Microamount determination and extraction of Mn(VII),Ni(II) as anion in different Vital and environmental samples with 2-[α-naphthol azo]-4,5-diphenl imidazole[α-NADPI]

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Abstract

Extraction Ni(II) as anion chloro complex $[NiCl_4]^{=}$ and Mn(VII) as $[MnO_4]^{-}$ as ion pair complex extracted to organic phase by un organic reagent 2-[α-naphthy azo]-4,5-diphenyl imidiazole [α-NADPI] as complexing agent , with definition all parameters effect on extraction activity such as, hydrochloric acid concentration, metal ion concentration, shacking time, as well as stoichiometry show ion pair complex extracted was 1:1:1. Thermodynamic study appear the complexation reaction was endothermic with both anion $[NiCl_4]^{=}$ and $[MnO_4]^{-}$, in addition to used this method to determination Ni(II) and Mn(VII) in different environmental and vital sample.

Key words: Liquid ion exchange, solvent extraction.

Introduction

Liquid ion exchange is one of important application of solvent extraction method for extraction of anion species as ion pair complexes. Extraction of Gold from acidic aqueous solution as Chloro complex anion $AuCl_4^-$ by different organic organic reagent include crown ethers, cryptand. Imidazol derivatives and high molecular weight amine dissolved in Chloroform, determined all optimum condition as well as studied organic solvent effect, stoichiometry for complex extracted and thermodynamic[1]. Liquid ion exchange method for extraction $CrO_4^{=}$, MnO_4^- and $FeCl_4^-$ by using high molecular weight amines Diphenyl amine,Triethanol amine dissolved in Chloroform, this study include determine HCl concentration for extraction by conversion amines to ion exchanger, as well as study all condition for extraction as well thermodynamic and organic solvent effect[2]. Separation and extraction of Chloroanion complexes of Zn(II), Cd(II) and Hg(II) by using different organic reagent α-NA,4-ABA, 4-CMePADPI and C222 by liquid ion exchange method. This study appear HCl concentration in aqueous solution, consider as effective parameter by conversion organic reagent into liquid exchanger, then studies all optimum conditions and stoichiometry, thermodynamic and organic effect solvent[3]. Extraction Zn(II) as $Zn(SO_4)_2^{=}$, $ZnCl_4^{=}$, $ZnCl_3$- according to liquid ion exchange, with determination all optimum condition[4]. Hg(II) was separated from 0.5M acetic acid by Aliquid 336S as liquid ion exchange, and extracted species was $[2R_4N^+:Hg(OAC)_4^{=}]$, this method suitable for separation from Zn, Cd, Ni, Co, Cu, Bi, Mn[5]. Different new liquid ion exchange[Etheylene bis(trioctyl phosphonium)](EBTOP) used for extraction of Pb(II), Cu(II), Cd(II), Zn(II) as well as Fe(III) and In(III)[6]. Zn, Cd and Hg were extracted from

