Joined Liquid Ion Exchange with Cloud Point Extraction Methods for Separation and Determination of Cr(VI), Mn(VII)

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الخلاصة

تم فصل وإغناء وإستخلاص أيوني (Cr(VI على هينة $Cr_2O_7^=$ و (Mn(VII على هينة MnO_4^- من وسط حامض HCl وباستخدام صبغة Janus green B لتكوين معقد الترابط الأيوني، دراسة الظروف المثلى للأستخلاص أظهرت التركيز الامثل لحامض الهيدروكلويك HCl 0.1M و 0.05M على التوالي وبوجود Mn(VII) 50µg أو Cr(VI) 20µg وبوجود TritonX-100 1% 0.8mL لاستخلاص (Cr(VI و 0.5mL لاستخلاص (Mn(VII وكانت 95 °C هي الدرجة الحرارية الملائمة وبزمن تسخين 15 min. لكلا الأيونين. أضافة الى دراسة تأثير المتداخلات والأملاح الألكتروليتية. واستخدمت هذه الطريقة لتقدير كلا الأيونين في نماذج مختلفة. وكان الطول الموجي لأعظم إمتصاص لمعقد الترابط الأيوني المستخلص λ_{max}=560 nm لمعقد المنغنيز و 603nm لمعقد الكروم.

Abstract

Sensitive and selective extraction method used for separation, preconcentration and spectrophotometric determination of Cr(VI) as $Cr_2O_7^=$ and Mn(VII) as MnO_4^- from HCl media by used Janus green B after formation ion pair association complex, studies the optimum condition for extraction demonstrated 0.1M and 0.05M of HCl suitable for extraction efficiency of Cr(VI) and Mn(VII) respectively, in presence 50µg Mn(VII) or 20µg of Cr(VI). with 0.8mL 1% TritonX-100 for extraction ion pair association of Cr(VI) as well as 0.5mL for Mn(VII) and 95°C suitable for formation CPL and extraction ion pair complex for both metal ions ,with 15 min. of heating time for both metal ions. Then study effect of interferences and electrolyte presence. This method applied for spectrophotometric determination of Cr(VI) and Mn(VII) in different samples. The wave length for maximum absorbance of ion pair complex extracted was λ_{max}=560 nm for Mn(VII) and 603nm for Cr(VI) complexes.

Key words: Manganese, Chromium, cloud point extraction, Janus green B.

Introduction

Extraction of Cr(VI) using azo dye 2- [benzenethiazolylazo]-4-benzenenaphthol after CPE in presence nonionic surfactant Triton X-100, the Cr(VI) detected spectrophotometrically at λ_{max}=475 nm. Enrichment factor of 270, DL=0.017µg mL^{-1}. The linearity of 0.1-2.0 µgmL^{-1} and ε=4.47×10^4 L.mol^{-1}.cm^{-1}. RSD%= 0.31. This method is applied in the determination of Cr (VI) in various environmental and botanical samples[1]. Separation and extraction of Pt(II) as chloroanion $PtCl_4^=$ according to CPE method used Triton X-100 in HCl media with Janus

green. The stoichiometric show that the more probable structure of extracted complex was $[JG^+;HPtCl_4^-]$, the main method for extraction show D.L=6.8028×10^{-6}, Sandell's sensitivity =0.003133 µg cm^{-1}, RSD%=0.00885 the λ_{max}=690nm and ε=6227.861 L.mol^{-1}.cm^{-1}[2]. Spectrophotometric determination of Mn using CPE. The method involved the formation of an ion association complex between MnO_4^- and brilliant green in acidic solution and in presence Triton X-100. Extracted complex having λ_{max} =657 nm. Enrichment factor of 282, DL=0.086µg mL^{-1}, with linearity of 0.2-3µg.mL^{-1}.RSD%=1.07%. This method is applicable in the determination of Mn in environmental and vital samples[3]. Extraction of Ni(II) as $NiCl_4^=$ by using DB18C6 according to CPE, extracted species has λ_{max} =295nm. Stoichiometry study shows ion pair complex extracted was 1:1. So this study includes application about determination Ni(II) in different samples[4].

1-(2-Pyridyl azo)-4-benzene naphthol used as reagent for determination Mg (II), after conversion Mg(II) to anion complex by reaction with oxine, initially the reagent (PABN) must be react with Ni(II) to form large cation complex produce ion pair complex with $Mg(OX)_3^-$ having λ_{max}=398nm, this method used for determination of Mg (II) in different samples[5]. The extraction of Cr(VI), was performed from acidic sulphate and alkaline carbonate media by using Aliquat 336 and Alamine 336 as extractants in kerosene. The results indicate that extraction of Cr(VI) from acidic media is more favored than from alkaline solution. This method was applied for the removal and recovery of Cr(VI) from electroplating waste solution[6]. Determination of trace chromium species by FAAS after separation of Cr(III) by CPE using alizarin-3-methyliminodiacetic acid as the complexing agent. Under the optimized conditions, the calibration graph of Cr(III) was linear in the range of 4–200 µg L^{-1}. DL= 1.0 µg L^{-1}. RSD%= 4.8%. The enhancement factor was 40.05. After reduction of Cr(VI) to Cr(III) with ascorbic acid, to determine total chromium. The proposed method has been applied to determine water samples and water-soluble chromium species in soil[7]. CPE procedure has been used for the determination trace amounts of Cr(III), Pb(II), Cu(II), Ni(II), Bi(III), and Cd(II) ions by using FAAS. This method was based on CPE of analyte metal ions without ligand using Tween 80 as surfactant. The surfactant-rich phase was dissolved with 1.0 mL 1.0 mol.L^{-1} HNO$_3$ in methanol to decrease the viscosity. This method was applied to several matrixes such as water, food and pharmaceutical samples [8].

