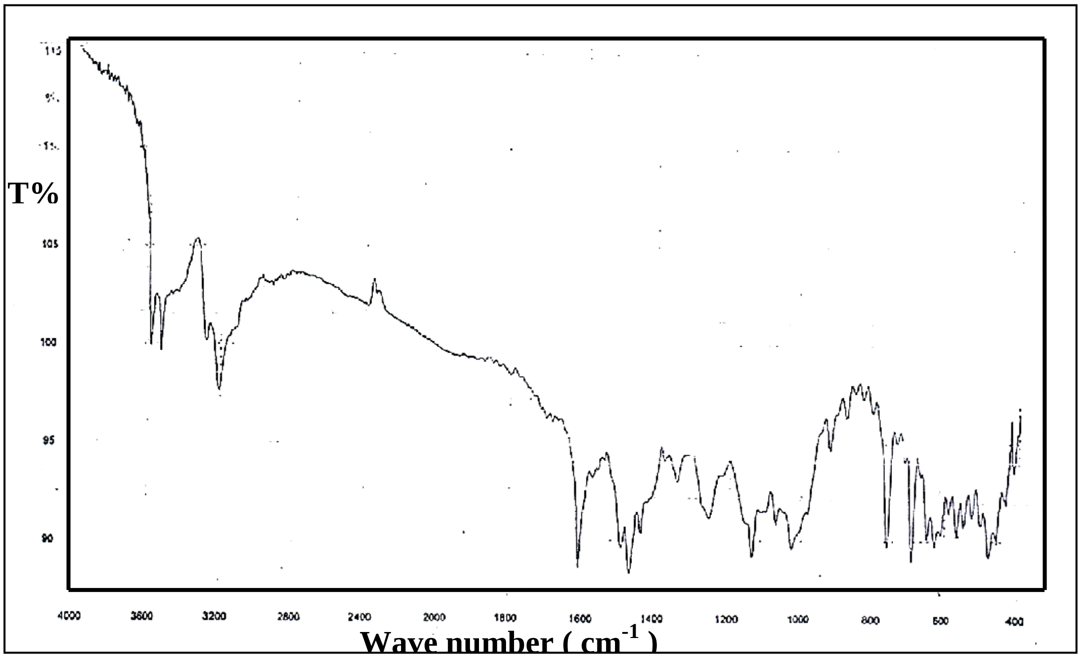


Fig.(3) : IR spectrum of (6 – NO_2 BTADI – Ag(I))

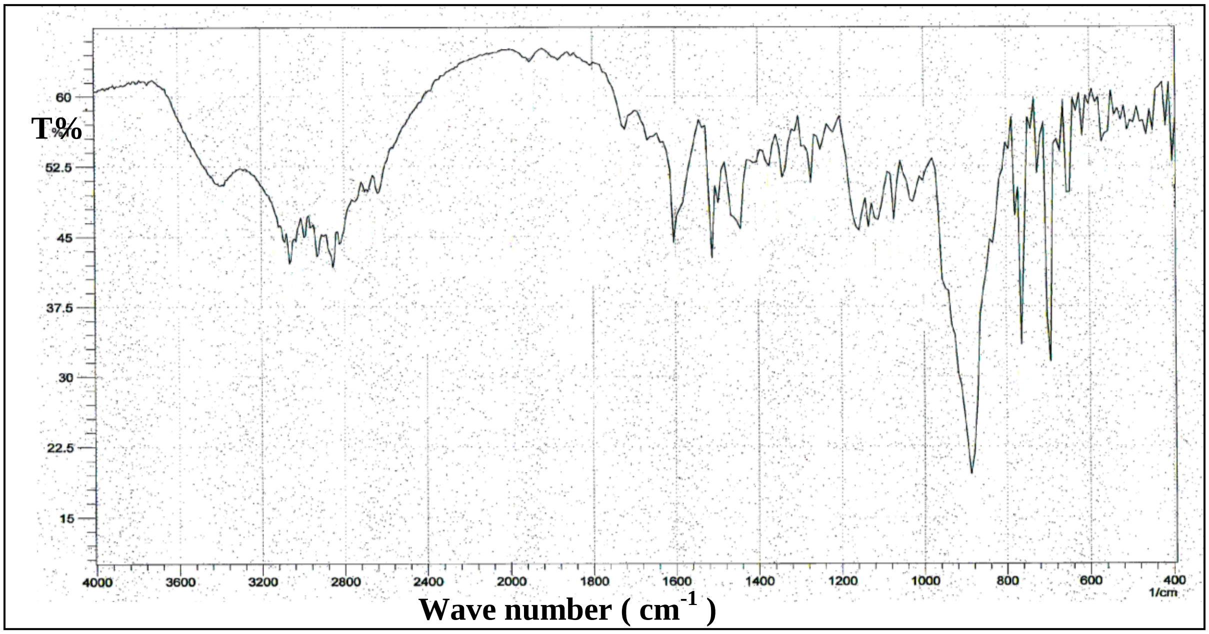


Fig.(4) : IR spectrum of (6 – NO_2 BTADI – Cr(VI))

