Via Cloud Point Extraction Methodology and Acidic HCl media Extracted of Iron (III) by DB18C6

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الخلاصة

بواسطة استخدام الايثر التاجي DB18C6 وفي وسط حامضي HCl استخلص ايون الحديد (III) كمعقد ترابط ايوني باستخدام تقنية استخلاص نقطة الغيمة بعد تغيير Fe^{3+} الى $FeCl_4^-$ ، هذه الدراسة وضحت 1.2 M HCl هو التركيز الامثل في وجود $5\times10^{-2}M$ من كلوريد الصوديوم NaCl و $1\times10^{-4}M$ من الايثر التاجي DB18C6 وكذلك 0.5mL من سطح لا ايوني 1%TritonX-100 اللازمة للحصول على اعلى كفاءة استخلاص ، وكذلك وضحت الدراسة الحرارية 85 °C هي الدرجة الحرارية الملائمة للاستخلاص وفق تقنية استخلاص نقطة الغيمة CPE بالإضافة الى الحاجة لتسخين المحلول في حمام مائي كهربائي عند 85 °C ولمدة 15 دقيقة . الدوال الثرموديناميكية هي انثالبي الاستخلاص $\Delta H_{ex}=0.159$ KJ mol^{-1} و الطاقة الحرة للاستخلاص $\Delta G_{ex}=-62.43$ KJ mol^{-1} واما قيمة انتروبي للاستخلاص $\Delta S_{ex}=174.83$ J mol^{-1} K^{-1}، التطبيق التجريبي بين ان التركيب الاكثر احتمالاً لمعقد الترابط الايوني المستخلص هو ; $[Na\ DB18C6]^+$; $FeCl_4^-$ ، وهناك تطبيق عملي لهذه الدراسة في نماذج حقيقية مختلفة .

Abstract

By use crown ether DB18C6 and from acidic HCl media extracted Fe^{3+} ion as ion association complex by application cloud point extraction methodology after change Fe^{3+} into $FeCl_4^-$, this study show 1.2M HCl was the optimum concentration in precence 5×10^{-2} M NaCl and 1×10^{-4} M Crown ether DB18C6 as well as show 0.5mL of Nonionic surfactant 1% TritonX-100 was necessary to obtained higher extraction efficiency , so that thermodynamic study illustrate 85ºC was favorable temperature for extraction according to CPE method in addition to needing heating the solution in electrostatic water bath at 85 ºC for 15 minutes . Thermodynamic data was $\Delta H_{ex}=0.159$ KJ mol^{-1} , $\Delta G_{ex}=-62.43$ KJ mol^{-1} , $\Delta S_{ex}=174.83$J mol^{-1} K^{-1} , experimental application offer the more probable stracture of ion pair association complex extracted was $[Na\ DB18C6]^+$; $FeCl_4^-$, there are another empirical application for this study in real samples .

Keywords: Iron ; cloud point extraction ; crown ether ; liquid ion exchange .

Introduction

CPE method is based on the distribution ion pair association complex formed between surfactant and aqueous phase and when the solution is heated to fixed temperature the micelles formed cloud point layer with smallest volume and higher density containing ion pair association complex of Ni^{2+} in equilibrium with aqueous solution[1,2]. A previous study used CPE methodology for separating Cu(II), Co(II), Pb(II) from different samples after complex formation with 1-phenyl thiosemicarbazide by used TritonX-114 coupled with flame atomic