Experimental

a) **Apparatus:** Biochrom model (80-7000-11) Libra S60 Cambridge CB40FJ spectrophotometer with 1 cm quartz cell was used for recording the absorbance spectra and absorbance. Electrostatic water bath (WNB7-45) (England) was used to maintain the temperature.

b) **Reagent and materials:** All analytical grade reagents were used without further purification as received from company. Doubled distilled water was strictly used for preparing solution and dilution of reagents and samples. Triton X-100 (Sigma Ultra). $KMnO_4$ (CHEMSUPPLY limited) and Janus green B (Merck). $K_2Cr_2O_7$ (BDH). The stock solution of Mn(VII) at 1mg mL^{-1} was prepared by dissolving of 0.2877g of $KMnO_4$ in 100mL distilled water in volumetric flask. The stock solution of Cr(VI) at 1mg mL^{-1} was prepared by dissolving of 0.2829g of $K_2Cr_2O_7$ in 100 mL distilled water in volumetric flask. 0.25% Diphenylcarbazide solution was prepared by dissolving 0.25g from it in 50 mL of acetone. Janus green B solution of $1\times10^{-2}M$ was prepared by dissolving 0.051g from it in 10mL distilled water in volumetric flask.

Principle Method for Extraction

10mL aqueous solution contain fixed quantity of Cr (VI) as $Cr_2O_7^{=}$ or Mn(VII) as MnO_4^{-} and optimum concentration of HCl in presence suitable concentration of organic reagent Janus green B and favorable mL of 1%TritonX-100, and heating the solution to 95^0C for suitable time until formation cloud point layer ,afterward separate CPL from aqueous solution and dissolved CPL in 5mL ethanol and measure the absorbance at λ_{max} against blank prepared at the same manner in absence metal ion, as well as aqueous solution treated according to spectrophotometric method[9] for each metal ion and after return to calibration curves **Figures 2** and **3** determine the remainder quantity of metal ion and subtraction this value from original quantity to determine transferred quantity to CPL as ion pair association at later calculate distribution ratio of extraction, as well as performed reference procedure to determine transferred quantity by stripping method after shaking alcoholic solution of CPL with to portion 5mL of 2M NaOH to dissociation ion pair complex and return metal ion to aqueous solution and determined the quantity of stripped metal ion by spectrophotometric

determination[9].the experimental procedure illustrate the quantity of transferred metal ion determined by stripping method equal to the same quantity of metal ion determined by subtraction .then followed the subtraction method because easier and faster.

Results and Discussion

Absorption spectra

Absorption spectra of the reagent Janus green B solution and its complex with MnO_4^- and $Cr_2O_7^=$ in surfactant-rich phase against blank prepared under similar conditions were recorded. The results as in **Figure 1:**
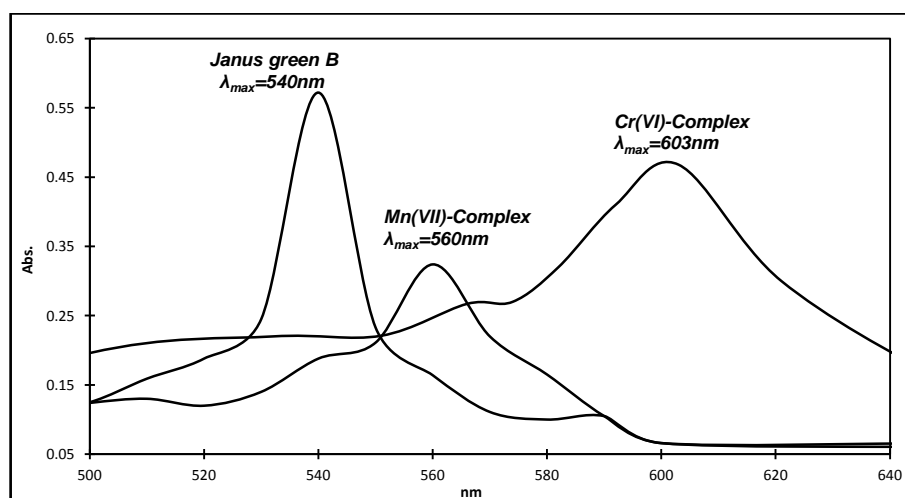
Figure 1: UV-Vis-spectra for organic reagent Janus green B and its ion pair complexes with MnO_4^- and $Cr_2O_7^=$.