Absorption Spectra and Characteristics of the Complexes

The UV- Vis spectrum of an ethanolic solution of the reagent (6 – NO_2BTADI) ($1.25x10^{-4}$ M) shown three peaks, the first and second peaks were observed at (224 nm) and (263 nm) were assigned to the moderate energy π- π^* transition of the aromatic rings. The third peak (λ max) was observed at the (471 nm) due to the (π-π^*) from aromatic ring through the azo group (charge transfer) was referred to the n- π^* transition of intermolecular charge- transfer taken place from benzene through the azo group(-N=N) (27).

Interaction of the metal ions Ag(I) and Cr(VI) with the reagent has been studied in aqueous ethanolic solution . A bathchromic shift of Ag(I) and Cr(VI) complexes show the absorption maxima of 566 and 570 nm with molar absorptivities (ε) of 4898.3 L mol^{-1} cm^{-1} and 1182.2 L mol^{-1} cm^{-1} obtained respectively while the reagent gave the absorption maxima of 471 nm as depicted in Fig. 5. The wave length different($\Delta \lambda_{max}$) is (99-85 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.

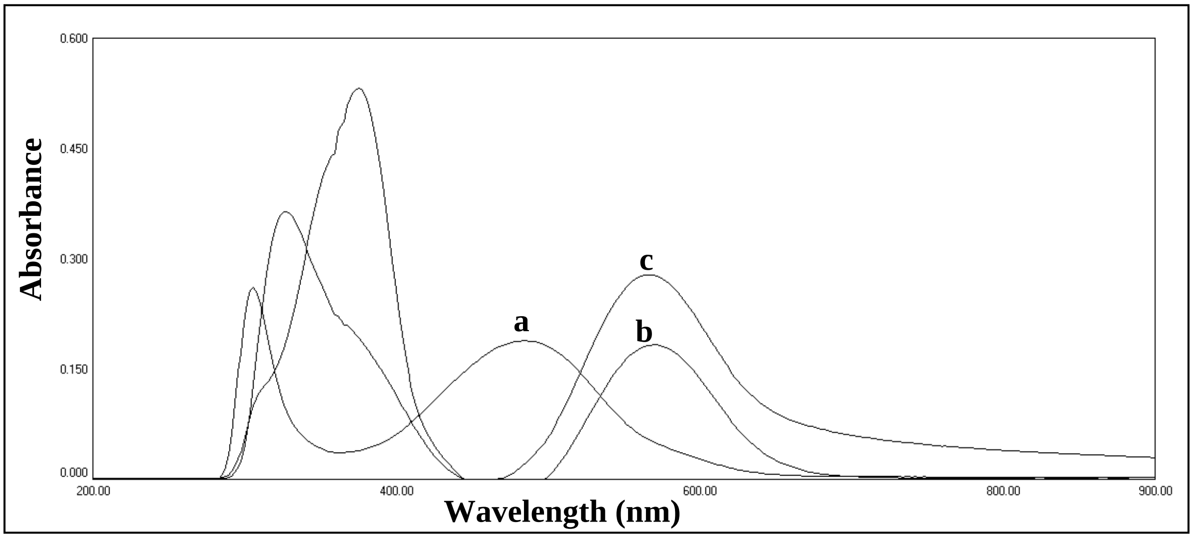


Fig.(5): Absorption spectra (a) Reagent (6 – NO_2BTADI) = 1.0 x 10^{-4} M (b) Cr(VI)-(6 – NO_2BTADI) complex , Cr(VI) = 27 µg mL^{-1} , 3 ml of (6 – NO_2BTADI)= 1.0 x 10^{-4} M , pH= 5.5 . (c) Ag(I))- (6 –NO_2BTADI)complex , Ag(I) = 10 µg mL^{-1} , 1.5 ml of (6 – NO_2BTADI) = 1.25 x 10^{-4} M , pH= 6.5

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 are summarized in Table (1).

