

Spectrophotometric Determination of Cr(VI) Ions Using New Benzothiazolyl azo Compound 2-[(6-Methyl-2-Benzothiazolyl) azo]-4-Chlorophenol

Aqeel Mahdi . J, Kasim . H .Kadhim , and Abbas. N .Al-Sharefy
*Dept. of Chemistry , College of Science , University of Babylon
 Babylon-Iraq*

(NJC)

(Received on 11 /4/2006) (Accepted for publication on 15/ 11 /2006)

Abstract

The new reagent 2-[(6 – Methyl – 2 – Benzothiazolyl) azo] – 4 - Chlorophenol (6-MeBTACIP) organic was synthesized, and used in the spectrophotometric determination of Cr (VI) ion . Sensitive, selective and rapid method was proposed. The reaction between the reagent and Cr(VI) ion occurs at pH = 7.4 , and the absorbance of the resultant solution remains stable for over 24 h.

The method allows for the determination of Cr(VI) over the range 0.2-9.0 $\mu\text{g.ml}^{-1}$, with molar absorptivity of $0.772 \times 10^4 \text{ L.mol}^{-1}.\text{cm}^{-1}$ in chloroform solvent, and a detection limit of 0.16 $\mu\text{g.ml}^{-1}$. Recovery and relative error values of precision and accuracy of method were found to be R.S.D%=0.449 , Re%=98.67 ,and Erel%=1.33. Study of complex nature showed that metal: reagent ratio was 1:2 at pH=7.4 ,and the stability constant of $(7.67 \times 10^9) \text{ l}^2 . \text{mol}^{-2}$, the interferences of ions (Cu^{2+} , Pb^{2+} , Hg^{2+} , Zn^{2+} , Cd^{2+} , Ni^{2+} , MoO_4^{2-} , WO_4^{2-}) and masking agents effect on absorbance were also studied.

The above mentioned procedure was applied in the determination of total chromium in residual water of alnajak dibajat factory as chromium(VI). Results came in agreement with those obtained by flame atomic absorption method for determination of Cr (VI).

-4-[(6 - Methyl - 2 - Benzothiazolyl) azo] - 2 - Chlorophenol
 (VI) (VI)
 . 24
 1- . (9.0-0.2) (VI)
 . 1- . (0.16) 1- . 1- . (10⁴x0.772)
 (98.67 =%Re) (0.449=%R.S.D)
 .(1.33=%E_{rel})

-Buffer solution (pH=7.4) was prepared by mixing aqueous solution of sodium acetate trihydrate (1.0 mol.l^{-1}) and glacial acetic acid (0.025 mol.l^{-1}).

Apparatus

Spectrophotometric measurements were recorded on a cintra 5-GBC scientific equipment and Sp8-100, Pye Unicam, England, measurements were carried out by using PW9421 pH meter, Philips, England. Temperature effect on stability of complex were studied by using a water bath - 90, Hambury, England. The flame atomic absorption spectrophotometer-500, Perkin-Elmer, U.S.A, were used for atomic absorption.

Procedure ;

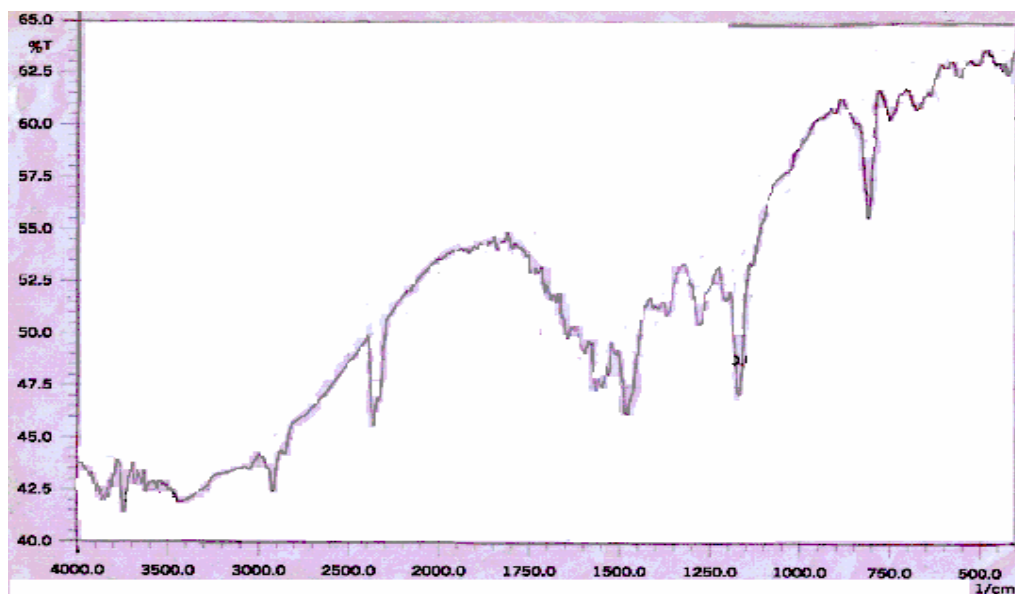
To an aliquot containing $\leq 100 \mu\text{g.ml}^{-1}$ of Cr(VI) in a 10-ml volumetric flask,