absorption with detection limit 3.42 µg/L for Pb(II) 1µg/L Co(II) and 0.67 µg/L Cu(II) .Extraction Cu(II),Ag (I) and Ni(II) after complexation with two ligand 2-[(4-formyl phenyl)azo]-4,5-diphenyl imidazole and 2-[(2-methylphenyl)azo]-4,5-diphenyl imidazole at optimum condition which is restricted experimentally [3] . By used CPE methodology coupled with flame atomic absorption determined micro amount of lead in different samples of soil and water after complexation with 1-[2-pyridyl azo]-2-naphthol and Triton X-114 at pH=8 [4] . By application of CPE methodology coupled with spectrophotometric technique for extraction and determination of Pb^{2+},Cd^{2+},Ni^{2+} in different samples [5] . Study for separation and determination of cadmium (II) by cloud point extraction coupled with flow injection atomic absorption by used methyltrioctyl ammonium to formation ion pair association complex with $CdI_4^=$ with using Triton X-114 [6] . By used BHIS as complexing agent for extraction Ag(I) at pH=8 in CPE methodology with Triton X-114 with detection limit 1.9 µg/L [7] . Separation and determination Pb(II) ,Cd(II) ,Pd(II) in some vital samples by CPE method coupled with flame atomic absorption by used IPAI as complexing agent at pH=8 with Triton X-114 this study illustrate D.L.=1.6 µg/L [8] by application of CPE methodology for separation and preconcentration small quantities of nickel(II) without using complexing agent as first step for determination by flame atomic absorption by used nonionic surfactant (PONPE7.5) [9] .

Experimental

It is important to note spectrophotometricaly and absorbance measurements was carry out by employed biochrome spectrophotometer (80-7000-11) Libra 560 cambridye CB40FJ , Jaban . So was used electrostatic water bath (WNB7-45 England) for maintain temperature .

Undoubtedly all chemicals used as received from trustworthy commerical company without farther purification stock solution of Fe^{3+} ion 1000 ppm prepared by dissolved 0.2922 g of $FeCl_3$ in 100mL distilled water contain 1mL of hydrochloric acid in volumetric flask , other working solution prepared by dilution with distilled water by used suitable volumetric flask,20% potassium thiocyanate solution prepared by dissolved 20 g in distilled water and acidify the solution with HCl into (pH=2).

The Fundamental Method

10 mL aqueous solution contain 50µg Fe^{3+} and optimum concentration of NaCl with suitable concentration of DB18C6 with 0.5mL nonionic surfactant 1%TritonX-100 then heating the solution in electrostatic water bath for suitable temperature and time until formation cloud point layer CPL separated this layer from aqueous solution and dissolved in 5ml ethanol afterword measure absorbance of ethanolic solution against blank prepared at the same manner in absence metal ion as well as aqueous solution treated according to spectrophotometer method[11] and after returned to calibration curve Figure (1) Calibration curve to determined reminder quantity to metal ion in aqueous solution after extraction and subtraction this quantity from main quantity to determine the transfer quantity to the CPL as ion pair complex and by dividing there quantities each over other to caluatate distribution ration (D) such as below

$$D = \frac{[Fe^{3+}]_{CPL}}{[Fe^{3+}]_{aq}}$$

to determine the transfer quantity of Fe^{3+} ion to the CPL follow another procedure which called stripping method involved shaking CPL after separation with two portion each one 5mL in volume of 0.5M NaOH to destroyed the ion pair complex and remain Fe^{3+} ion in aqueous basic solution then used spectrophotometric method (thiocyanate method)[10] . The experimentes show the transferred quantity of Fe^{3+} ion to CPL as ion pair determined by stripping method was equal the quantity determined by subtraction remainder Fe^{3+} ion from origin quantity so that in all experimental studies determined the transfer Fe^{3+} to CPL by subtraction method because easyer and faster .

Results and discussion
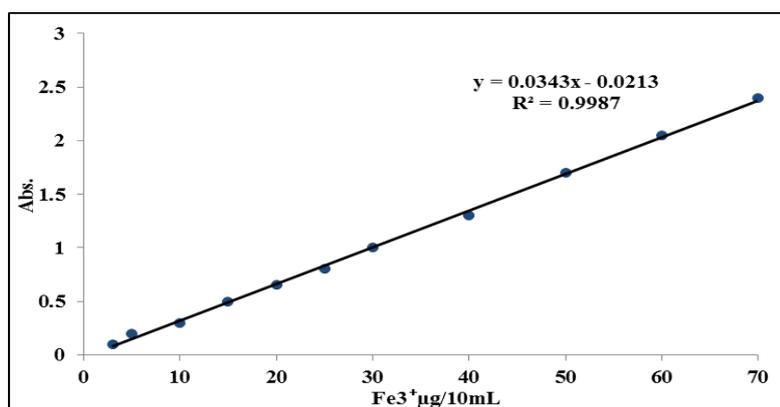
Figure 1. Calibration curve for determination remainder Fe^{3+} ion in aqueous solution