Table (1): Method validation of the spectrophotometric determination of Ag(I) and Cr(VI)

Parameter	Ag(I)	Cr(VI)
λ_{max} (nm)	566	570
Regression equation	A=0.0288C+0.0009	A= 0.0061C + 0.0086
Correlation coefficient(r)	0.9990	0.9995
C.L. for the slope (b± tsb) at 95%	0.0288±0.00021	0.0061± 0.00087
C.L. for the intercept (a± tsb) at 95%	0.0009±0.0028	0.0086± 0.0051
Concentration range (µg mL^{-1})	٠.2-12.5	0.8-30
Limit of Detection (µg mL^{-1})	0.11	0.77
Limit of Quantitation (µg mL^{-1})	0.37	2.59
Sandell's sensitivity (µg.cm^{-2})	0.0220	0.0227
Molar absorptivity (L.mol^{-1}.cm^{-1})	4898.3	1182.2
Composition of complex (M: L)	1:1	1:1

RSD% (n=7) at 4 µg Ag (I) mL^{-1} and 15 µg Cr (VI) mL^{-1}	1.3	1.62
Recovery%	99	97.54

Optimization of Procedure

Effect of pH

The effect of pH on formation of the (Ag(I) ,Cr(VI))- (6- NO_2BTADI) complexes was determined by recording their absorbance signals at λ_{max} ,over the range of 3-9 ,using different pH acetate buffer solutions. The results are shown in Fig.6.

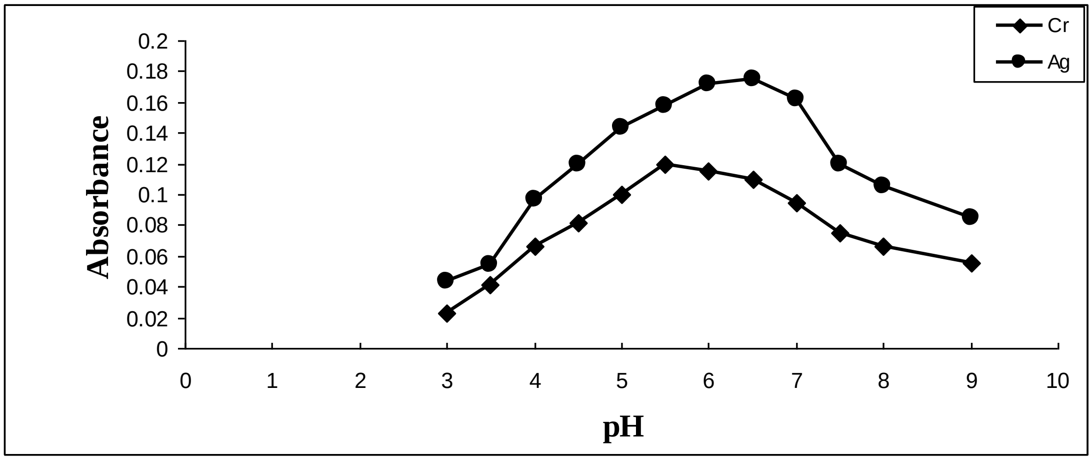


Fig.(6): Effect of pH on the formation of(6- NO_2BTADI)- M complexes formed with Ag (I) and Cr (VI)). Conditions : Ag(I) = 6 µg mL^{-1} , 1.5 ml of (6-NO_2BTADI) =$1.0x10^{-4}$ M .and Cr(VI) = 18 µg mL^{-1} , 3 ml of (6-NO_2BTADI)=$1.0x10^{-4}$ M

As can be seen in Fig.(6), the absorbance first increased with increasing pH and reached a maximum at pH 5.5 and 6.5 for Ag(I) and Cr(VI) complexes ,respectively. The absorbance gradually decreased because of partial dissociation of the complexes at higher pH. Therefore, pH 5.5 and 6.5 were selected as the optimum pH's for complete formation of for Ag(I) and Cr(VI) complexes respectively .

Effect of Temperature and Time

The effects of the temperature and the 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 Ag(I) and Cr(VI) ions. The temperature was varied from 10 ^{O}C to 80 ^{O}C in a search of optimum value. It can be seen from Fig. 7 that the highest absorbance signals were achieved when the temperature at 40 ^{O}C.

