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Sensitive Liquid Ion Exchange For Accurate Separation And Determination Mn(VII)

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Abstract

Liquid ion exchange method one of the important applications of solvent extraction to separation and determination of metal anionas ionpair association complexes, used very sensitive and accurate method for separation and determinationof Mn^{7+} an MnO_4^-, spectrophotometric study of ion pair association of MnO_4^- with 3-Aminophenol extracted to the organic phase → show up wave length of maximum absorbance was $\lambda_{max=}$449nm,all studies about optimum condition appear higher extraction efficiency need 0.5M HCl, 50 µg/5mLof MnO_4^-, 1x10^{-4}M 3-Aminophenol , 15min shaking time, the research involve another studies about influential parameters.

Keyword: Liquid Ion exchange, solvent extraction, 3- Aminophenol, ion pair association complex

Introduction

Manages is one of the elements in biochemistry that plays as co-factor several anzymes[1]. Extraction Mn(III) and Ni(II) asion pair association $[MnO_4]^-$ and $[NiCl_4]^=$ as chloroanion complexes extracted by used 2-[α-naphthol azo]-4,5-diphenyl imidazole in some different vital samples[2]. 2-(2-hydroxy naphtha-1-yl azo]-pyridin is agood chromogenic reagent for the separation and determination of Fe(III), Mn(II), Co(II), Ni(II) and Cu(II) ions in aqueous buffer solution and the procedure was applied on natural samples [3].Determination of Mn using CPE extraction developed with spectrophotometry by formation of an ion association complex between brilliant green MnO_4^- in presence of 1% Triton X-100 and complex was extracted at optimum conditions on extraction efficiency such as metal ion concentration, Organic reagent and thermodynamic by using ethanol as asolvent[4]. Liquid ion exchange used as indirect method for determination Cd(II) and Hg(II) by sing suitable reagent[5]. By CPE and liquid ion exchange as extracted Pt(II) ion from acidic media and used Janus green in different samples[6].Spectrophotometric

technology is applied with cloud point extraction for determination the number of metalions and studied several effective parameters on extraction[7-18]. (4-hydxoxy phenyl azo)-4-benzene naphthol as organic reagent is used for separation of Mn in acidic media forming an ion pair association complex (MnO_4^-) and used TritonX-100 surfactant[19]. Separate and extract Mn(VII) as [$HPANN^+$; MnO_4^-] by using 3-[(pyridyl azo)]-1-nitroso-2-naphthol via applying liquid ion exchangetechnology with CPE in amedium of HCL and triton X-100 as surfactant, the statistical criteria for the method are LOQ of (0.0260) LOD of (0.0080) and sandell's sensitivity of (72.5×10^{-7}) $\mu g/cm^2$ [20].

Experiment

Instruments

For Spectrophotometric studies and absorbance measurements used double beam UV-Vis spectrophotometer, Biochrom Libra S60, Altravard Bio Science Company, Cambridge (UK), as well as for exact weightused electrical balance , A&D company Limited , Dool, CE, HR200, made in Japan., so that used pH-meter (WTW. Listed / 8693, Laboratory Equipment, E 163694 , CE, made in Germany), for heating the solutions used Electrical Water bath (Hamburg-90) England.

Chemicals & solutions

All chemicals are obtained from certified companies, and used without farther more purification, stock solution of Mn(VII)asMnO_4^- in (1mg/mL) concentration prepared by dissolved 0.2877 g of $KMnO_4$ in 100ml Distilled water in volumetric flask.

For spectrophotometric determination of Mn(VII) in aqueous solutions prepare special solution it's composition 75g of Mercuric sulfate $HgSO_4$ dissolved in 100 mL Concentrate Nitric acid HNO_3 , and 200Ml distilled water with 200 mL of 85% phosphoric acid solution H_3PO_4 , and 0.03 g Silver nitrate $AgNO_3$, and complete the solution by distilled water to 1 liter volume in volumetric flask.

As well as prepare solution of organicreagent (3- Amino phenol) in $1x10^{-2}$M concentration by dissolved 0.0109 g in l00mLchloroform.