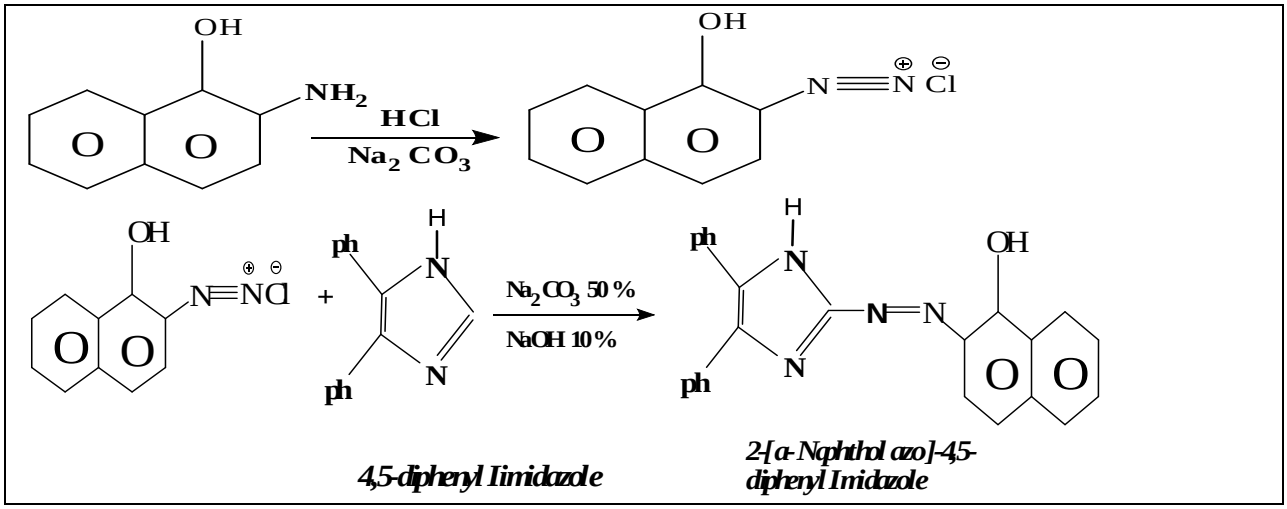
chloride and sulphate media by solvation and liquid ion exchange methods and studies the extracted species[7]. Hg[II] extracted as chloro complexes anion by different high molecular weight amines and tetra ammonium salts with distribution the effective parameters and extracted species[8]. Kostova and Kamburova studied the optimum conditions for spectrophotometric determination of Mn(II) as ion pair complex with crystal Violat(CV) as complexing agent as well as this study demonstrate more probable structure of ion pair complex extracted was 1:1 MnO_4^- : CV^+ [9]. Another study for Kostenko to spectrophotometric determination Pb(II) in dranking water in solid phase spectrophotometric determination by used chromazurol S as ion exchanger and this method give sensitivity (0.02) [10]. Mohsen and et el used haphthalene methyl trictyl ammonium as adsorption layer for micro amount determination of Cd(II), Pb(II) as $PbI_4^=$, $CdI_4^=$ after that used FAAS for determination, as well detection limit for this methanol was 0.42 ngL^{1-} for Cd(II) and 0.072 ngL^{-1} for Pb(II) [11]. By two layer method (ABS) contain many cations Ni^{+2}, Cs^+, Hg^+, Fe^{+3}, Cd^{+2}, Co^{+2}, Eu^{+3} with (PEG 2000 $NH_4)_2SO_4$ by used four azo-derivalives for extracted Hg^{+2} as anion complex, this study giving high distribution ratio with $Co^{=2}$, Ni^{+2}, Fi^{+3}[12].

Instruments

All spectrophotometric measurements and absorbance were registered by using a double beam (UV-Vis) spectrophotometer shimadz UV 1700 (Japan) and a Single beam (UV-Vis) spectrophotometer TRIUP international corp. TRUV 74,S (Italy), IR-Spectra for the complexes were recorded by using FTIR S 8400 (England). Skaker used HY-4 vibrator with AD just about speed multiple(Italy).

Materials

All chemicals used provided from Fluka and Merck such as nickel chloride six hydrate, ammonia,dimethyl glyoxime, potassium persulphate, , reagent2-[α-naphthol azo]-4,5-diphenl imidazole [α −NADPI]synthesized as in privates study [13]. , potassium permanganate , chlorobenzene ,methanol.



Fig(1) : reagent2-[α-naphthol azo]-4,5-diphenl imidazole [α –NADPI]

General extraction procedure

Shaking fixed volume of ligand solution with HCl solution at optimum concentration in order to conversion ligand to liquid anion exchang .Then shaking anion exchanger formed with aquueous solution contain analyte metal as $NiCl_4^-$ or MnO_4^- for suitable time to compet equilibrium of ion exchange, and then separate two layers and measure the absorbance of organic phase contain ion pair complex extracted against organic reagent at λ_{max}. as well as calculate distribution ratio value by determine remaining quantity of metal in aqueous solution after extracted and quantity transferred to organic layer by appliction spectrophotometric method suitable for each metal.

Results and Discussion

UV-Vis spectrum for [α −NADPI] shows maximum absorbance at(λ_{max}= 460nm), but the spectrum of the complex between [α −NADPI] and Nickel(II) as $NiCl_4^=$ giving maximum absorbance at (λ_{max}= 508nm) but the complex with Mn(VII) as MnO_4^- was (λ_{max}=572nm).