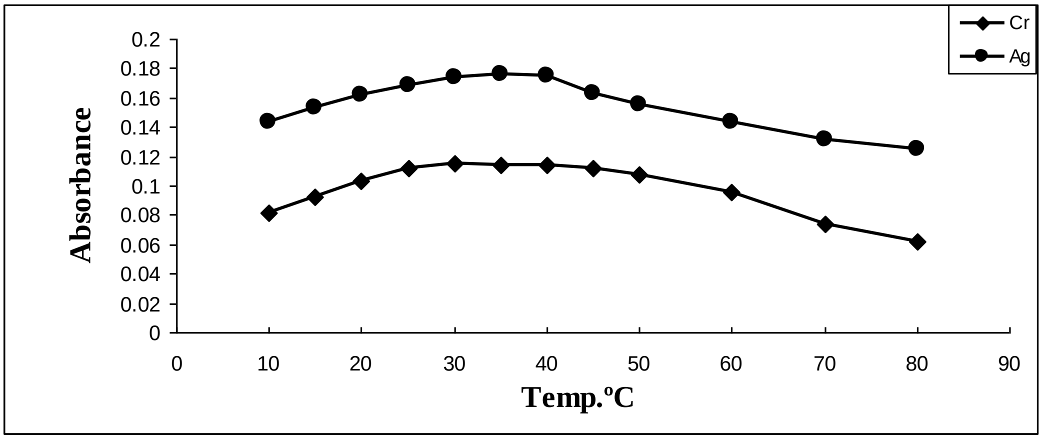


Fig.(7): Effect of the temperature on the absorbance for (6- NO_2BTADI)- M complexes formed with Ag (I) and Cr (VI)). Conditions : Ag(I) = 6 µg mL^{-1} , 1.5 ml of (6- NO_2BTADI) =$1.25x10^{-4}$ M and Cr(VI) = 18 µg mL^{-1} , 3 ml of (6- NO_2BTADI) =$1.25x10^{-4}$ M

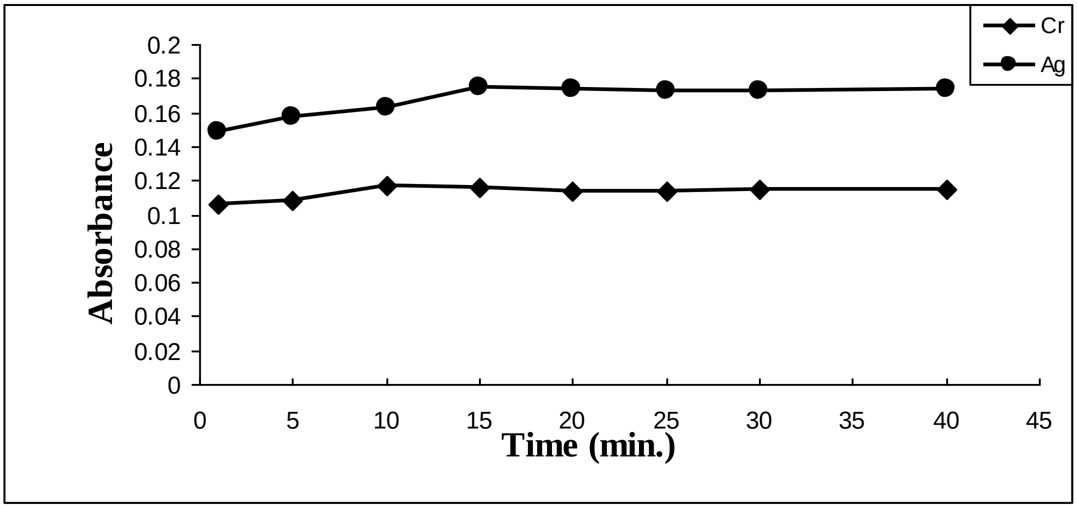
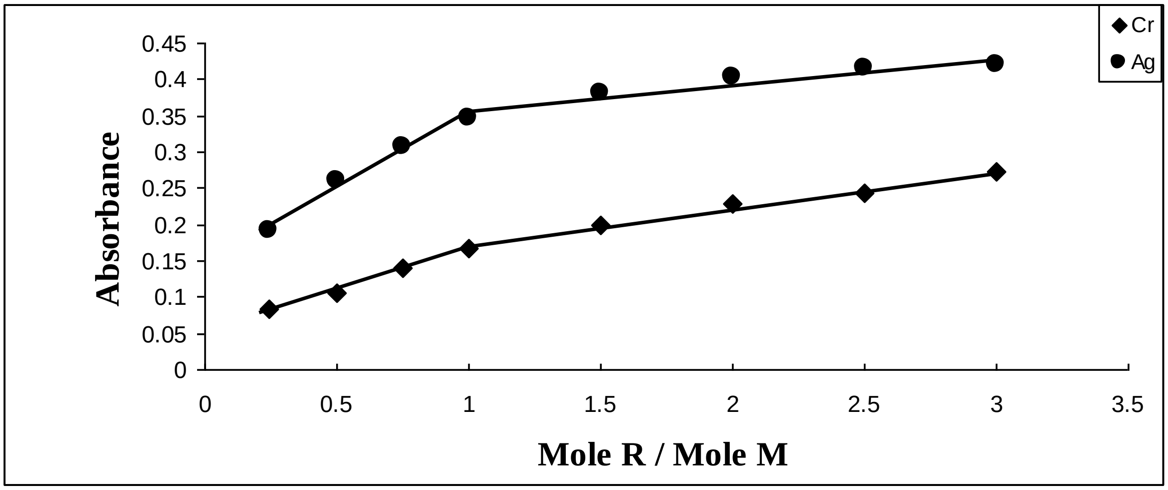