Spectrophotometric Studies

10mL aqueous solution contain 50µg Fe^{3+} ion and 1.0M HCl 5×10^{-2} M NaCl and 1×10^{-4} M DB18C6 shaking the solution for 5 minutes then added 0.5mL 1%TritonX-100 and heating the solution in electro static water but at 85ºC for 15 minutes until complete formation cloud point layer with smaller volume and higher density separated this layer from aqueous solution and dissolved in 5ml ethanol and taken the Absorption UV-visible spectrum for ethanolic solution against blank prepared at the same manner without Fe^{3+} ion the result was illustrated in Figure (2) .
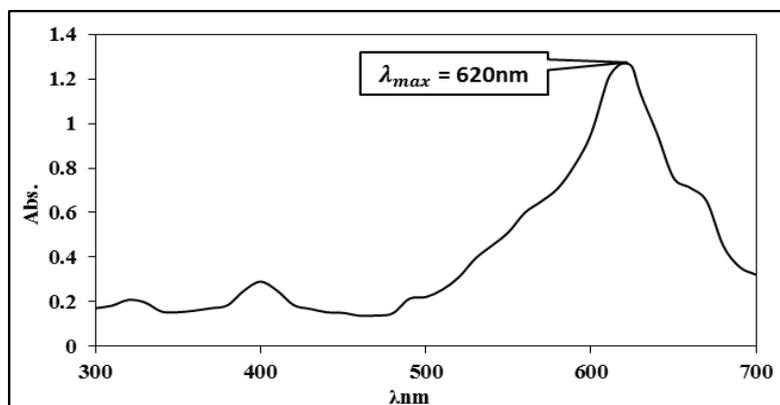

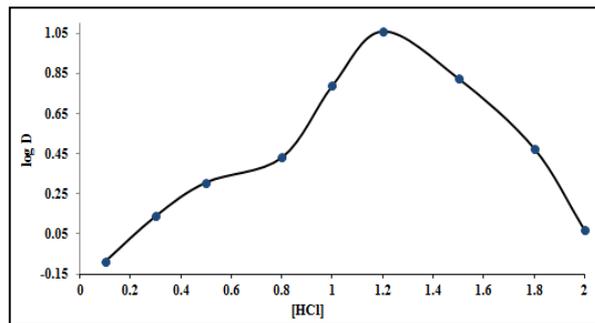**Figure 2. UV-VIS spectrum of the ion-pair complex extracted to cloud point**

The spectrum show maximum absorbance for ion pair complex extracted to CPL was $\lambda_{max}=360$ nm .

Alteration HCl Concentration

10mL aqueous solution each one contain 50µg Fe^{3+} ion rising concentrations of HCl ,5×10^{-2} M NaCl ,1×10^{4}M   DB18C6 shaking all there solutions for 5 minutes then added 0.5mL of 1%Triton X-100 ,heating there solutions in electrostatic water bath at 85ºC for 15 minutes until formation CPL ,separate CPL from aqueous solution and follow the procedure detailed in fundamental method ,the results was as in Figures (3,4) .
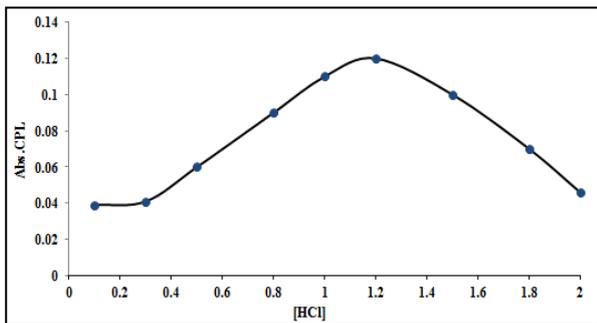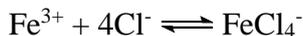

| **Figure 3. Effect of HCl concentration on complex concentration in CPL** | **Figure 4. Effect of HCl concentration on extraction efficiency and D-values** |

The results show 1.2M was the optimum concentration of HCl which is suitable for giving best thermodynamic equilibrium to form $FeCl_4^-$ as well liquid ion exchanye to formation ion pair association such as below.