Comprehensive method

By taken aqueous solution 5 mL in volume contain optimum quantity of Mn^{7+} as MnO_4^- and exact concentrations of hydrochloric acid HCl, afterward add 5 ml organic solution of 3-Amino phenoldissolved in chloroform, then shake the solution for fixed time in electrical

shaker, at latter separate the organic phase from the aqueous phase, and measure the absorbance of the organic phase against organicsolution as blank at λ_{max} of Ion pairassociation complex in organic solvent, But the aqueous phase treated according to special solution spectrophotometric method [21], to determination the remain quantity of Mn^{7+} in aqueous solution from calibration curve in Fig2, after extraction, then subtraction the remain quantity of Mn^{7+} from the original quantity in aqueous solution to determine the transfer quantity of Mn^{7+}intoorganic phase to formation ion association complex, in the end calculate distribution ratio(D)

$$D=\frac{[Mn^{+7}]org}{[Mn^{+7}]ag}$$

Results and Discussion

Spectrophotometer Study

Prepare 5 mL aqueous solution contain 50 µg of Mn^{7+} as $MnO4^-$ with 0.5 M Hydrochloric and HCl, added to this solution 5 ml solution of 3-Amino phenol dissolved in chloroform in $1x10^{-4}$ Mshake the solution in electrical shaker for suitable time, then separatedorganic phase from the aqueous phase, and be taken UV-Vis spectrum for organic phase against organic solution of 3-Amino phenol, the spectrum appear obviously in Fig 1.

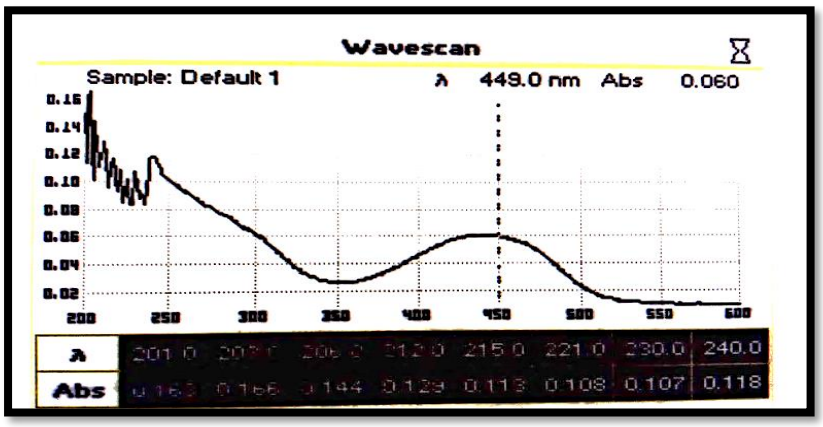
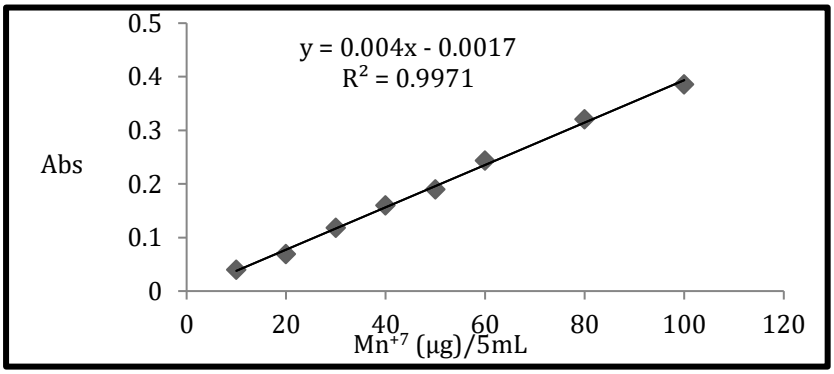


Fig (1): UV-Vis Spectrum for Ion pairassociationComplex of Mn^{+7} as $MnO4^-$ and 3-Amino phenol.

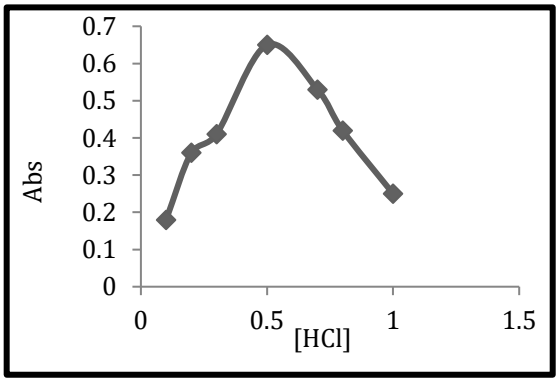
Variation HCl concentration

Preparing a number of aqueous solution 5 mL involume contain 50µg Mn^{7+}as MnO_4^- , added to each solution 5 mLorganic solution of 3- Amino phenol dissolved in chloroform and at $1x10^{-4}$ M concentration, then shake the solutions an electrical shaker for suitable time,