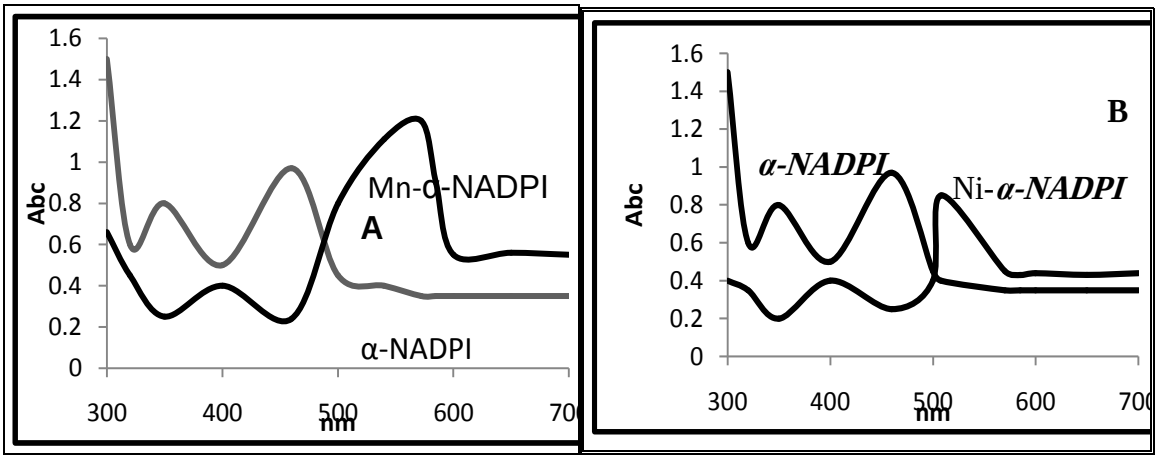
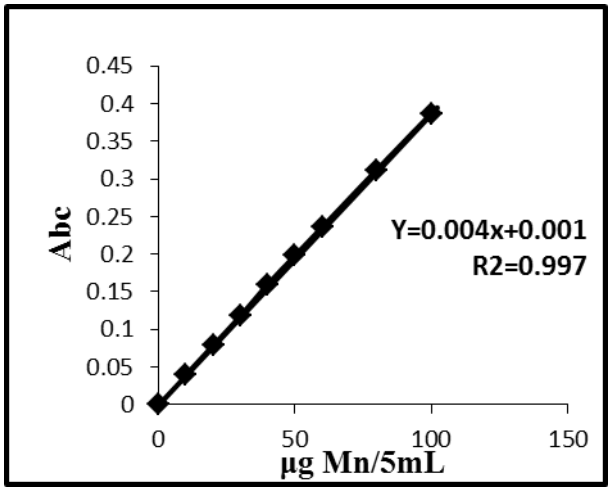


Fig (2): UV-Vis spectra for (A): Mn(VII) complex with α-NADPI and (B): Ni(II) complex with α-NADPI

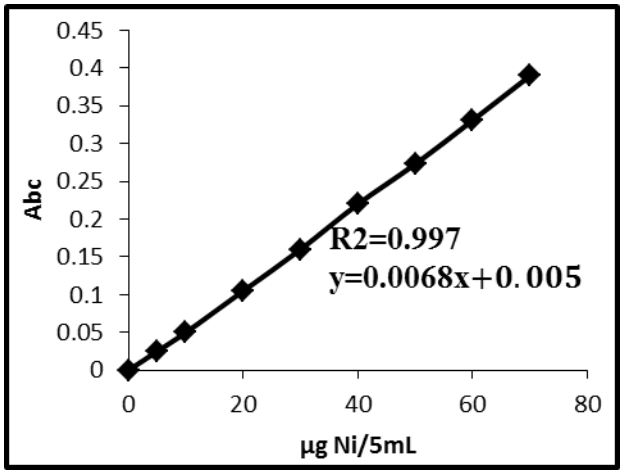
Calibration Curve for determination Mn(VII) and Ni(II) in aqueous phase

Different aqueous solution contain rang of Mn(VII) (5-100µg) in 5ml in volume treated according to specific spectrophotometric method for determination of Mn (VII)[14], the result giving straight line as in Fig(3).