$Fe^{3+} + 4Cl^- \rightleftharpoons FeCl_4^-$
$DB18C6 + NaCl \rightleftharpoons [Na\ DB18C6]^+;Cl^-$
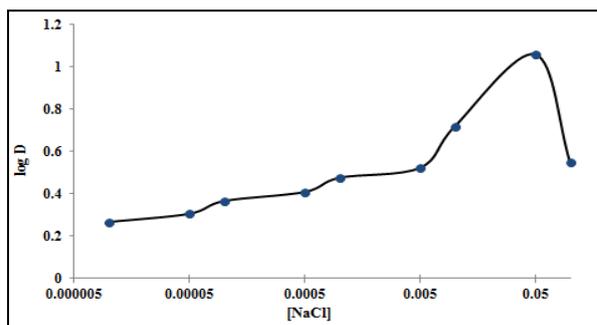$[Na\ DB18C6]^+;Cl^- + FeCl_4^- \rightleftharpoons [Na\ DB18C6]^+;\ FeCl_4^- + Cl^-$

Any concentration less than optimum not allow to reach thermodynamic equilibrium and decrease extraction efficiency undoubtedly decline absorbance and D-value but any concentration more than optimum value effect to decline absorbance and D-value also because increase dissociation equilibrium and increase the species $H_9O_4^-$, $FeCl_4^-$ which being stable with increase acidity of solution and minimizing ion pair complex formation and extraction .

Variation NaCl Concentration

Extracted 50µg Fe^{3+} ion from 10mL aqueous solution in presence 1.2M HCl and rising concentrations form NaCl 1×10^{-4} M DB18C6 , shaking these solution for 5 minutes then added 0.5mL 1%TritonX-100 and heating these solutions in electrostatic water bath at 85ºC for 15 minutes until formation CPL separated and dissolved in 5ml ethanol the complex as detailed in fundamental method , the results shows as in Figures (5,6) .
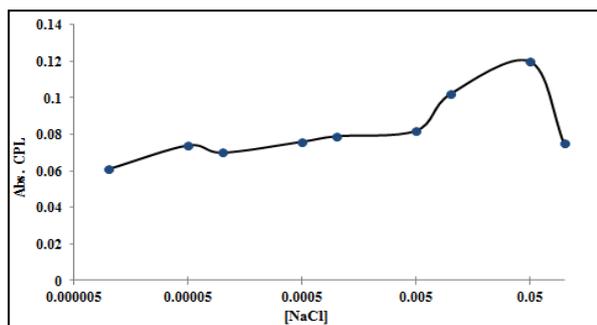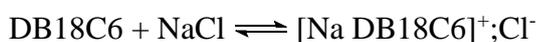
Figure 5. Effect of NaCl concentration on formation and stabilit of liquid ion exchanger


Figure 6. D=F[NaCl]

The results show 5×10^{-2} M NaCl was optimum value appear higher extraction efficiency because effect to reach thermodynamic equilibrium for formation ion exchanger . with high concentration and stability as bellow

$$DB18C6 + NaCl \rightleftharpoons [Na\ DB18C6]^+;Cl^-$$

This formation and stability help to increase extraction of $FeCl_4^-$ by liquid ion exchang ,any concentration less than optimum value dicreare concentration and stability of liquid ion exchanger $[NaDB18C6]^+;Cl^-$ and reflect decline in extraction efficiency ,but any concentration more than optimum value decrease extraction efficiency also because increase dissociation equilibria by effect of mass action law and Le Chatelier prineiple .