add 2 ml of the acetate buffer, and 3 ml of ($1 \times 10^{-4} \text{ M}$) of (6-MeBTACIP) solution and was diluted to the mark with distilled water. The whole content of the flask was transported to 50-ml separation funnel and extracted with 10 ml chloroform. The absorbance of the resultant organic layer was measured after 15 minute, at 517 nm at 25°C against the reagent solution as a blank that prepared under the same conditions.

Results and Discussion

1- FT-IR spectrum of the reagent (6-MeBTACIP)

FT-IR spectrum of the reagent (6-MeBTACIP) shows in Fig. 1, and the (table 1) shows the main frequencies of the absorption bands corresponding to the function groups of the reagent:



Fig(1);FTIR-Spectrum of (6-MeBTACIP) reagent

Table 1: The characteristic I.R Spectra of (6-MeBTACIP)

Wave number (Cm ⁻¹)	Groups
3200-3750	ν O-H,N-H
2856	ν C-H Aliphatic
2922	ν C-H Aromatic
1700	ν C=N
1483	ν N=N
1510	ν C=C
1173	ν C-S
816	ν C-Cl
1280	ν C-O Phenolic

2-Properties of the (6-MeBTACIP), and Isobestic Point

(6-MeBTACIP) reagent is a red powder slightly (hardly) soluble in water. It's solution is orange and stable

for suitable period time , but in basic medium $\text{pH} \geq 8.0$ the solution becomes pink , which can be interpreted in the following equilibria ;

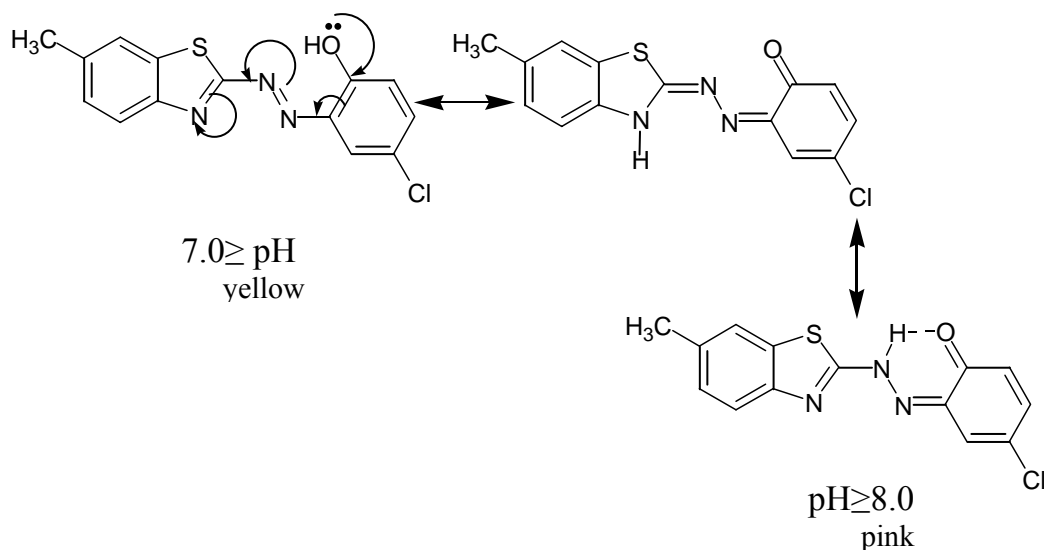
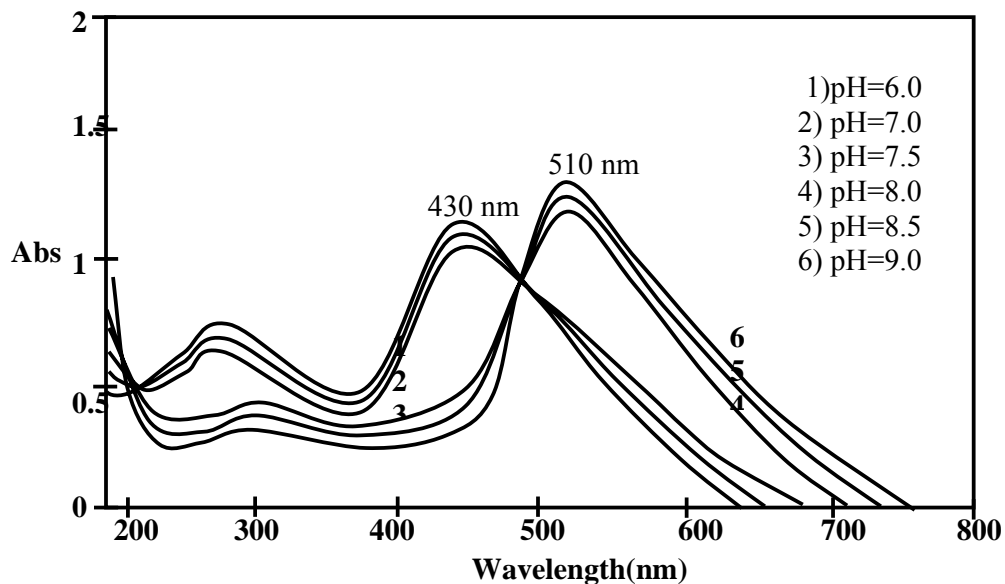