Variation HCl Concentration

Extracted 50µg of Cr (VI) and Mn (VII) from 10 mL aqueous solutions contain different concentrations of HCl and 0.5 mL 1% TritonX-100 and 1×10^{-4}M Janus green B and heating these solutions at 95^0C for suitable time until formation CPL so separate CPL from aqueous solutions and determined absorbance of alcoholic solutions of CPL and calculate D-values by followed principle method. The results were as in **Figures 4** and **5**:
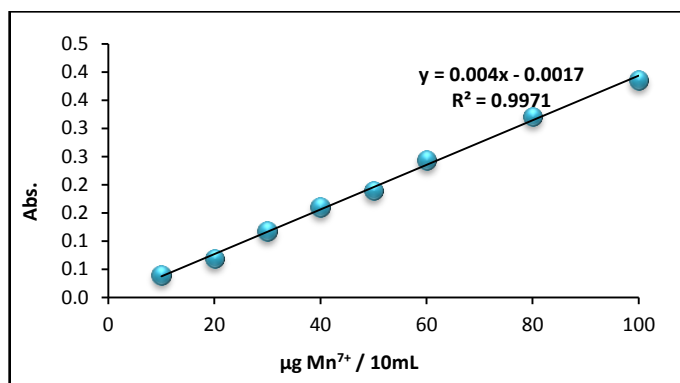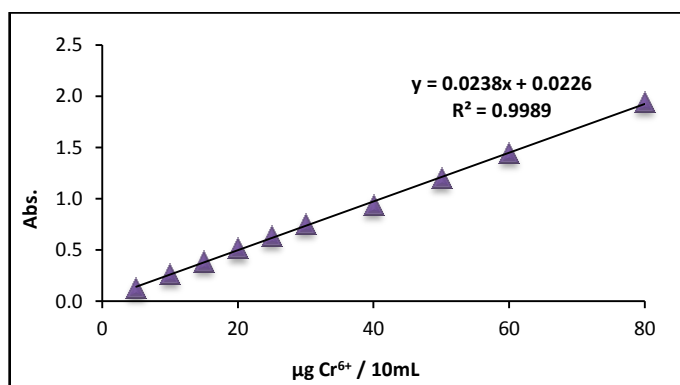
Figure 2: Calibration curve for Mn^{7+} ion.
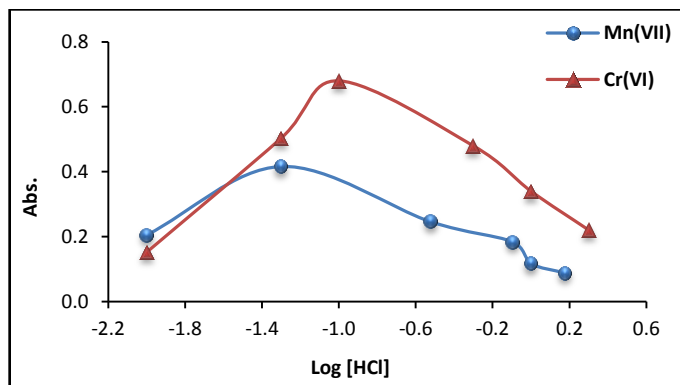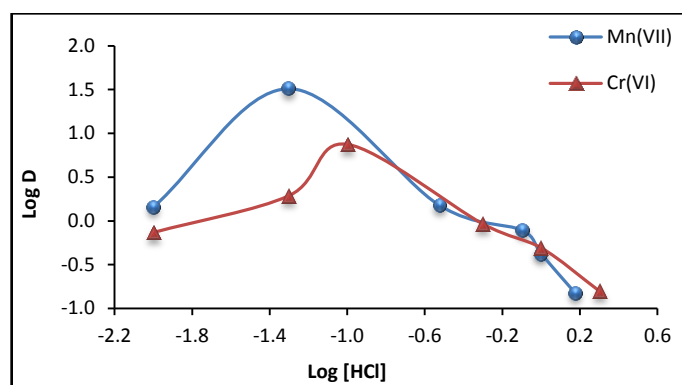

Figure 3: Calibration curve for Cr^{6+} ion.

Figure 4: Effect of HCl concentration on complex formation and extraction

Figure 5: D = f (log [HCl])

The results show optimum values for extraction $Cr_2O_7^{=}$ was 0.1M HCl and for MnO_4^{-} was 0.05M HCl and at these concentration reached favorable thermodynamic equilibrium for extraction which giving higher absorbance and D values, according to liquid ion exchange equilibrium any concentration of HCl less than optimum value not enough to reach thermodynamic equilibrium and causing decrease in absorbance and D value. Whilst at higher than optimum value of HCl, there is a difficulty of exchange of $Cr_2O_7^{=}$ and probably due to the reduction of Mn(VII) ion to Mn(II) thus preventing the formation of ion-pair complex in cloud point layer.