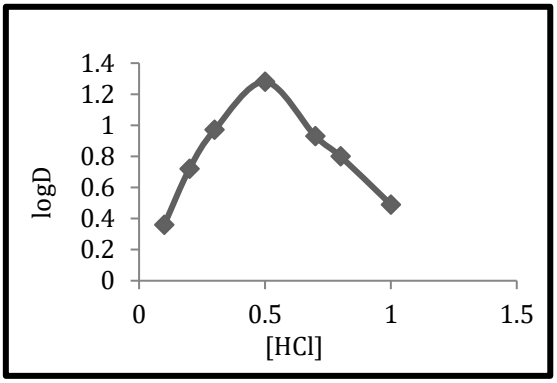
eventually separated the organic phase from the aqueous phase and complete the experiment as in comprehensive method the results were an in Fig 3,4



Fig(2): Calibration curve for determination Mn^{7+}in aqueous solution by special solution spectrophotometric



Fig(3): Effect of HCl Concentration on formation and stability of Ion pair association complex



Fig(4): Effect of HCl concentration on extraction efficiency and D-value

The results illustrate 0.5M HCl in the optimum concentration of HCl to give higher extraction efficiency, because this concentration give the faster formant relating to the on pair association complex with higher concentrations goanna transfer into organicphase with greater stability .

Variation Metal ion Concentration

Necessary supply many 5mL aqueous solutions contain different quantity of Mn^{7+} as MnO_4^-, added to each solution 5 mL organic solution of 3-Amino phenol dissolved in chloroform in $1x10^{-4}$M All these solutionshacked in electrical shaker for optimum time, in the end separate organicphase from aqueous phase, then complete the work as in comprehensive method, the results were as in Fig 5,6.

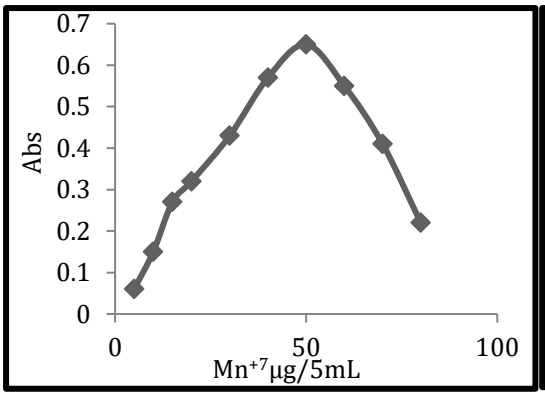


Fig5: Effect of metal ion concentration on the Formation and stability of ion pair association complex extraction to organ phase

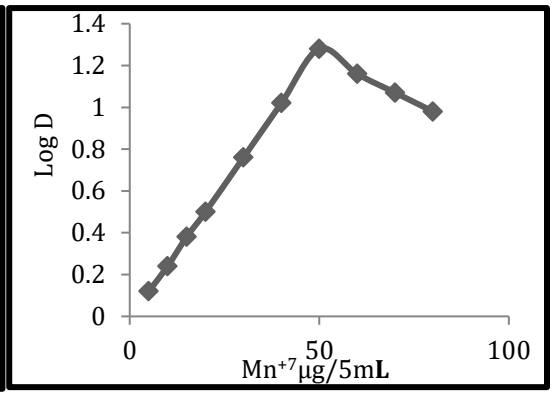
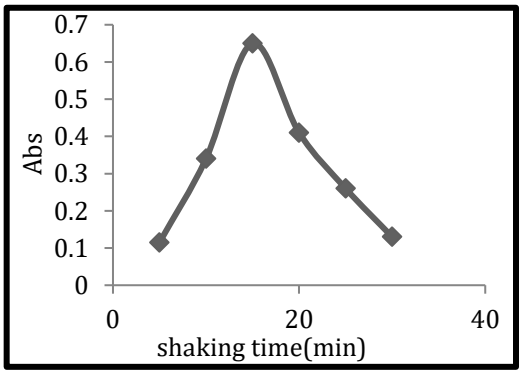


Fig6: Effect of metal Ion cone on extraction efficiency and D-value.