Fig.2 shows the isobestic point of the reagent was obtained at 492 nm by measuring the spectra at the uv – visible regions for solution reagent at pH (6-9).



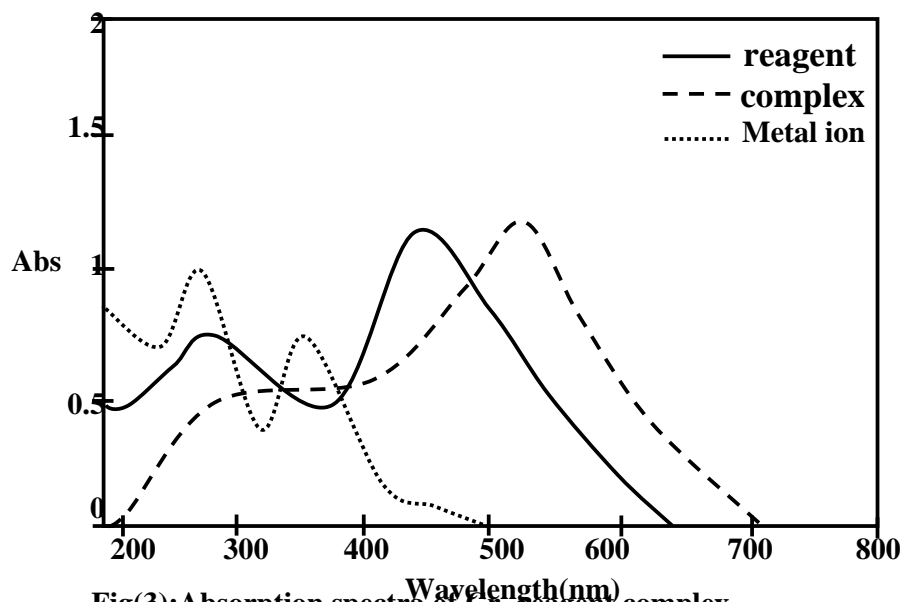
Fig(2);Absorption spectra of (6-MeBTACIP) reagent at various pH

Study of chromium (VI)_(6-MeBTACIP) complex

Absorption spectra

a-Ultra violet - visible absorption spectra of (6-MeBTACIP) reagent , Cr(VI) ion , and Cr(VI)- (6-

MeBTACIP) complex solutions are show in fig(3).The reagent showed an absorption maximum at 430 nm , the chromium ion at 352 nm , and the complex at 517 nm .