Fig(3): Calibration Curve for determination Mn(VII) in aqueous solution

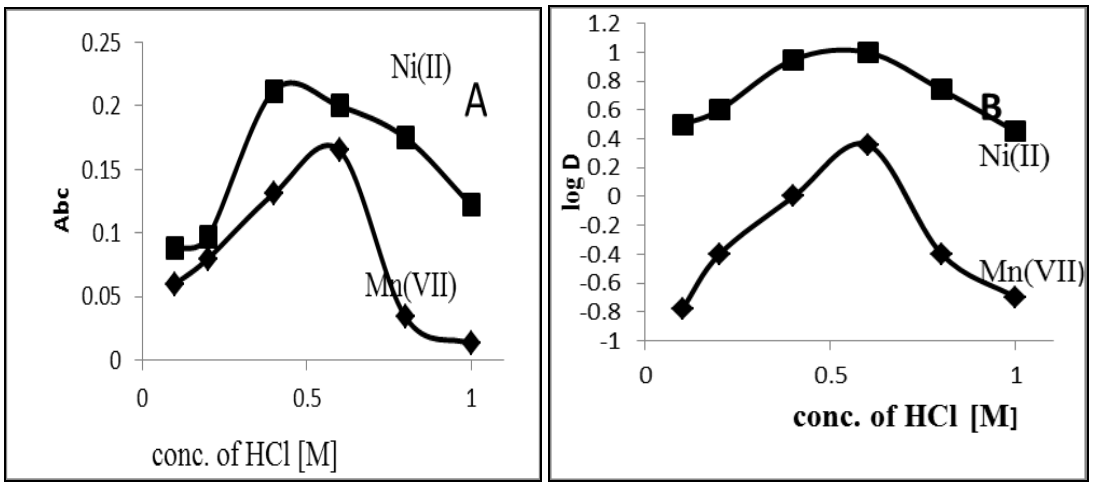
But for determination Ni(II) in aqueous solution contain (5-70µg) of Ni(II) used Dimetheyl glyoxim method [14],the results giving straight line as in Fig(4) .



Fig(4): Calibration Curve for determination Ni(II) in aqueous solution

Effect of HCl concentration on Efficiency of extraction

Extracted $[MnO_4]^-$ & $[NiCl_4]^=$ from acidic aqueous solution media contain different concentration of HCl (0.1-1M) according to liquid ion exchange method, the result shown in Fig:5(A&B).



Fig(5)Effect of HCl concentration efficienly of extracted according to liquid ion exchanger

The results shows absorption value and distribution ratio(D) increase with HCl concentration increase to (0.6M) for extraction MnO_4^- and (0.4M) for

$[NiCl_4]^{-2}$,HCl concentration less than optimum value not allow to reach equilibrium for extraction and effect to decrease absorbance and D value as well HCl concentration more than optimum value decline absorbance and D value by effect of dissociation equilibrium.

Effect of Metal ion concentration

Extracted Mn(VII) & Ni(II) as $[MnO_4]^-$, $[NiCl_4]^{-2}$ from aqueoue solution contain rang concentration (5-70µg) according to liquid ion exchange method at optimum HCl concentration , the results appear as in Fig :6(A&B).