Changing DB18C6 Concentration

10mL aqueous solution contain 50µg Fe^{3+} ion and 1.2 M HCl ,5×10^{-2}M NaCl ,different concentrations of DB18C6 shaking these solutions for 5 minutes and then added 0.5mL 1%TritonX-100 after ward heated these solutions in electrostatic water bath at 85ºC for 15minutes after complete formation CPL separated and dissolved in 5ml ethanol there complete as in the procedure detailed in fundamental the results was as in Figures (7,8) .
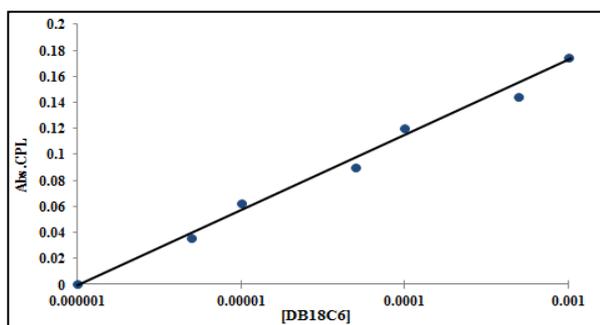
**Figure 7. Increasing complex formation with increasing DB18C6 concentration**
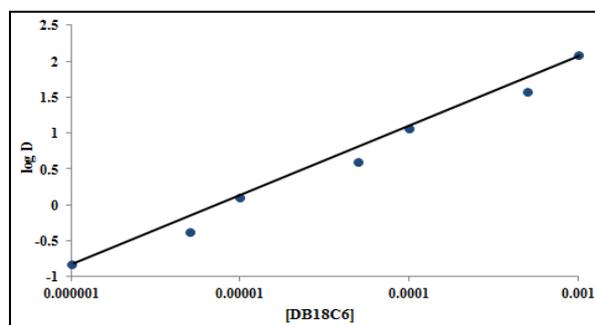
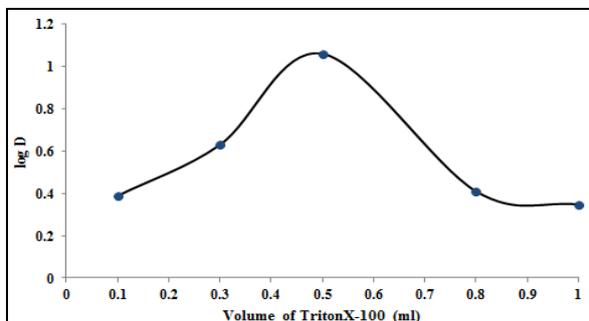**Figure 8. Increasing extraction efficiency and D-value with increasing DB18C6 concentration**

The results show there is linear relation for effect of DB18C6 concentration on absorbance and D-values which is mean increasing extraction efficiency as a function for DB18C6 concentration .

Fluctuation TritonX -100 Volume

Extracted 50µg Fe^{3+} ion from 10mL aqueous solution at optimum condition in presence different volume of 1%TritonX-100 according to procedure detailed in fundamental method the results as in Figures (9,10) .
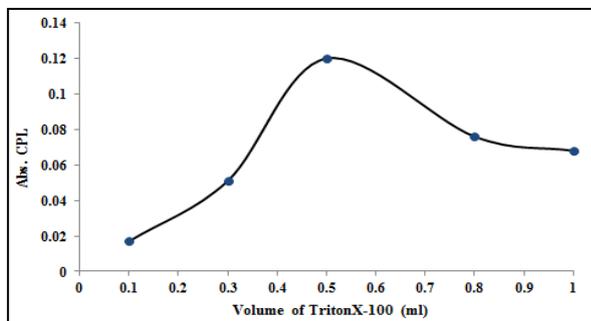
Figure 9. Effect of surfactant volume on ion pair transfer and absorbance


**Figure 10. Effect of surfactant volume extractio efficiency and D-value**

The results show 0.5mL was the optimum volume which is more suitable for higer extraction efficiency because this volume opplicability form good cloud point layer hold larger quantity of ion pair complex ,any concentration less than optimum not enough to form this layer effect to decrease extraction efficiency ,as well as any volume more than optimum increasing diffusion of micelles and decline extraction efficiency also.