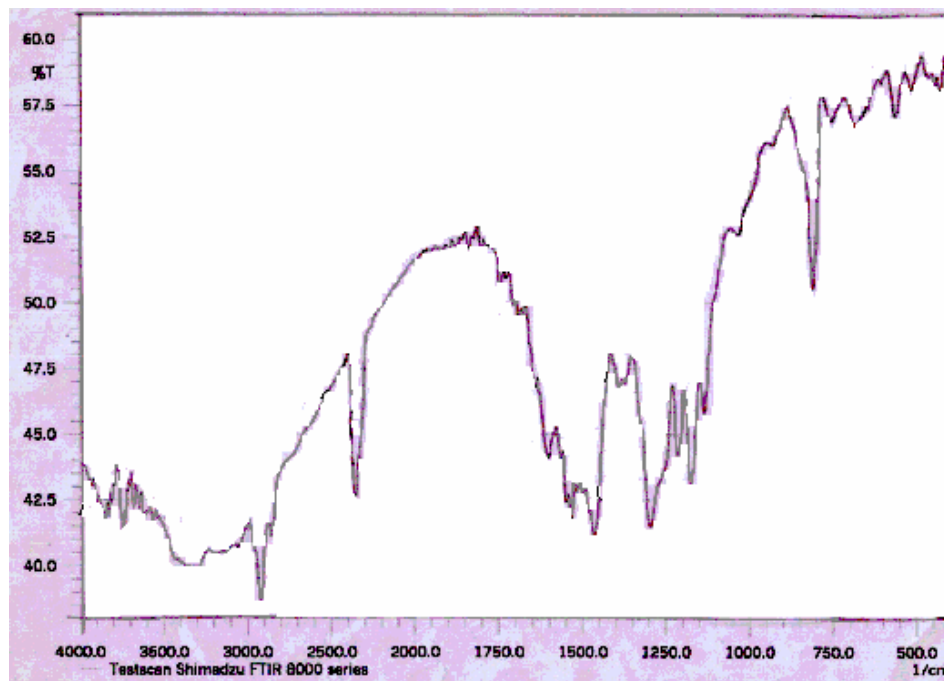


Fig(3);Absorption spectra of Cr-reagent complex.

b-FT-IR of Cr(VI)- (6-MeBTACIP) complex

FT – IR spectrum of the Cr (VI)- (6-MeBTACIP) shows in Fig.4, and the

(table 2) show the main frequencies of absorption that return to function groups of complex



Fig(4);FTIR-Spectrum of Cr(VI)- (6-MeBTACIP) complex

Table 2: The characteristic I.R Spectra of Cr(VI)- (6-MeBTACIP) complex

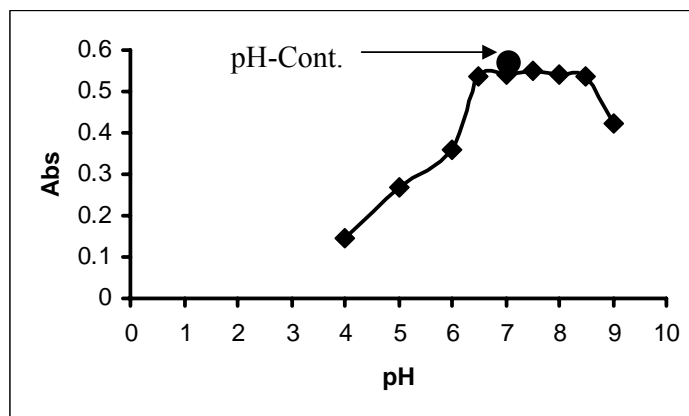
Wave number (Cm ⁻¹)	Groups
3200-3750	ν O-H,N-H
2854	ν C-H Aliphatic
2920	ν C-H Aromatic
1685	ν C=N
1463	ν N=N
1510	ν C=C
1175	ν C-S
814	ν C-Cl
1294	ν C-O Phenolic
410	ν N-M
420-500	ν O-M

Effect of pH

The influence of pH was studied over the range (3-9) adjusted by means of dilute HCl and NaOH solutions. Fig(5) shows the effect of pH , where the

maximum absorbance obtained in the range of pH=(6.8-7.8) .At pH values less than 6.5 and higher than 8 absorbance was decrease. Therefore ,

the optimum pH was 7.4 , where the absorbance was maximum and stable .