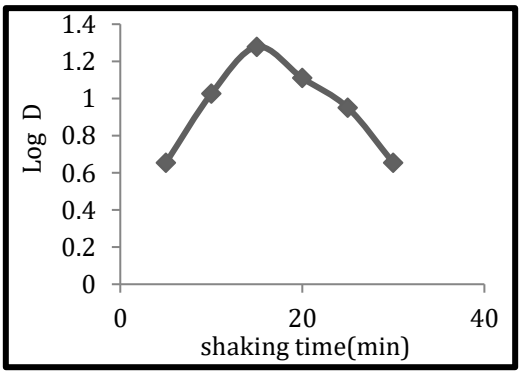
The results show up 50 µg $Mn^{7+}$was the optimum concentration give higher extraction efficiency because this concentration give format rate for thermodynamic relative to formation Ion pair complex extracted to organic phase so that higher concentration, because this results give good evidence that the metalionconcentration consider as thermodynamic data.

Effect of shaking time

Many aqueous Solutions 5 mL in volume contain 50µg Mn^{7+}as $MnO_4^-$and 0.5 M hydrochloric acid HCl, added to each solution 5 ML organic solution of 3- Amino Phenol dissolved in chloroform in $1x10^{-4}$M, shake all these solutions for different Time in electrical shaker , eventually separate organic phase from aqueous phase and complete the woke as in comprehensive method, the results were as in Frig 7,8 .



Fig(7): Effect of shaking time on the formationand stability of ion pair associationcomplex extracted



Fig(8): Effect of shaking time on extraction efficiency and D-value

The results demonstrate 15 min. was the optimum Shaking time give higher extraction efficiency and maximum concentration Ion pair association complex extracted into organic phase, because shaking time represent kinetic side of extraction methodsliquid ion exchange.

Effect of organic solvent

A number of 5 mL aqueous solutions prepared each one contain 50 µg on Mn^{7+} $MnO4^-$ and 0.5 M of HCl , added to these solutions 5 mL of organic solution to 3- Amino phenol dissolved in different organic solvents at $1x10^{-4}$M concentrations, shake these solutions for 15 min. in electrical shaker in the end separate the organicphase from the aqueous phase and complete the experiment an in comprehensive method the results were as in Table1.

Table (1): Effect or organic solvent on extraction efficiencyof Mn^{7+}as MnO_4^- On according to Liquid in exchangewith 3-Amino phenol.

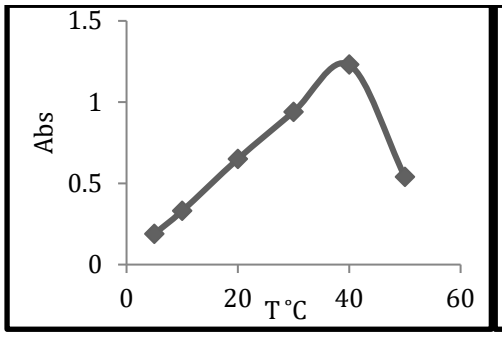
Organic solvent	Abs. of organic phase at λ_{max}=449nm	D
Nitrobenzene	0.46	11.5
Amyl alcohol	0.81	31.7
Benzene	0.73	21.8
Toluene	0.79	27.4
Dichloromethane	0.55	16.5
1,2-Dichluroethan	0.70	20.2
chloroform	0.65	19.0

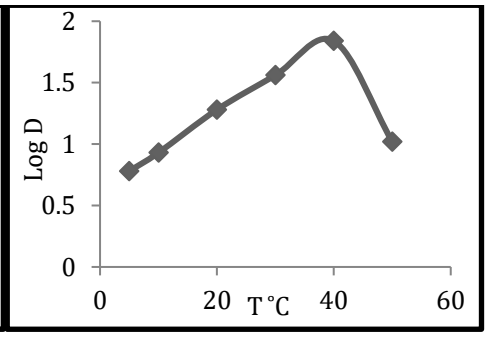
The results show up there is different extraction efficiency with different organic solvent because the variation behavior for each organic solvent which is participate in the formatIon pair association complex, as well as there is not any linear relation between D-values and dielectric constant of organic solvent , that is prove there is not any effect for polarity on extraction efficiency of Mn^{7+} with 3- Amino phenol an ion association complex .