Fig.(8): Effect of time on the absorbance for (6- NO_2BTADI)- M complexes formed with Ag (I) and Cr (VI)). Conditions : Ag(I) = 6 µg mL^{-1} , 1.5 ml of (6- NO_2BTADI) =$1.25x10^{-4}$ M and Cr(VI) = 18 µg mL^{-1} , 3 ml of (6- NO_2BTADI) =$1.25x10^{-4}$ M

It was also observed that the incubation time of 15 min and 10 min are sufficient for the maximum absorbance of Ag(I) and Cr(VI) ,respectively.

Composition and stability of complexes

The composition of the chelat complexes were determined by mole ratio and continuous variation method Fig. 9 and Fig.10. Both methods showed that the molar ratio of Ag(I) and Cr(VI) ions to reagent (6- NO_2BTADI) are 1:1 and the suggested related chemical structures are shown in Figures 11,12 . The stability constant are found to be 0.3456 x10^6L.mol^{-1} and 0.0796 x10^6L.mol^{-1} for Ag(I) and Cr(VI) respectively .



Fig(9): Mole ration method for Ag(I)-complex at pH=6.5 and Cr(VI)-complex at pH=5.5

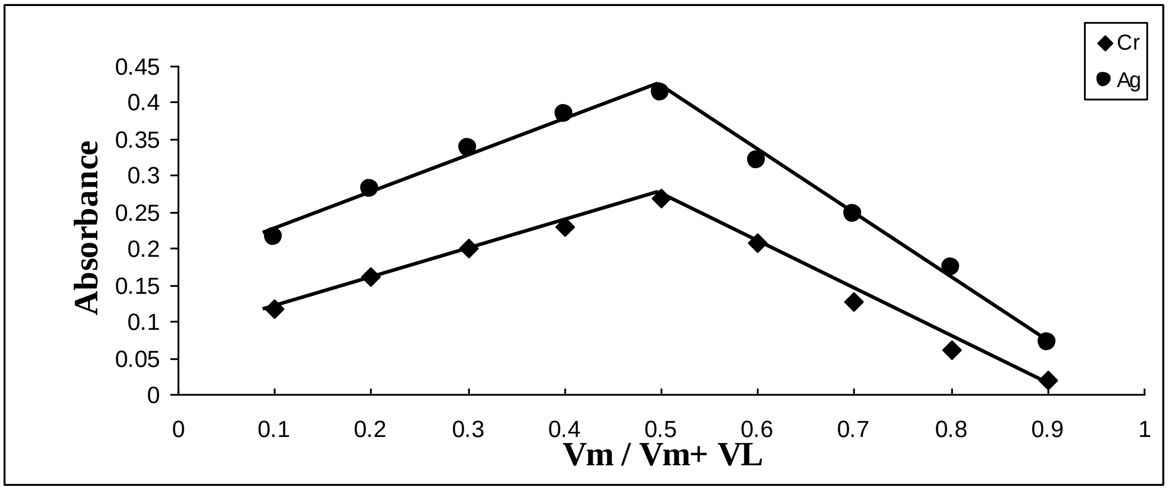


Fig.(10): Continuous variation method for Ag(I)-complex at pH=6.5 and Cr(VI)-complex at pH=5.5.