Metal Ion Concentration Effect

Extracted Cr (VI) and Mn (VII) each one alone from 10 mL aqueous solutions contain increasing quantity of each ion and 0.1 M HCl for Cr (VI), 0.05M HCl for Mn(VII) and 1×10^{-4}M Janus green B and 0.5 mL of 1% TritonX-100, the solutions heating at 95^{0}C for 15 min afterward separate CPL from aqueous solutions and determined absorbance and D-values such as general method. The results were as in **Figures 6** and **7**:
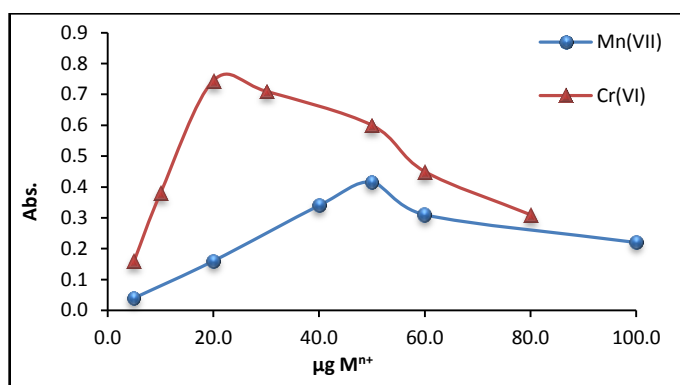
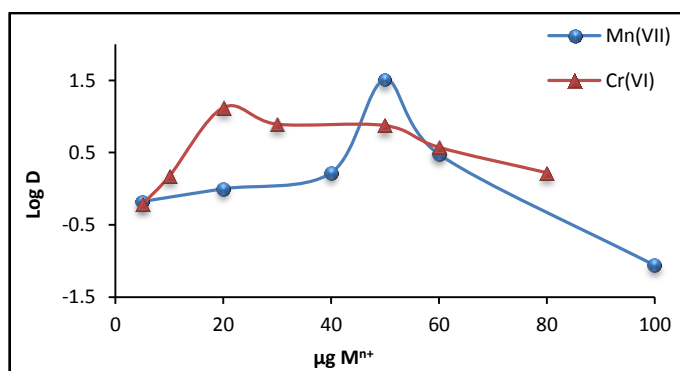**Figure 6:** Effect of metal ion concentration on complex formation and extraction.


Figure 7: D= F [metal ion]

The results show extraction efficiency change as a function of metal ion concentration and giving a straight line relation to optimum value of metal ion which is 20μg/10mL for Cr(VI) and 50μg /10 mL for Mn(VII), this concentration effect to reach the favorable thermodynamic equilibrium and giving enhancement in the rate of forward direction of equilibrium. For that produced high concentration of ion pair complex extracted in CPL, but any concentration less than optimum value not enough to reach the best thermodynamic equilibrium and causing decrease in the rate of forward direction and reduce absorbance and D-value, so that concentration more than optimum effect to decrease extraction efficiency by effect of mass action law and Le Chatlier principle.
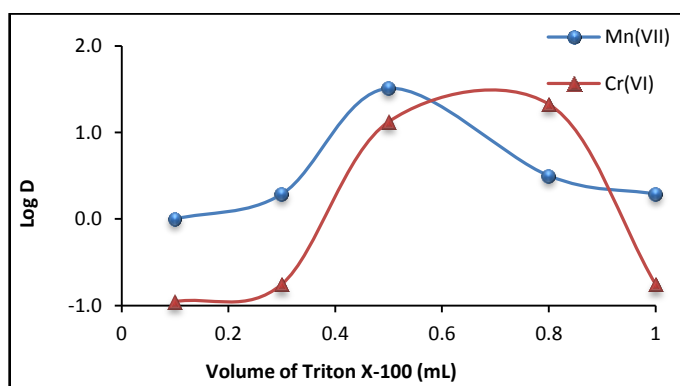
Surfactant Volume Effect

Extracted Cr (VI) and Mn (VII) at optimum concentration for each ion and HCl from 10 mL aqueous solutions in presence 1×10^{-4} M Janus green B and different volume of TritonX-100, heated the solutions to 95^{0}C for 15min then separated CPL from aqueous solution

.Afterward determined absorbance of alcoholic solution of CPL and calculated D-values according procedure detailed in general method .The results were as in **Figures 8** and **9**:
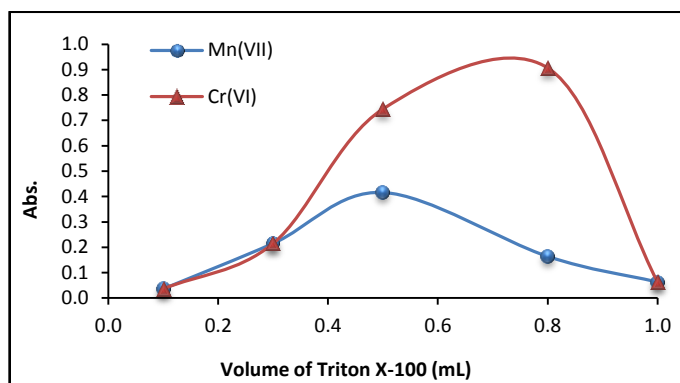
Figure 8: Effect of surfactant volume on extraction efficiency of ion pair complex.