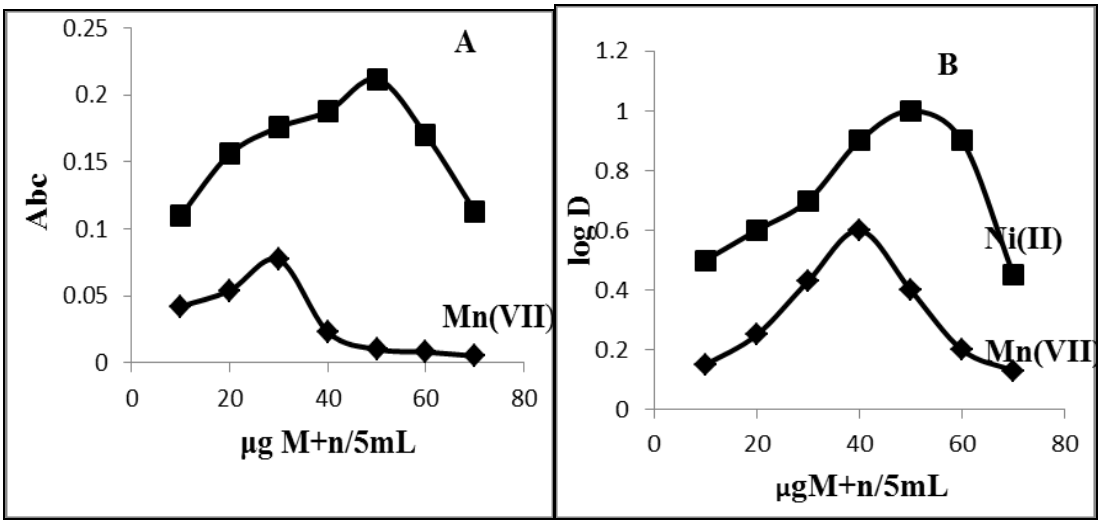


Fig (6): Effect of Metal ion concentration on extraction ability

The results demonstrate optimum concentration of Mn(VII) was 30µg but Ni(II) was 50µg, metal concentration less than optimum value not allow to reach Thermodynamic equilibrium for extraction, as well metal concentration more than optimum value decline the absorbance and D value by effect of dissociation equilibrium according to mass action low and le schatlier principle.

Effect of shaking time

Extraction Mn(VII) & Ni(II) according to liquid ion exchange method. At different shacking time (3-25) min illustrate 10 min was the favorable shaking time to giving higher absorbance and D value as in Fig (7).

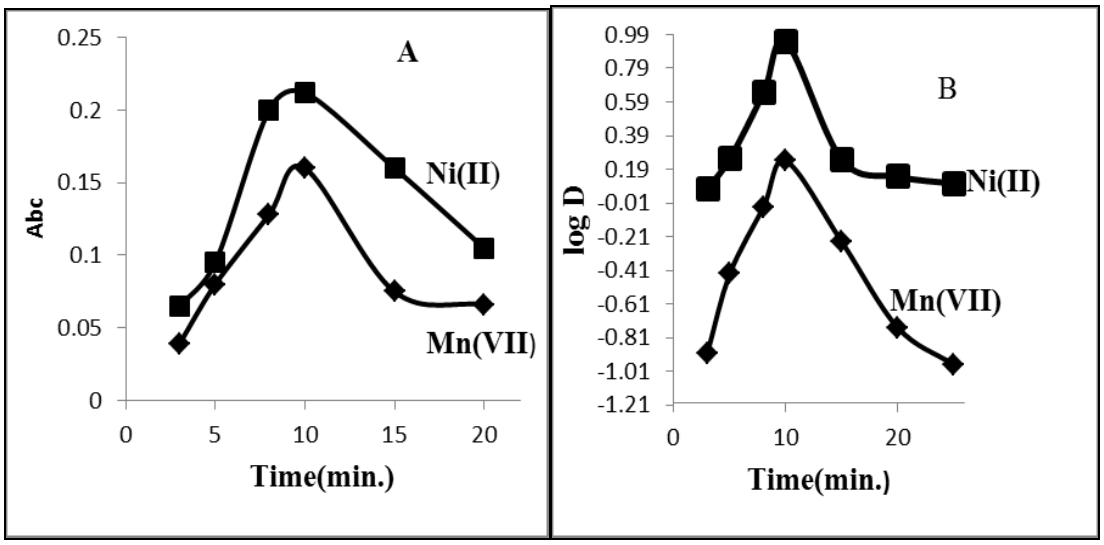


Fig (7). :Effect of shaking time extraction efficienly according to liquid ion exchange

The results shows 10 min was favorable shaking time for extraction both metal ion by reach higher thrmodynamic and kinetic equilibria to giving maximum absorbance and distribution ratio.

The stoichiometry

1-Slope analysis

Extraction metal ion from aqueous solution optimum concentration in foundation different concentration of ligand (1×10^{-3} - 1×10^{-6} M) , the results obtained as in Fig(8).