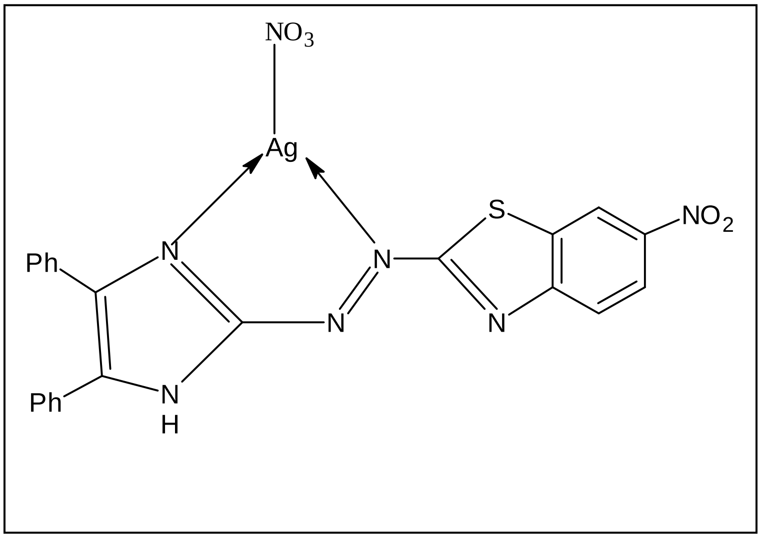


Fig.(11) : The proposed structural formula of Ag(I) complex

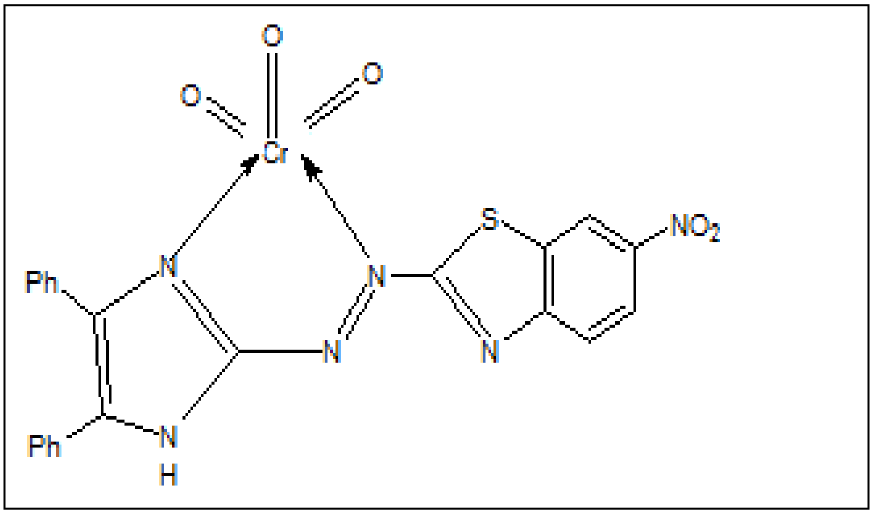


Fig.(12) : The proposed structural formula of Cr(VI) complex .

Precision and Accuracy

Seven replicate analyses of 4 μg mL^{-1} silver and 15 μg mL^{-1} chromium solutions following the general procedure gave repeatability in term of relative standard deviation (RSD) of 1.30% and 1.62% respectively (Table 1).

In order to assess the validity of the proposed method, the method was applied for the quantitative determination of silver and chromium in water samples were spiked by adding known amount of silver (I) and chromium (VI) determined by the proposed method and then the same steps were followed with the general procedure. The results were tabulated in Table 3.The results are found satisfactory.

Table (2): Accuracy of the proposed method

Amount metal ion taken (μg mL^{-1})		Amount metal ion found(μg mL^{-1})	Rec (%)	E_{rel} (%)
Ag	1	1.03	97.0	-3.0
	4	3.89	97.25	2.75
	8	8.09	98.88	-1.12
Cr	5	4.89	97.8	2.2
	10	10.11	98.9	-1.1
	15	15.19	98.74	-1.26

Conclusions

In this paper, (6-NO_3BTADI) reacts with Ag(I) and Cr(VI) and forms water insoluble complexes. Spectrophotometric method has been found to be quite simple, rapid, cheap, less time consuming and gave reproducible results, than most of the other methods, applicable for the determination of these metals in the presence of each other, which makes it an alternative to the existing methods for the determination of these metal ions.