**Figure 9:** Effect of surfactant volume on D-values.

The results demonstrate the optimum volume was 0.8 mL for extraction Cr(VI) and for Mn(VII) was 0.5mL these volumes of surfactant suitable to reach the critical micelles concentration (CMC) to produce cloud point layer with smaller volume and higher density thermodynamically giving favorable extraction efficiency. Any volume less than optimum not suitable to reach thermodynamic equilibrium for best extraction efficiency and effected to decline absorbance and D-values. So surfactant volume more than optimum effect to increase diffusion of micelles in aqueous solution and decreased in extraction efficiency also.
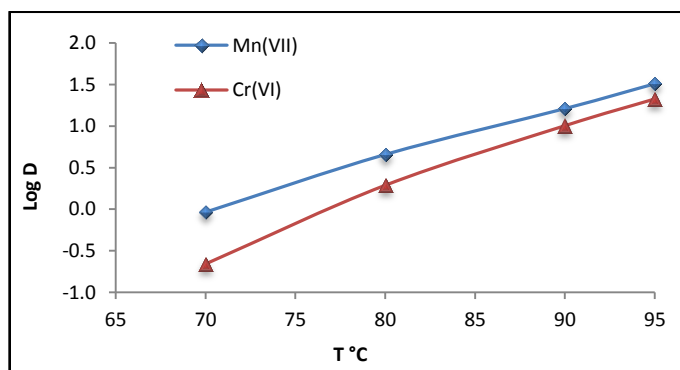
Effect of Temperature

Extracted Cr (VI) and Mn (VII) at optimum concentration for each ion from 10 mL aqueous solution in presence 1×10^{-4}M Janus green B and optimum concentration of HCl and optimum volume of TritonX-100 with each ion heating these solutions in electrostatic water

bath at different temperature, afterward determine absorbance and D-values at each temperature according to procedure detailed in general method. The results were as in **Figures 10** and **11**:
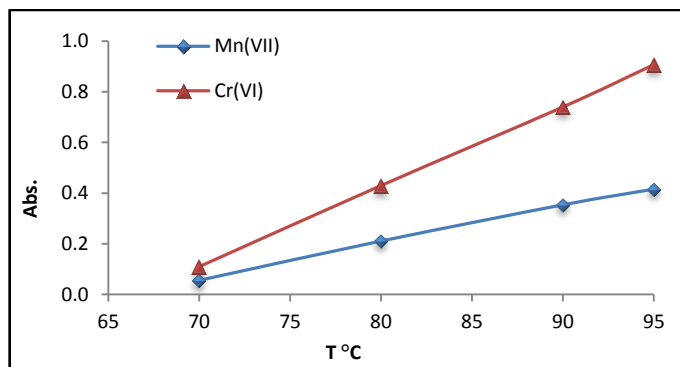
Figure 10: Effect of temperature on separation activity.
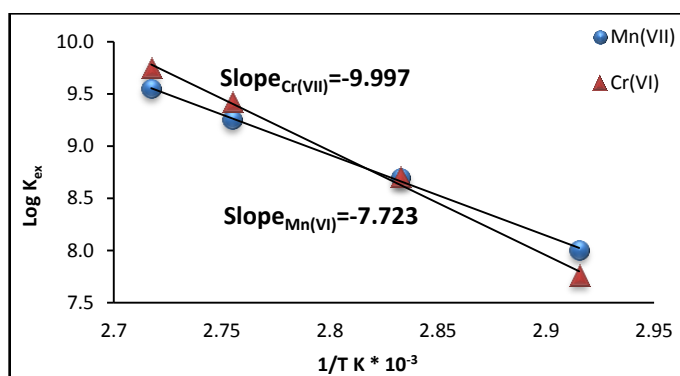

Figure 11: Effect of temperature on D-values

The results show 95°C was the optimum temperature suitable for separation and extraction both ions because at this temperature reach produce favorable aggregation of micelles and dehydration to giving CMC which necessary for higher extraction efficiency. So that calculated extraction constant K_{ex} at each temperature from the relation below:

$$K_{ex} = \frac{D}{[metal\ ion].[JGB]}$$

After that plotted log K_{ex} against 1/T K the results were appear in **Figure 12**:

Figure 12: Effect of temperature on K_{ex} for extraction Mn(VII) and Cr(VI).

From the slope of straight line relation above calculate enthalpy of extraction:

$$slope = \frac{-\Delta H_{ex}}{2.303R}$$

As well as calculate ΔG_{ex} and ΔS_{ex} from the relation below

$\Delta G_{ex} = - R\ T\ ln\ K_{ex}$

$\Delta G_{ex} = \Delta H_{ex} - T\Delta S_{ex}$

The results were:

M^{n+}	$\Delta H_{ex}\ kJ.mole^{-1}$	$\Delta G_{ex}\ kJ.mole^{-1}$	$\Delta S_{ex}\ J.mole^{-1}K^{-1}$
Mn(VII)	0.148	- 67.28	183.23
Cr(VI)	0.191	- 68.63	187.01