Thermodynamic study

In order to seen Effect of temperature on the extraction efficiency take a number of 5 mL aqueous solution each one contain 50 µg Mn^{7+} as $MnO4^-$with 0.5 MHCl , added to each solution 5ml of 3- Amino Phenol solution dissolved in chloroform at $1x10^{-4}$M concentrations, shake the solutions for 15 min at different temperature eventually separate the organic

phase from the aqueous phase and completeness the work as detailed in comprehensive method the results demonstrate in Fig 9, 10.

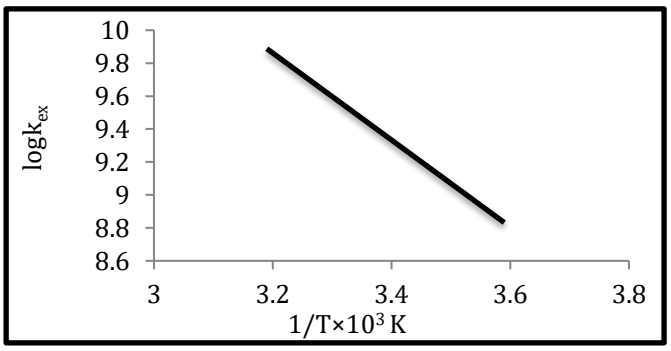




Fig(9): Effect of temperature on Formation and stability or ion pairComplex extracted association

Fig (10): Effect of temperature on Extraction efficiency and D-value

These results show up extraction method liquid Ionexchange for Mn^{7+} as $MnO4^-$ by using of 3-Amino phenol was endothermic relation give maximum extraction efficiency at 40°CAfterward calculate extraction constant k_{ex} from D-values at each temperature the results give straight line relation in Fig11, with slope equal to (-2.65), and from the slope value and thermodynamic relations calculate thermodynamic data an illustrated below.



Fin (11) = Effect of temperature on extraction Constant Value.

ΔH_{ex} = 15.883 k J mol^{-1}

ΔG_{ex} = -53.217 k J mol^{-1}

ΔS_{ex} = +220.77 J $mol^{-1} k^{-1}$

The lower value of enthalpy ΔH_{ex} reflect the large convergence of ion pair association complex structure, so that the large value of entropy ΔS_{ex}demonstrate this method of extraction is entropic in region.

Stoichiometry

In order to see the composition of ion pair association complex extracted of Mn^{7+} as $MnO4^-$ with 3- Aminophenol used two spectrophotometric methods, Slope analysis and slope ratio methods at optimum conditions the results demonstrated in

Figs: 12,13,14

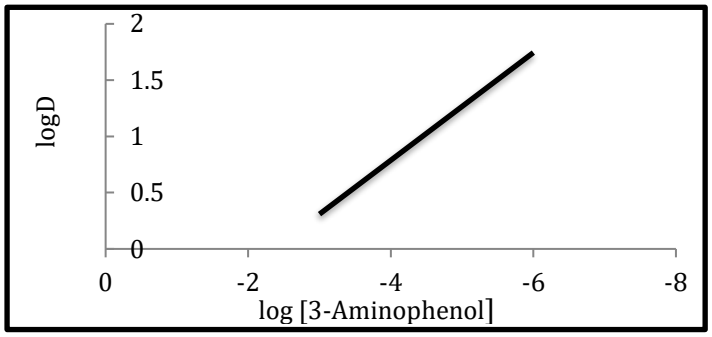
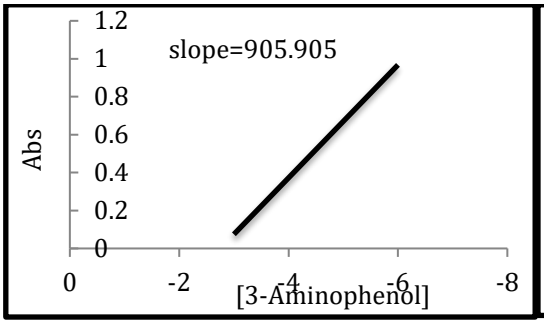
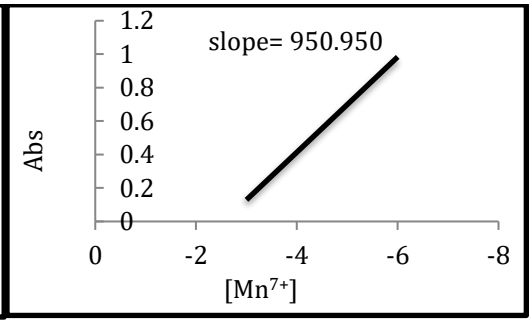