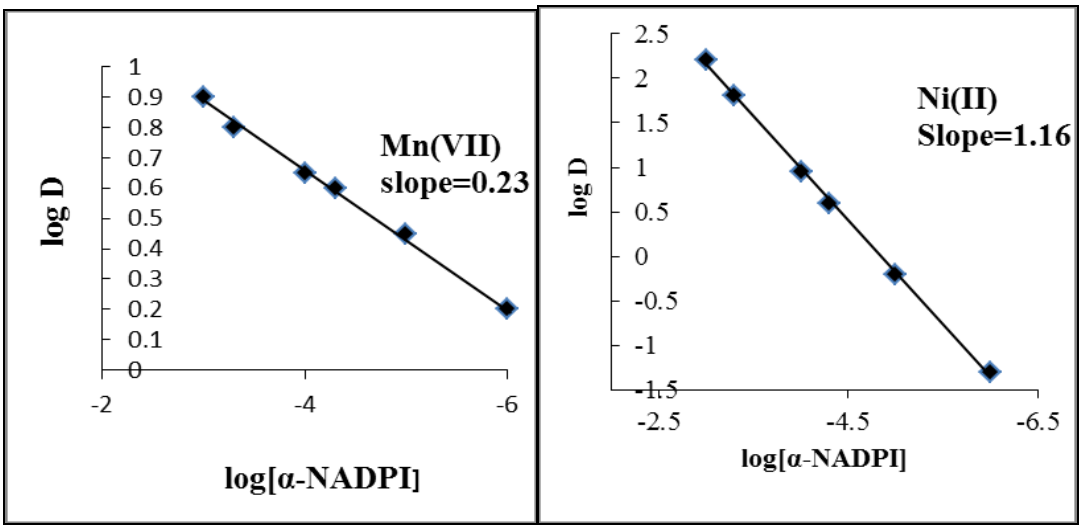
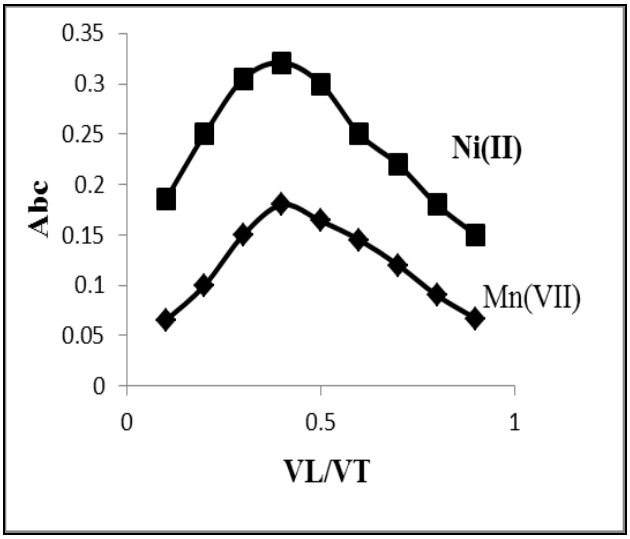


Fig (8):The slope analysis method for α-NADPI

Straight line relation givin slope=0.23 for Mn(IIV) and slope= 1.16 for Ni(II) demonstrate the more probable structure of complex was 1:1 $[HL]^{+}[MnO_4]^{-}$, $[HL]^{+}[HNiCl_4]^{-}$ or $[HL]^{+}[NiCl_3]^{-}$.

2- Continuous Various method

By mixing different volume of metal ion solution at 1×10^{-4} M with α- NADPI solution dissolved in chloro benzene at 1×10^{-4} M for total volume 10 ml at optimum conditions , the results shown in Fig(9).