References

1- F. Karipcin, E. Kabalcilar, S. Ilican, Y. Caglar, M. Caglar,(2009), Synthesized some 4-(2-thiazolylazo)resorcinol complexes: Characterization, thermal and optical properties, Spectrochimica Acta Part A 73 174–180.

2- M.R. Yazdanbakhsh, A. Mohammadi, M. Abbasnia ,(2010) , Some heterocyclic azo dyes derived from thiazolyl derivatives; synthesis; substituent effects and solvatochromic studies , Spectrochimica Acta Part A ,77, 1084–1087

3- S.S. Chavan , V.A. Sawant , (2010) , Synthesis, structural characterization, thermal and electrochemical studies of Mn(II), Co(II), Ni(II) and Cu(II) complexes containing thiazolylazo ligands ,Journal of Molecular Structure ,965, 1–6.

4- L. S. Carvalho, A. C. S. Costa, S. L. C. Ferreira and L. S. G. Teixeira, (2004), Spectrophotometric Determination of Chromium in Steel with 4-(2- Thiazolylazo)-Resorcinol (TAR) Using Microwave Radiation, J. Braz. Chem. Soc., Vol. 15, No. 1, 153-157.

5- L.L. Wang, J.Q. Wang, Z.X. Zhengb and P. Xiao, (2010), Cloud point extraction combined with high-performance liquid chromatography for speciation of chromium(III) and chromium(VI) in environmental sediment samples, Journal of Hazardous Materials 177 ,114–118.

6- X.H. Yang, J. Ling , J. Peng, Q.E. Cao , L. Wang, Z.T. Ding and J. Xiong, (2013) ,Catalytic formation of silver nanoparticles by bovine serum albumin protected-silver nanoclusters and its application for colorimetric detection of ascorbic acid, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 106 ,224–230.

7- R. M. Naik , R. K. Tiwari ,P. K. Singh ,S. B. S. Yadav and A. Asthana , (2008) , Kinetic determination of silver at trace level based on its catalytic effect on a ligand substitution reaction, Transition Met Chem ,33:615–623

8- X. Wen, L. Kong, M. Chen, Q. Deng, X. Zhao and J. Guo , (2012) , A new coupling of spectrophotometric determination with ultrasound-assisted emulsification dispersive liquid–liquid microextraction of trace silver, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 97 ,782–787.

9- N. Dalali, N. Javadi and Y. K. Agrawal, (2008) ,On-line Incorporation of Cloud Point Extraction in Flame Atomic Absorption Spectrometric Determination of Silver, Turk J Chem ,32, 561 – 570.

10- J. L. Manzoori and G. K. Nezhad,(2003),Selective cloud point extraction and preconcentration of trace amounts of silver as a dithizone complex prior to flame atomic absorption spectrometric determination, Analytica Chimica Acta 484 ,155–161 .

11- S. Chen, X. Zhang, L. Yu, L. Wang and H. Li, (2012) ,Simultaneous determination of Cr(III) and Cr(VI) in tannery wastewater using low pressure ion chromatography combined with flow injection spectrophotometry, Spectrochimica Acta Part A 88 ,49– 55.

12-R. E. Shaffer, J. O.Cross, , S. L. R. Pehrsson, and W. T Elam, (2001), Speciation of chromium in simulated soil samples using X-ray absorption spectroscopy and multivariate calibration. Analytica Chimica Acta, 442, 295.

13- M.V. B. Krishna and K. Chandrasekaran, (2005) ,Speciation of Cr(III) and Cr(VI) in waters using immobilized moss and determination by ICP-MS and FAAS, Talanta 65, 135–143.

14- L. Hua, Y.C. Chan, Y.P. Wu and B.Y.Wu, (2009),The determination of hexavalent chromium (Cr6+) in electronic and electrical components and products to comply with RoHS regulations, Journal of Hazardous Materials 163 ,1360–1368.

15- A. W. Al-Shawi, and R. Dahl ,(1999), Determination of total chromium in phosphate rocks by ion chromatography. Journal of Chromatography A, 850, 137–141.

16- R. Michalski, (2004), Ion chromatography method for the determination of trace levels of chromium (VI) in Water. Polish Journal of Environmental Studies, 13,73–77.

17- L.Yarong, N. K Pradhan, R. Foley, K. C. Low Gary,(2002), Selective determination of airborne hexavalent chromium using inductively coupled plasma mass spectrometry. Talanta, 57, 1143–1153.