<u>Heating Time Effect</u>

Extracted Cr (VI) and Mn (VII) at optimum concentration for each ion from 10 mL aqueous solutions in presence $1 \times 10^{-4}M$ Janus green B, optimum concentration of HCl and volumes of TritonX-100 and heating these solutions in electrostatic water bath at 95°C for different times at later determine absorbance and D-values according to procedure detailed in general method. The results were as in **Figures 13** and **14**:
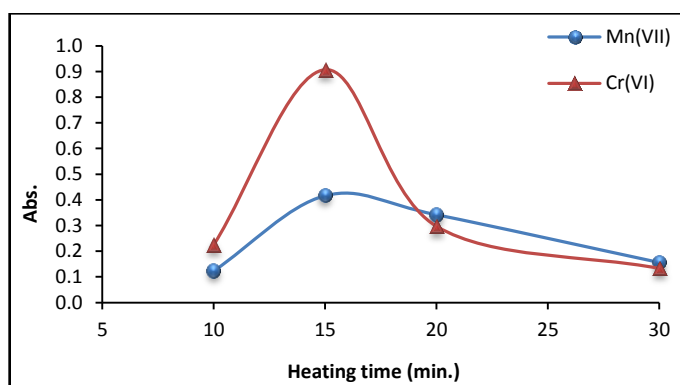
Figure 13: Effect of heating time on separation activity and absorbance values
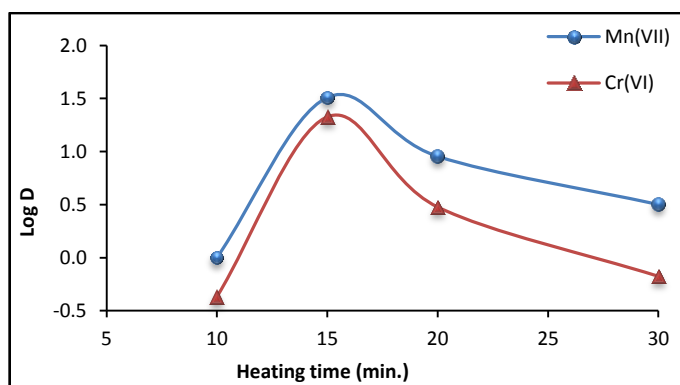
Figure 14: Effect of heating time on extraction efficiency and D-values

The results illustrate optimum heating time for extraction was 15 min. for both metal ions this time help to reached best thermodynamic equilibrium and giving optimum dehydration and produced favorable aggregation for CMC with smaller volume and higher density and giving higher absorbance and D-values .While heating time less than optimum not enough to reached thermodynamic equilibrium and reduced the extraction efficiency, so that heating for time more than 15min. effect to decrease extraction efficiency also be effected of increase diffusion of micelles.

Stoichiometry

Ion pair complex structure for both ions known through spectrophotometric studies: slope analysis and slope ratio methods[10]. As well as the results of these two methods illustrated in **Figures 15, 16** and **17**:
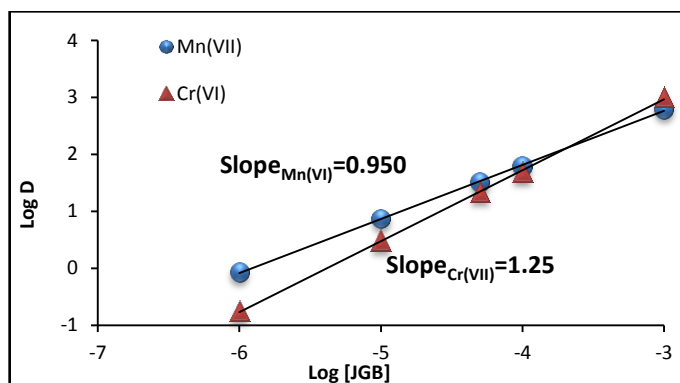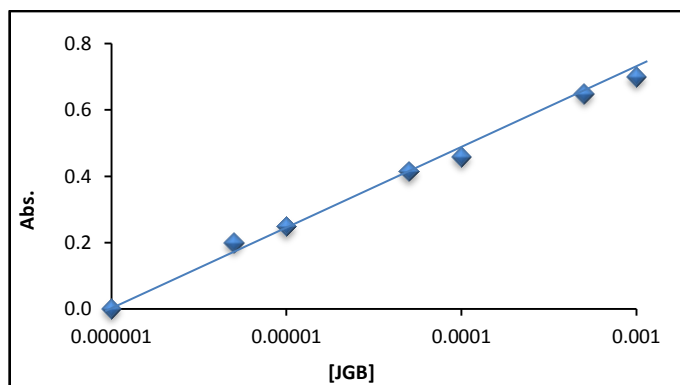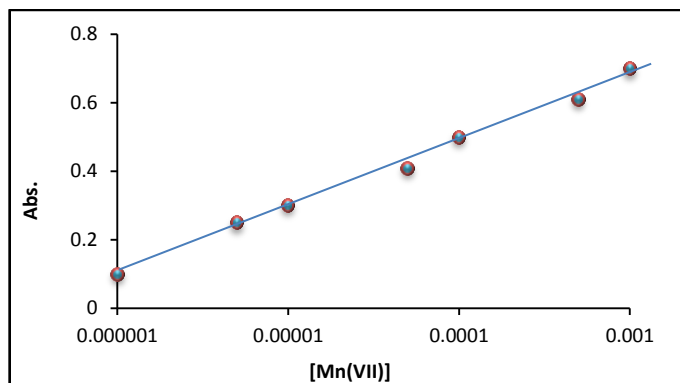
Figure 15: Slope analysis method for both metal ions Mn(VII) and Cr(VI)
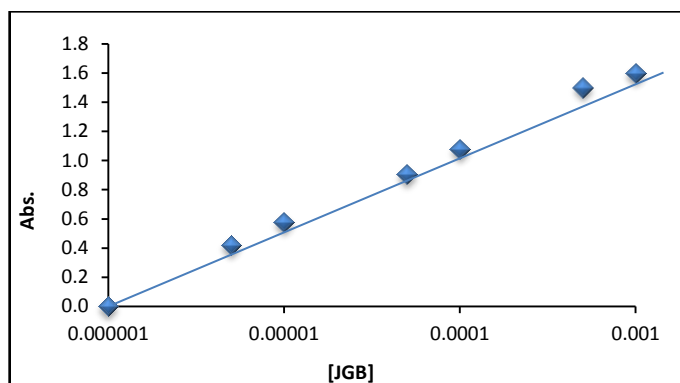