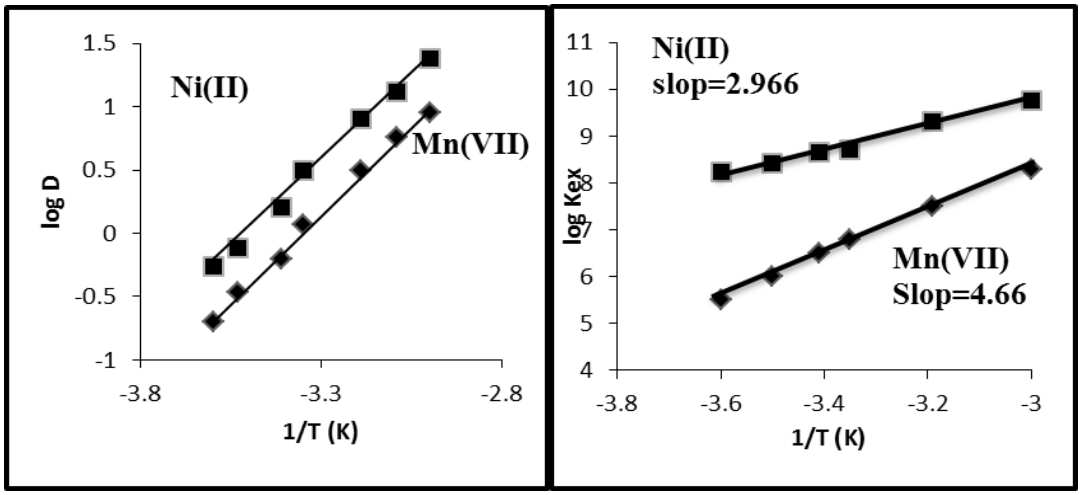


Fig(9) :Various continuous method

The graph relation givin relation for Mn(IIV) and Ni(II) demonstrate complex extraction was 1:1 $[HL]^{+}[MnO_4]^{-}$, $[HL]^{+}[HNiCl_4]^{-}$ or $[HL]^{+}[NiCl_3]^{-}$.

Effect of Temperature

Extracted metal ion at optimum condition at different temperature (5-60C°), the results in Fig(10).



Fig(11):temperature effect on extraction constant K_{ex} and disstribution ratio(D)

$$\frac{\Delta \log K_{ex}}{\Delta 1/T} = \frac{-\Delta H_{ex}}{2.303\,R} \quad \text{.....(1)}$$

From the straight line relation for K_{ex} determine enthalpy of extraction by used the slope to the straight line :

$$Slope = \frac{-\Delta H_{ex}}{2.303R} \quad \text{.....(2)}$$

Free energy of extraction ΔG_{ex} and entropy ΔS_{ex} from relation below :

$$\Delta G_{ex} = -R\,T\,ln\,K_{ex} \text{ .....(3}$$

$$\Delta G_{ex} = \Delta H_{ex} - T\Delta S_{ex} \text{.....(.4)}$$

Table (1) :Thermodynamic value for Mn(VII) & Ni(II)

ion	*α-NADPI*		
	ΔH_{ex} K.J. mol^{-1}	ΔG_{ex} K. J. mol^{-1}	ΔS_eK.J. mol^{-1}
Mn(VII)	*0.0873*	*55.58*	*166*
Ni(II)	*0.0514*	*60.82*	*182.48*

The results shown extraction of metal ion Mn(VII) & Ni(II) according to liquid ion exchange was endothermic.

Effect of organic solvent

Extraction of Mn(VII) & Ni(II) at optimum condition according to liquid ion exchange method by use different organic solvent differ in dielectric constant giving the results in Table(2).

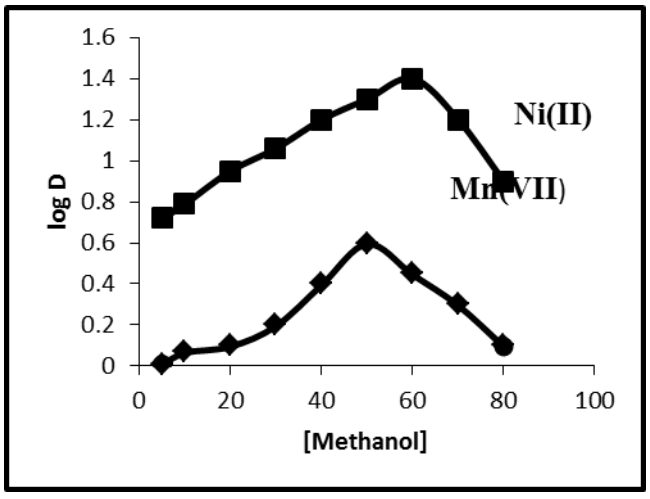
Table(2): effect of organic solvent

solvent	α- NADPI				
	Mn(VII)			Ni(II)	
	Dielectric constant(ε)	D	E%	D	E%
Nitro benzene	35.470	0.50	33.33	2	66.6
Amyl alcohol	15.800	0.71	41.52	2.5	71.40
Dichloro methane	9.080	1.00	50	5.0	83.30
Chloro benzene	5.708	4.40	81.48	9.0	90.00
Benzene	2.804	0.82	45.05	3.2	75.00
Toluene	2.438	0.91	47.8	4	80.00

The results appear there is not any linear relation between D-value and dielectric constant *(ε)* for organic solvent that is mean there is not any effect for polarity of organic solvent on extraction efficiency but there is an effect for organic solvent structure on extraction ability.