Thermodynamic

Extracted 50µg Fe^{3+} ion from 10ml aqueous solutions at all optimum conditions according to procedure detailed in fundamental method except heating at different temperatures the results was as in Figures (11,12) .
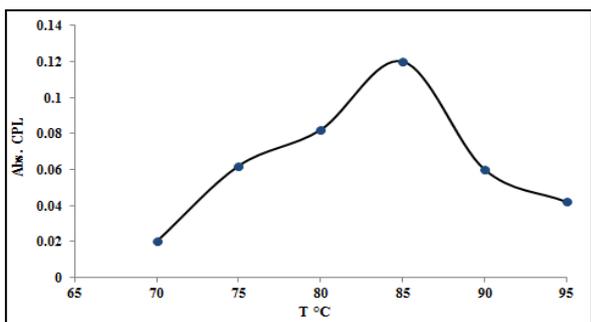
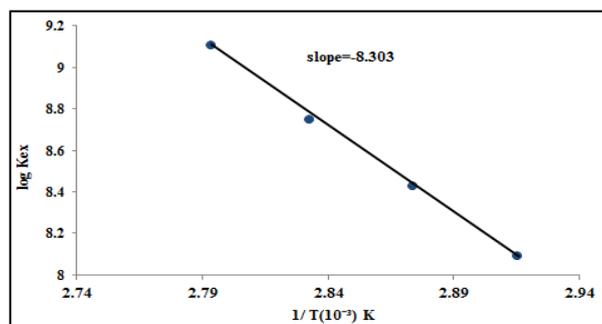**Figure 11. Effect of temperature on concentration of complex extraction and absorbance**
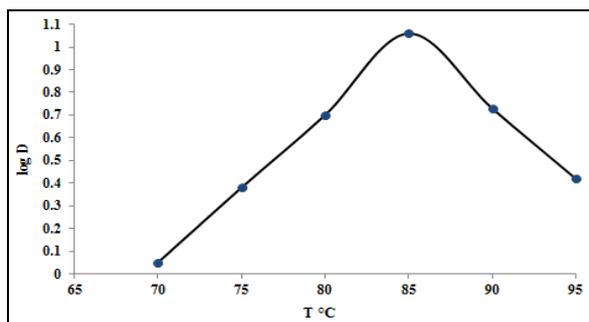
Figure 12. Effect of temperature on extraction efficiency and D-values

After caculated extraction constand temperature by application relation below .

$$K_{ex} = \frac{D}{[Fe^{3+}][DB18C6]}$$

ploted log K_{ex} against 1/T K , the result was as in figure 13 .

Figure 13. Effect of temperature on extraction constant value

From slope of straight line relation in figure (13) and thermodynamic relation calculate thermodynamic .

$\Delta H_{ex} = 0.159$ KJ mol^{-1}

$\Delta G_{ex} = -62.43$ KJ mol^{-1}

$\Delta S_{ex} = 174.83$ J mol^{-1} K^{-1}

Results show extraction of Fe^{3+} by cloud point extraction method was endothermic as well as the very small value of enthalpy offer the two ions of ion pair complex is closely near to each other where as the large value of entropy reflect the nature of extraction method in entropic inregion .

Effect of heating time

Extracted 50µg Fe^{3+} ion from 10mL at optimum condition except heating the solutions for different time according to the procedure detailed in fundamental method the results shows in the Figures (14.15) .
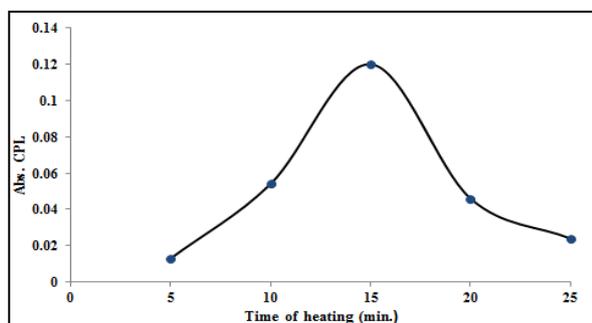
Figure 14. Effect of heating time on ion pair complex to CPL and absorbance
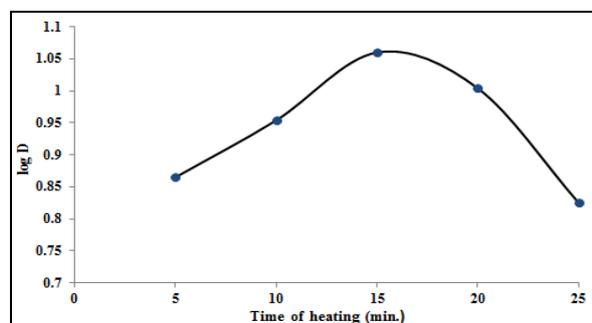