Fig(5);Effect of pH on the stability of Cr(VI) complex

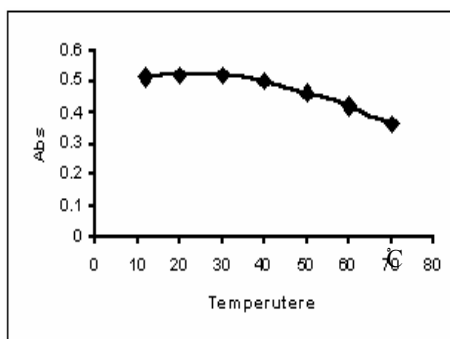
Effect of time

The stability of absorbance of the complex was studied from (0-120)min with 5 min intervals till 24 h . Fig (6) shows that maximum absorbance has reached after 15 min , after preparation of complex until the end of 24 h .

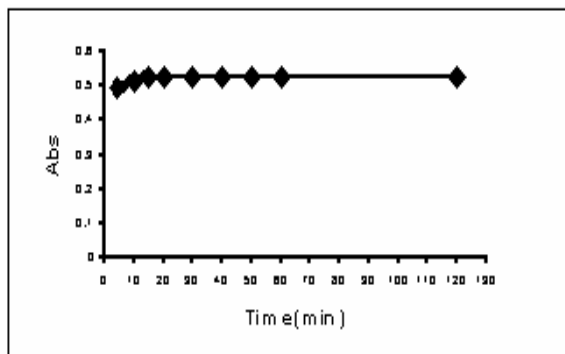
Effect of temperature

The effect of temperature on the absorbance of complex was studied at

temperatures range (10-80) °C using a water bath-90 ,Hambury ,Fig (7). Maximum absorbance was obtained when the temperature between (20-30) °C which was regarded as a proper temperature range of the complex formation. At a temperature higher than 40 °C the absorbance has decrease due to the dissociation of the complex gradually



Fig(7) effect of temperature on the stability of the complex

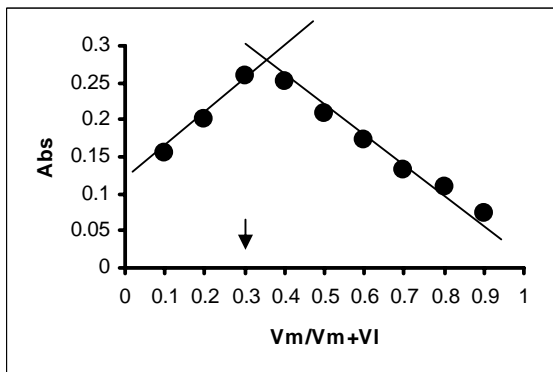


Fig(6) effect of time on the stability of the complex

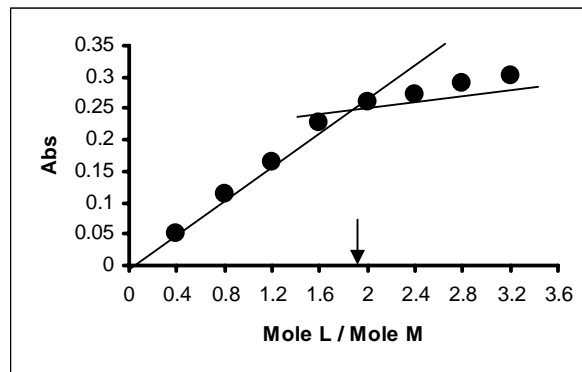
Determination of stoichiometry and formation constant

The composition of complex was studied by Jobs method of continuous variations and mole-ratio method⁽¹²⁻¹³⁾. Fig(8,9) show that both methods

indicate that , the ratio of metal ion to reagent molecules (M:L) was (1:2) at pH=7.4 . The formation constant calculated by the applied procedure , was found to be $(7.67 \times 10^9) \text{ l}^2 \cdot \text{mol}^{-2}$.



Fig(8);Jobs plot [Reag]=[Cr(VI)]
= 1×10^{-4} ,pH~7.4



Fig(9);Mole ratio plot[Reag]=[Cr(VI)]
= 1×10^{-4} ,pH~7.4

Molar conductivity

The molar conductivity of the prepared solid complex was measured by dissolving an adequate weight in two solvents of different polarity like methanol and acetone separately (

Table 3) , and measuring the value of molar conductivity by using the conductivity measuring device (Digital conductivimeter – alpha – 800 . Courteloud – England)