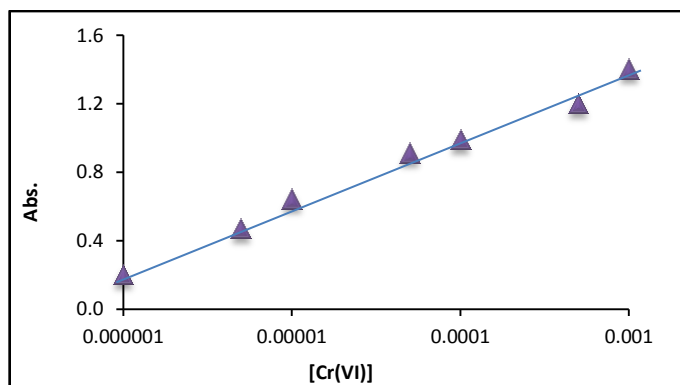a- Effect of different concentrations of organic reagent

b-Effect of different concentrations of Mn(VII) ion

Figure 16: Slope ratio for Mn(VII)

$$\text{Slope ratio} = \frac{528.72}{6474.74} = 1.15$$

a-Effect of different concentrations of organic reagent

b- Effect of different concentrations of Cr(VI) ion

Figure 17: Slope ratio for Cr(VI)

$$\text{Slope ratio} = \frac{1225.44}{889.79} = 1.38$$

The results appear were probable structure of ion pair complex extracted to CPL was 1:1 $[JGB]^+;MnO_4^-$, $[JGB]^+;HCr_2O_7^-$:
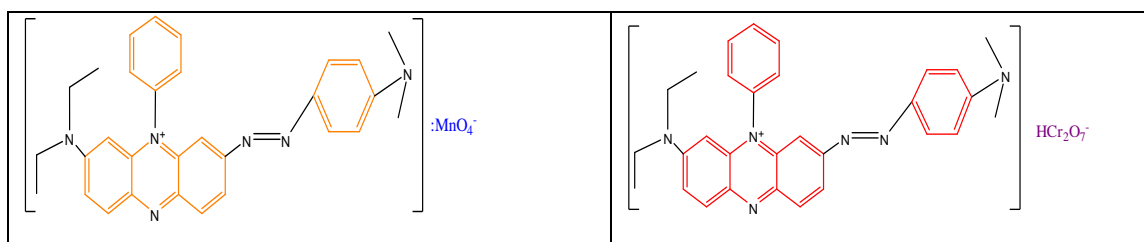
Figure 18: More probable structure of ion pair complexes for Mn(VII) and Cr(VI) with JGB.

Interferences Effect

Extracted Cr (VI) and Mn (VII) at optimum concentration for each ion from 10 mL aqueous solution contain optimum concentration of HCl for each ion and volume of TritonX-

100 in presence 0.1 M of different anion. And heating these solutions at $95^{\circ}C$ for optimum time, at latter determined the absorbance and D-values according to procedure detailed in general method .The results was as in **Table 1**.

Table 1: Interferences effect of different anion on extraction efficiency

Interferences	Mn(VII)			Cr(VI)		
	Abs.at λ_{max}=560nm	D	% E	Abs.at λ_{max}=603nm	D	% E
$C_2O_4^=$	0.194	3.55	78.00	0.346	0.82	45.00
$WO_4^=$	0.256	5.25	84.00	0.645	1.50	60.00
SCN^-	0.099	2.57	72.00	0.134	0.43	30.00

The results show there is an interference for the anions in the extraction of Cr(VI) and Mn(VII), this interference reflect the participation of these anion in the formation of ion pair association complex with organic reagent Janus green B, but depend on the nature and behavior of each anion in the aqueous solution as well as each anion needing special optimum conditions. Whereas absorbance and distribution ratio (D) values without any interferences were 0.416 and 32.33 respectively for Mn(VII) as well as 0.907 and 21.22 respectively for Cr(VI).