Figure 15. Effect of heating time on extraction efficiency and D- values

The results appear 15 minutes was the optimum heating time which is giving best aggregation for micelles to from CPL at CMC state to from best layer with smallest volume and higher density and layer efficiency for extraction any time less than optimum not suitable for extraction and effect to decline extraction efficiency so that any time more than optimum increase diffusion of micelles and decrease extraction efficiency .

Stoichiometry

To limitation the more probable structure of ion pair complex for Fe^{3+} ion extracted to CPL followed two spectrophotometric accurate method which is named . slope analysis method and
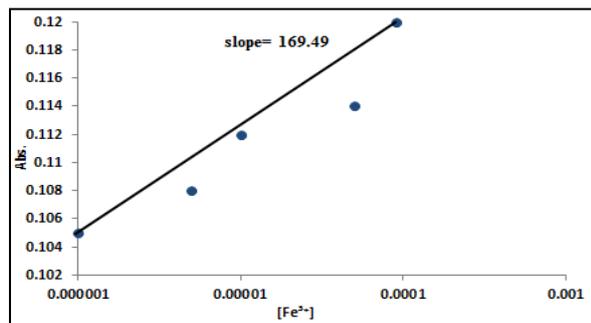
slope ratio method by application the procedure detailed in fundamental method. Where as the first method involved extracted Fe^{3+} at different concentration of DB18C6 at latter plot absorbance of log D against log[DB18C6]. The second method involved to experiments one extracted different concentration of Fe^{2+} in 10mL under all optimum condition at latter plot absorbance against molar concentration of Fe^{3+} ion by different concentration of DB18C6 at latter plot absorbance against molar concentration of DB18C6 .The results was as in Figures (16,17,18) .
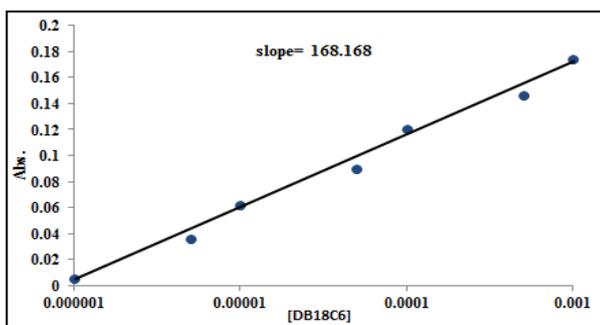
Figure 16. Slope analysis method
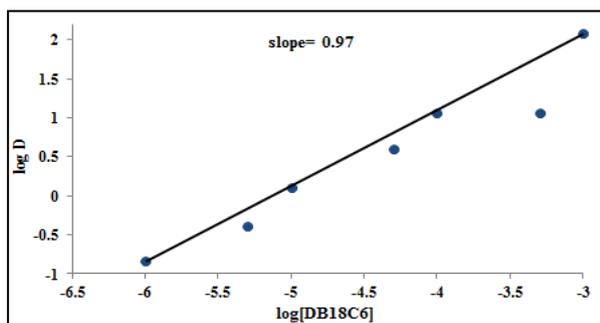
Figure 17. Effect of DB18C6 concentration on absorbance	**Figure 18. Effect of Fe^{3+} ion concentration on absorbance**

Slope ratio = 0.99

The results show more probable structure of ion pair complex extracted was 1:1
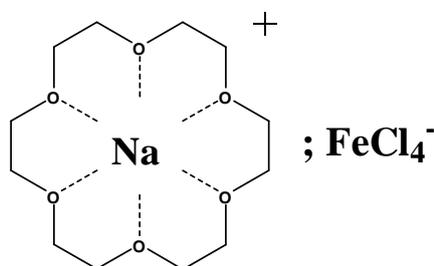
Grown ether kind effect

Extracted 50µg Fe^{3+} ion from 10mL aqueous solution at optimum conditions by different crown ethers and cryptand C222 according to procedure detailed in fundamental method the results was as in Table (1) .