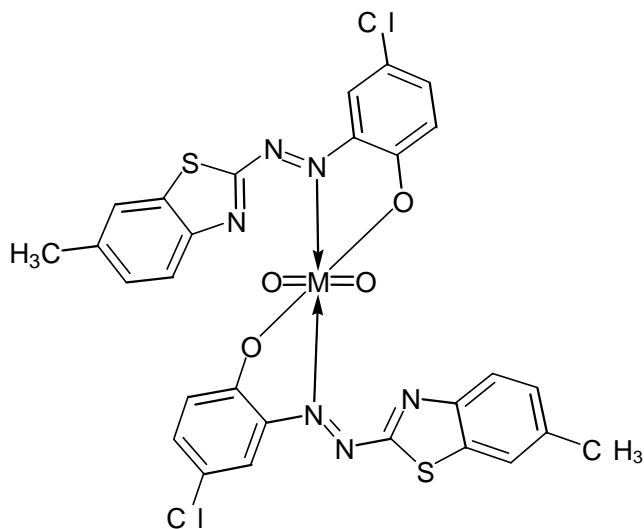
Table 3 : Molar conductivity of complex in acetone and methanol solvents

Molar conductivity , $\text{Cm}^2 \cdot \text{Ohm}^{-1} \cdot \text{mol}^{-1}$		Cr – (VI)-(6-MeBTACIP) ₂
methanol	acetone	
167	173.2	

From the results shown in the table 3 can deduce that the Cr(VI) complex with the reagent (6-MeBTACIP) is a weak electrolyte which contains no ionic properties. This result is coincidence with metal to reagent ratio (M:L) obtained experimentally⁽¹⁴⁻¹⁵⁾ .

From the obtained results of metal to reagent ratio,FTIR-Spectrum ,and depending on thiazolylazo compounds properties; the following structure can be suggested :

Suggestion of structural formula of Cr(VI)- (6-MeBTACIP) complex



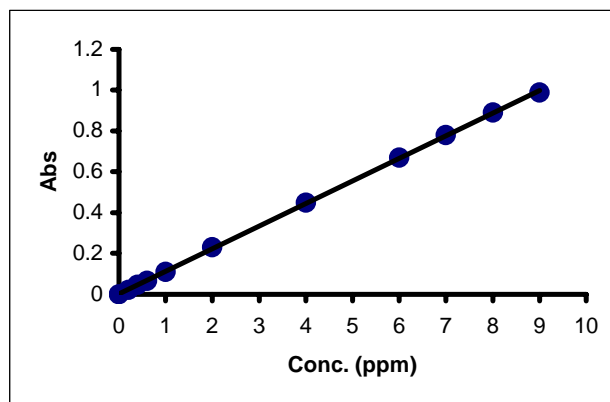
Where M=Cr

Analytical characteristics

Calibration curve

Linear calibration graph through the origin was obtained which obeyed Beers law over the range (0.2-9.00) $\mu\text{g}.\text{ml}^{-1}$ of Cr(VI). The average molar

absorptivity was found to be $(7.72 \times 10^3) \text{ l. mol}^{-1}.\text{cm}^{-1}$ in chloroform. The Sandell's sensitivity⁽¹⁴⁾ was $(0.0018) \mu\text{g. of Cr(VI).Cm}^{-2}$, and correlation coefficient (r) was 0.9986 (Fig.10).



Fig(10); Calibration curve of Cr(VI)- (6-MeBTACIP) complex in chloroform solvent.

Precision and accuracy

The relative standard deviation (R.S.D%) , evaluated from seven independent determinations of $10\mu\text{g}.\text{ml}^{-1}$ of Cr(VI) was 0.45% , this result showing that the method has good precision . Also the accuracy of

this method was determined by calculating the $E_{rel}\%$ for (10) ppm standard solution of Cr(VI) which was found to be 1.33 and $R_{e}\%=98.67$.

Analytical application

A total chromium in a waste water of (alnajaf – dibajat factory) as form

chromium (VI) was determined using this spectrophotometric method after applied the optimum conditions of formation of complex Cr(VI) - (6-

MeBTACIP) and compared with AAS method. The results obtained shown in table 4 .

Table 4 : Total concentration of chromium in waste water of alnajaf – dibajat factory

Sample No.	Total conc. of Cr , ppm	
	Spectrophotometric method	AAS
1	1.40	1.60
2	1.41	1.58

From these results it has been shown that there is a good conformity between the two analytical methods used. Therefore it was concluded that the spectrophotometric method mentioned in this research work can be used for the determination of trace concentrations for this element in different matrices with a good precision and sensitivity.