Electrolyte Effect

Extracted Cr (VI) and Mn (VII) at optimum concentration for each ion from 10 mL aqueous solution contain optimum concentration of HCl for each ion and optimum volume of TiritonX-100 in presence 0.1 M concentration of electrolyte salts, Heating these solutions at 95^0C at optimum time until formation cloud point layer and complete separation of ion association complex .Afterward determined absorbance and D-values in presence each electrolyte salts. The results were as in **Table 2**.

Table 2: Effect of electrolyte salts on extraction efficiency.

| Electrolyte salt	Mn(VII)			Cr(VI)		
	Abs.at λ_{max}=560nm	D	% E	Abs.at λ_{max}=603nm	D	% E
LiCl	0.753	65.82	98.50	1.88	40.15	97.57
NaCl	0.642	51.70	98.10	1.67	31.23	96.89
KCl	0.598	42.61	97.71	1.54	28.71	96.63
NH_4Cl	0.518	35.33	97.25	1.13	24.71	96.11
$MgCl_2$	0.612	48.44	97.98	1.47	27.85	96.53
$CaCl_2$	0.576	39.54	97.53	1.36	25.48	96.22

The results demonstrate the presence of electrolyte salts in the aqueous solution appear increasing of the extraction efficiency with enhancement in absorbance and D-values due to increasing in the ionic strength of the aqueous solution and help to increase dehydration of CMC layer, as well as enhancement destroyed of hydration shell for anion and help to increase the chances of formation ion pair association complex and good aggregation of micelles to form proper layer of cloud point with smaller volume and higher density. Whereas absorbance and distribution ratio (D) values without any electrolyte salts were 0.416 and 32.33 respectively for Mn(VII) as well as 0.907 and 21.22 respectively for Cr(VI).

Spectrophotometric determination of Cr(VI) and Mn(VII)

For spectrophotometric determination analyte metal ions we are need to preparing calibration curve by application the general method at optimum condition for aqueous solution contain different concentrations of metal ion Cr (VI) and Mn (VII). The results in the **Figures 19** and **20**:
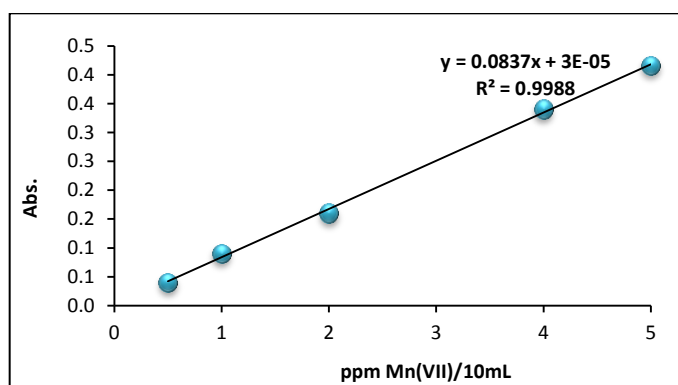
Figure 19: Calibration curve for spectrophotometric determination of Mn(VII)
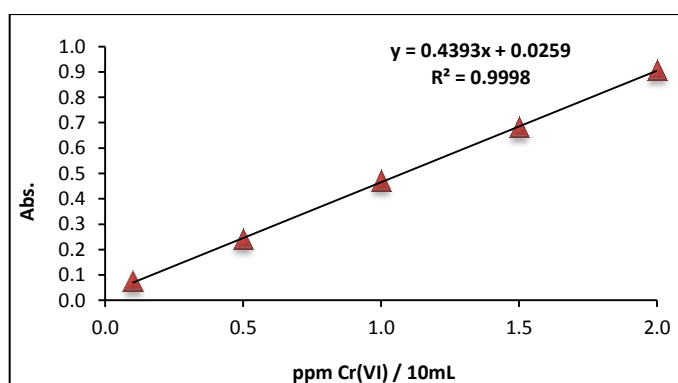
Figure 20: Calibration curve for spectrophotometric determination of Cr(VI).

Analytical parameters	Mn(VII)	Cr(VI)
Molar absorptivity (L.mol^{-1}.cm^{-1})	4632.16	22843.50
RSD%	0.0096	0.0070
Sandell's Sensitivity (µg/cm^2)	0.01186	0.0024
Detection limit (µg/mL)	5.25×10^{-6}	4.062×10^{-6}

This method used for spectrophotometric determination of Cr (VI) as $Cr_2O_7^=$ and Mn (VII) as MnO_4^- in different samples, where samples solution prepared according to wet digestion method[11], and aqueous solution of sample treated as general method for extraction and used the suitable masking agent for each ion. The results as in **Table 3**:

Table 3: Applications.

Sample No.	Sample Name	Mn(VII) ppm	Cr(VI) ppm
1	Non agriculture soil (Al-Mishikhab)	53.47	5.67
2	Agriculture soil (Al-Mishikhab)	77.61	3.15
3	Agriculture soil (Al-Huria)	80.44	0.998
4	Agriculture soil (Al-Abasia)	69.99	1.43
5	Tomato	54.22	0.24
6	Cucumber	17.33	2.65
7	Potatoes	47.39	0.47
8	Cow meat (beef)	13.44	0.072
9	White meat of chicken	2.20	0.046
10	Farmers fish	2.64	0.086

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