Fig:12 slope analysis method





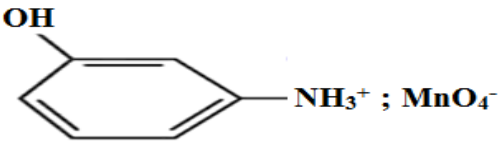
Fig(13): Effect of 3-Aminophenol Cons. on formation and stability of ionon pair association Complex

Fig(14): Effect of Mn+4 concentration formation and stability of ion pair association Complex

slope ratio = $\frac{905.905}{950.950}$ = 0.953

These results appear the composition of ion pair association Complex extracted into organic phase was 1:1

$[H\text{- 3 Aminophenol}]^+$; MnO_4^-



Ion pair association complex of Mn^{7+} with 3 Aminophenol

Electrolyte effect

A Number of 5 mL aqueous solution was prepared each one contain 50 µg Mn^{7+} as MnO_4^- and 0.5M HCl with existence 0.01M of strong electrolyte , added to each Solution 5ml organic solution of 3-Aminophenol dissolved in chloroform, shake all these solutions for 15 minutes in electrical shaker, In the end separate organic phase from the aqueous phase and complete the experiment as in comprehensive method the results illustrated in Table (2)

Table (2): Effect of Electrolytes on extraction efficiency of Mn^{7+}as $MnO4^-$.

0.01M Electrolyte	organic phase Abs at λ_{max}=449nm	D
LiCl	1.150	55.41
NaCl	0.940	42.56
KCl	0.853	33.86
NH_4Cl	0.766	27.13
$MgCl_2$	0.980	49.29
$CaCl_2$	0.743	25.64

The results show up existences of electrolyte in the aqueous phase side by side to Mn^{7+} effect to increase extraction efficiency, because the electrolyte impact to decrease polarity anddielectric constant of aqueous solution, that is mean farther destroy hydration shell on MnO_4^-, and increasing formation and stability of ion pair association complex extracted into organic phase .

Effect of Methanol

Anumber of 5 mLaqueous solution prepared each one contain 50 Mn^{7+} as MnO_4^-and0.5M HCl with existencedifferent concentrative of methanol CH_3OH, added to each solution 5mL of organic solution of 3- Aminophenol dissolved in chloroform , Shake all these solution for 15 minutes in electrical shaker, In the end separate organic phase from aqueous phase continue as in comprehensive method, the results were as in Figs 15,16

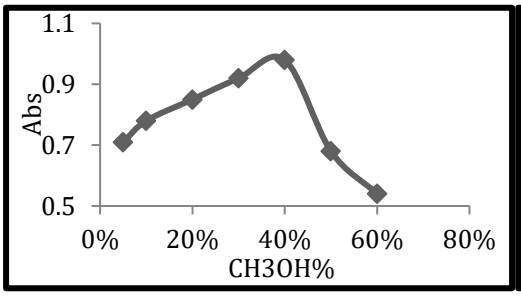


Fig (15) : Effect of methanol and stability of Ion pair association complex extracted

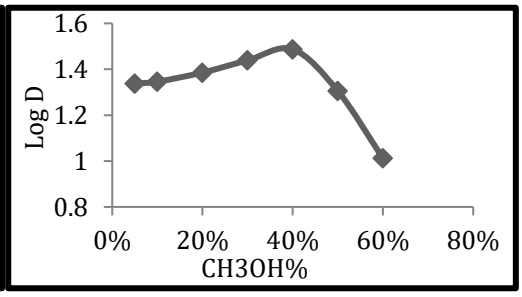


Fig (16): Effect of methanol on extraction efficiently and D-value

The results show up existence methanol in aqueous phase with metal Ion Mn^{7+} as MnO_4^- effect to increase extraction efficiency, and This efficiency increase with increasing percentage of methanol in aqueous solution to give maximum extraction efficiency in 40% methanol , because methanol in aqueous solution effect to decrease polarity and dielectric constant of water, and that is effect to destroy the hydration shell or metal anion MnO_4^- and increase the rate of thermodynamic formation of ion pair association complex, as well as this behavior increase with increasing percentage of methanol to reach maximum at 40% methanol.Increasing percentage of methanol more than 40% effect to decline extraction efficiency to a large degree and in this case transfer 3-Aminophenol to the aqueous solution and decrease formation of ion pair associations complex extracted into organic phase