Interferences :

The selectivity of Cr(VI) – (6-MeBTACIP) system is tested by carrying out of determination of 5 ppm in the presence of foreign ions. These ions (MoO_4^{2-} , WO_4^{2-} , Cu^{2+} , Pb^{2+} , Hg^{2+} , Zn^{2+} , Cd^{2+} , Ni^{2+}) which also reacts with the reagent 6-MeBTACIP during its reaction with Cr(VI). Above cations were masked by using suitable masking agents. The results obtained are summarized in table 5 :

Table 5 : study of interferences

Foreign ion	Form add	Amount add, ppm	Relative error
Ni^{2+}	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	10	-3.4
Cd^{2+}	$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	15	+5.2
Zn^{2+}	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	10	+1.2
Hg^{2+}	HgCl_2	20	+2.6
Pb^{2+}	$\text{Pb}(\text{NO}_3)_2$	15	+1.7
Cu^{2+}	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	20	-2.1
WO_4^{2-}	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	15	-10.3
MoO_4^{2-}	$(\text{NH}_4)_2\text{MoO}_4$	10	11.6

In order to enhance the selctivity various masking agents are examined. These are oxalic acid, citric acid, tartaric acid, 5-sulphosalicylic acid, 1,10-phenanthroline, sodium fluoride,

ascorbic acid, EDTA and Na_2HPO_4 . The results are shown in table 6 :

Table 6: effect of masking agents

Cr(VI) conc. ppm	Masking agent (2)ml, [0.01]M	Absorbance
5	Complex without any addition	0.620
5	Oxalic acid	0.331
5	Citric acid	0.602
5	tartaric acid	0.224
5	5-sulphosalicylic acid	0.625
5	1,10-phenanthroline	0.185
5	sodium fluoride	0.589
5	ascorbic acid	0.164
5	EDTA	0.182
5	Na ₂ HPO ₄	0.617

From the result shown in the table 6 can concluded that oxalic acid, tartaric acid, 1,10-phenanthroline, ascorbic acid and EDTA caused masking for Cr(VI), while other masking agents have no or little effects on the absorbance of Cr(VI)-6-(MeBTACIP) complex.

References

- Othmer . K., "Encyclopedia of Chemical Technology" , John Wiley & Sons; Newyork , 1981
- Boef . G ., W.Jong .,G.C.Krijin , and H.Poppe .*Anal.Chim Acta.*, 1960, **23**,557.
- Luciene . S.C.,A.C.S.Costa , S.L.C.Ferreira, and L.S.G.Texeirra , *J.Braz.Soc.*, 2004, **15**,1.
- Azhar . A.G.,M.Sc.Thesis, University of Babylon(2003).
- Revansiddapa.H.D.,and T.N.K.Kumar,*Chem.Anal.*, 2002, **47**,311.
- Zhao.Y,and G.Han ,*Talanta.*, 1994, **41**,1247.
- Fu-Sheing.W,Z.Yu-rui,Q.Pel-hau,Y.Fang, and S.Nai-kui, *Mikrochim . Acta*, 1982, **2**,67.
- Texeira. L. S. G., A. C. S. Costa, S. L. C. Ferreira, C. M. S. Carvalho, and , M. L. Freitas, *J.Braz.Chem.Soc.*,1999, **10**, 519.
- Rathaiah.G.V,and M.C.Eshwar, Bull .*Chem.Soc.Jpn*, 1985, **58**, 2447.
- Subrahmanyam.B.,and M.C.Eshwar, *Mikrochim.Acta*, 1976, **11**,579.
- S.I.Gusev, M.V.Zhvakina , and I.A.Kozhevnikov, *Zh. Analit.Khim.*, 1971, **26** , 859.
- Jop,*Ann.Chim.*, 1928, **9**,113.
- A.E.Harvey,andD.L.Manning,*J .Am.Chem.Soc.*, 1950, **72**,4488.
- Marczenko.Z, "Spectrophotometric Determination of Element", John Wiley & Sons, Inc., Warsaw(1976).

15. I. Salomi and A. Al-Daher,
Iraqi J. Sci., 1983, **13**, 2141.
16. A.Z. Al-Rubaie, H.A. Al-Shirayda, P. Grenger and S. Chapelle, *J. Organometal. Chem.*, 1985, **4**,321.