18- G. Yang , Q. Hu , J. Yang and J, Yin, (2002), Spectrophotometric determination of silver, with 2-(2-quinolylazo)-5-diethylaminophenol as chromogenic reagent, Anal Bioanal Chem ,374 :1325–1329

19- S. L. Narayana , S. A. N. Reddy , Y. Subbarao , H. Inseong , A. V. Reddy ,(2010),A simple and highly sensitive spectrophotometric determination of Cr(VI) in food samples by using 3,4-dihydroxybenzaldehydeisonicotinoylhydrazone (3,4-DHBINH), Food Chemistry 121 ,1269–1273

20- L. Narayana and SUVARAPU ,(2009),Simultaneous Spectrophotometric Determination of Chromium(VI) and Vanadium(V) by using 3,4-Dihydroxybenzaldehyde isonicotinoyl hydrazone (3,4-DHBINH), E-Journal of Chemistry, 6(S1), S459-S465

21- A. M. Jamaluddin and H. M. Reazul , (2011), A Rapid Spectrophotometric Method for the Determination of Chromium in Environmental Samples using Bis (salicylaldehyde) orthophenylenediamine, J. Chem. Sci Vol. 1 (1) April Res.

22- Khalid J. Al – adilee , (2007), Synthesis and Spectrophotometric study of Co,Ni and Cu Ions complexes with some new azo dyes containing 4,5-diphynel imidazole, J. Nat. Chem. ,28 :585 .

23- R.M. Silverstein , (1996), " Spectrometric Intentification of organic compound "6th , Ed, Jhon Willey and Sons.

24- M .Asniza, I. A.Am Abdeul Khalil, (2011), Synthesis and characterization of a new Hetrocyclic azo pigment, J.Sains Malaysiana, Chem, 40,7,7498- 7508.

25- L. Mangsup , S. Siripasisarnpipat and N. Chaichit , Crystal structure of bis(2-(2-thiazolylazo)-methylphenol) cobalt(III) chlorid ,Anal.Sci (2003),19,1345.

26- N. Nakamoto,(1997),Infrared Spectra and Raman Spectra of Inorganic and Coordination Compounds, 5th ed., Wiley, New York.

27- M.R. Mahmoud, A.M. Hamman and S.A. Ibrahim ,(1994), Chromium Complexes of O,O-Dihydroxyazo Dye, Z. Phy. Chem 265,3:203.

التقدير الطيفي Ag(I) وCr(VI) باستخدام الكاشف ٢-(٦- نايترو ٢- بنزوثيازوليل ازو) -٤، ٥ ثنائي فنيل اميدازول ككاشف تحليلي

أزهار عبيس غالي

جامعة القادسية –كلية التربية –قسم الكيمياء

طريقة طيفية حسّاسة وسريعة وبسيطة لتقدير ايونات الفضة (I) و الكروم (VI) باستعمال(2 –[6-نايترو 2 – بنزوثيازول ازو)] – 4 ، 5- ثنائي فينل اميدازول (6-NO_2BTADI) ككاشف تعقيد. يَعطي الكاشفُ لونَ ورديَ شديد عند تفاعله مع تلك الايونات في محلول ألخليك المنضم . الامتصاص الأعظم عند ٥٦٦ نانوميتر و٥٧٠ نانوميتر على التوالي. معامل الامتصاص المولاري وحساسية ساندل لمعقدات الفضة (I) و الكروم (VI) ٠.٤٨٩٨×١٠^{٤} لتر.مول.سم$^{-١}$ ٠.١١٨٢ ×١٠^{٤} لتر.مول.سم$^{-١}$ على التوالي. ثابت الاستقرارية ١:١[فلز:عضيدة] لمعقدات الفضة (I) و الكروم (VI) 0.3456 ×10^6 و 0.0796 × 10^6 لتر.مول$^{-١}$ على التوالي. مدى الخطية (٠.٢-12.5)جزء بالمليون و (0.8-30) مع حد الكشف ٠.١١ مايكرو غرام مللتر$^{-١}$ و ٠.٧٧ مايكرو غرام مللتر$^{-١}$ والانحراف القياسي النسبي لسبع قياسات متكررة (٤ مايكروغرام مللتر$^{-١}$ فضة و١٥ مايكروغرام مللتر$^{-١}$ كروم) 1.30%و 1.62% ووجد مدى الاسترجاع ٩٩ و ٩٧.5لايوني الفضة (I) و الكروم (VI)على التوالي. طبقت الطريقة لتقدير الفضة (I) و الكروم (VI) في نماذج ماء .