Table 1. Effect of type extractant

Extractant	Abs.360nm	D
12C4	0.015	3.36
15C5	0.077	8.54
18C6	0.186	20.82
DB18C6	0.120	11.5
DB24C8	0.103	9.64
C222	0.08	7.35

The results show 18C6 giving highest extraction efficiency more than DB18C6 because phenyl group effect to decreanr electron density on oxygen atom by effect of with drawing. Which is increasing stability of ion exchanger [Nacrow]$^+$;Cl$^-$ in addition to agreement of Na$^+$ diameter with cavity size of crow ether and cage of cryptand .

Electrolyte effect

Extraction 50µg Fe^{3+} ion from 10mL aqueous solution at optimum condition and in presenter 0.05M different electrolytes according to procedure as mentioned earlier the results was as in Table (2) .

Table 2. Effect of electrolyte

Electrolytes	Abs.360nm	D
LiCl	0.110	6.692
NaCl	0.120	11.500
KCl	0.275	24.000
NH$_4$Cl	0.154	2.333
MgCl$_2$	0.257	19.000
CaCl$_2$	0.255	15.666
SrCl$_2$	0.115	8.285
BaCl$_2$	0.081	5.666

Extraction efficiency differ by different electrolyte salt of alkali and alkali earth elements because metal cations of there salts giving different agreement between metal cation and cavity size of DB18C6 The results show KCl giving higher distribution ratio with higher agreement between K$^+$ and DB18C6 .

Effect of interferences

Extracted 50µg of Fe^{3+} ion from 10mL aqueous solution of optimum condition in presence 0.05M some interferences according to procedure detailed in fundamental method the results was as in Table (3) .

Table 3. Effect of interferences

Interferences	Abs.360nm	D
Cd^{2+}	0.012	7.333
Hg^{2+}	0.106	8.090
Ni^{2+}	0.070	9.000
Cr$_2$O$_7^=$	0.076	10.111
MnO$_4^-$	0.103	6.692

The results show metal latiom and anions used all the giving interferences but in different degree because each one need specific optimum condition as well as there is appear different behavior in aqueous solution .
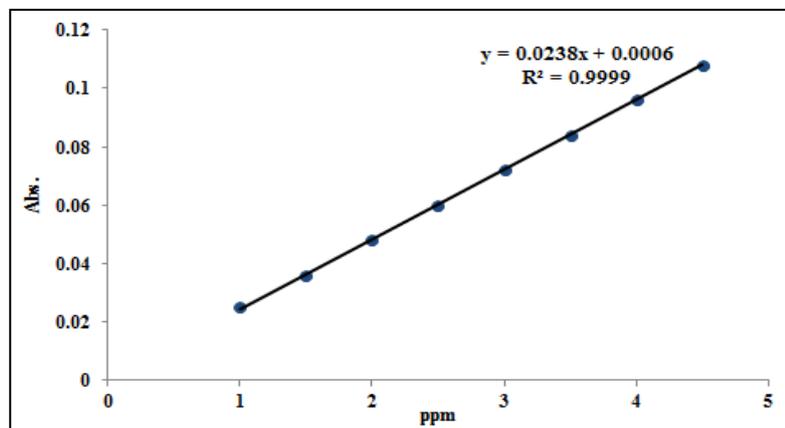
Spectrophotometric determination

Figure 19. Calibration curve for spectrophotometric determination of Fe(III)

Table 3. Determination of Fe(III) in various samples

S. No.	Sample	Fe(III)
1	Soil Shatt al-Kufa	23
2	Agriculture soil of Al.Mishkab	
4.5		
3	Orange	5
4	Fragaria x ananassa	5.8
5	Apiumgraveolens	27
6	Solanum lycopersicum	7.2
7	Allium cepa	21
9	Lens culinaris	38.5
10	Chickens meat	12

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