Interferences effect

Prepare many 5ml aqueous solutions each one contain 50 µg Mn^{7+} as MnO_4^-,, and 0.5 MHCl with existence0.01M of different metal anions, added to each solution 5mL of organic phase of 3-Aminophenal dissolved in chloroform, shake all these solution for 15min in electrical shaker, eventually separate organic phase from aqueous phase, and complete the work as in comprehensive method. The results were demonstrated in Table 3.

Table (3): Effect of interferences on extraction efficiency of Mn^{7+} as MnO_4^- in by LiquidIon exchange with 3-Aminophenol

0.01M interferences	Organic phase Abs at λ_{max}=449nm	D
$Cr_2O_7^=$	0.35	8.30
NO_3^-	0.54	16.4
MoO_4	0.43	12.6
WO_4	0.38	10.2
ClO_4	0.26	6.70

The Results illustrated all these metal anions give decline in extraction efficiency of Mn^{7+}as MnO_4^-, because all there metal anions considered an interferences, that is mean all these anions participate to formation Ion pair association complexes with 3-Aminophenol, and this behavior effect to consumption some of HCl and 3-Aminophenol and deline there concentrations less than optimum value which is necessary to extraction Mn^{7+} as MnO_4^- with higher extraction efficiency, and because each anion have different behavior in aqueous solution gives different effect.

Spectrophotometric Determination manganese

The manganese was determination spectroscopically according to the general method of extraction using suitablemasking agent in different environmental and vital samples ,The calibration curve is shown in Fig17,Analytical parameters of the extraction method in the Table4.

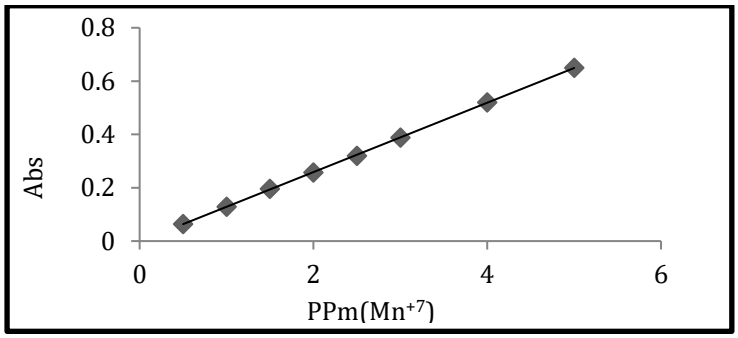


Fig17: Calibration curve of Mn(VII)

parameters	Mn(VII)
λ_{max}(nm)	449
Parameter linearity (ppm)	(0.5-5)
Molar absorptivity (L.mol^{-1}.cm^{-1})	7466
LOD(ppm)	1.031
LOQ(ppm)	3.125
Sandell's sensitivity(µg/cm^2)	7.576×10^{-3}

Table4: Analytical parameters of manganese

The samples were prepared by according to wet digestion method [22] the adopted method and at optimal conditions, and through the absorption values, the manganese ion was determined in the different samples. The results are shown in Table 5.

Table 5 : Manganese content (ppm) in different samples

No	Sample	Applied method (ppm)	FAAS method (ppm)
1	Agricultural soil	4.200	2.110
2	non-agricultural soil	2.410	2.380
3	cucumber	2.210	2.130
4	tomatoes	1.990	1.920
5	celery	0.540	0.510

6	Beans	2.440	2.410
7	Fish	2.800	2.700
8	Euphrates river water	0.180	1.720
9	drinking water	0.021	0.200

Conclusion

1. Liquid ion exchange method special method for separation and determination metal anions only.

2. Acidic medium of hydrochloric acid HCl help to change organic reagent into ion exchanger .

3.It's possible to usedelectrolyte salt the increase extraction efficiency and rising sensitivity of determination metal anion.

4. It's possible also to used fixed percentage of methanol in the aqueous solution alone or with electrolyte to farther increasing sensitive determination of any metal anion.

5- When the extraction method is endothermic we are could be confirmed the extraction in temperaturehigher than room temperature to get high extraction efficiency.

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