Methanol effect

Extraction Mn(VII) & Ni(II) from aqueous solution at optimum conditions with foundation of methanol in aqueous solution at rang 5%-80% . The results as in Fig(12):



Fig(12): Methanol effect

The results shows methanol effect to increase extraction efficiency to optimum value 50% for Ni(II) and 60% for Mn(VII) which is effect to destroy the hydration shell of anion which is effect to decrease the energy needing for transition to organic phase, but methanol more than optimum decline extraction by effect of increase transfere organic reagent to aqueous phase

Effect of interferences

Extraction of $[MnO_4]^-$ and $[NiCl_4]^=$ according to liquid ion exchange by α- NADPI in foundation of different ions giving the results as in Table(3).

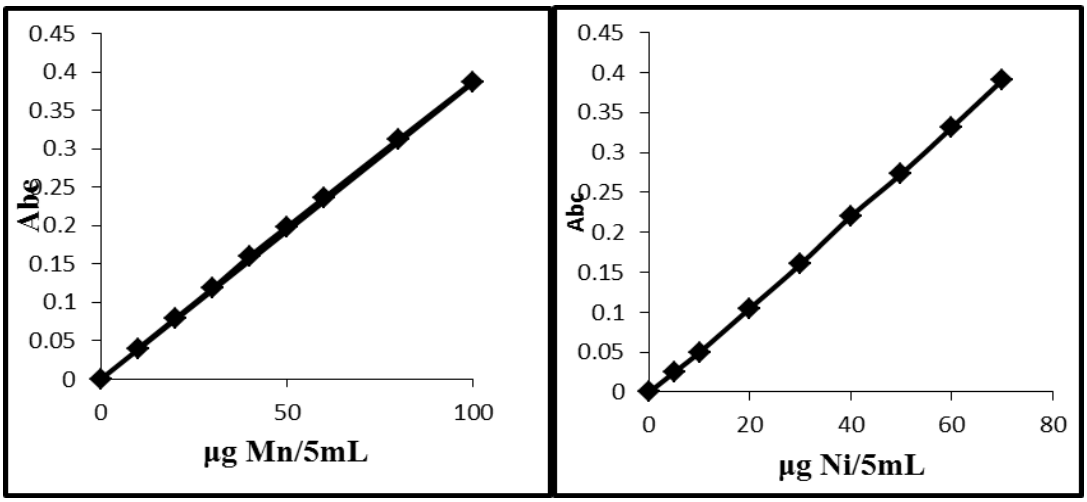
Table(3): Effect of interferences

Ions	*α- NADPI*			
	Mn(VII)		*Ni(II)*	
	D	*E%*	*D*	*E%*
CH_3COO^-	*4.8*	*82.75*	*10.2*	*91.07*
NO_3^-	*5.2*	*83.87*	*10.5*	*91.3*
CrO_4^{-2}	*5.8*	*85.3*	*10.7*	*91.45*
$Cr_2O_7^{-2}$	*6.2*	*86.66*	*10.9*	*91.59*
I^-	*6.1*	*85.3*	*11.5*	*92*
Cl^-	*6.3*	*86.3*	*11*	*91.6.*
Na^+	*8*	*88.8*	*13*	*92.82*
K^+	*7.5*	*88.23*	*12.5*	*92.6*
NH^{4+}	*7.2*	*87.8*	*12*	*92.3*

The results shows all of cation and anion giving increase in D values for extraction Mn(VII) and Ni(II) by the effect of electrolyte solution to withdrawing water molecule from the hydration shell of $[MnO_4]^-$ & $[NiCl_4]^=$ and increase trasnfered to organic layer to form ion pair complex extracted.

Calibration Curve for Spectrophotometric determination Mn(VII) & Ni(II)

By un liquid ion exchange method at optimum conditions determination the absorbance of ion pair complex extracted to organic phase $[MnO_4]^-$ and $[NiCl_4]^=$ at different amount of analyte metals Mn(VII) and Ni(II) and after plot Absorbance values against µg of Mn(VII) or Ni(II) the results giving straight line in Fig(13):



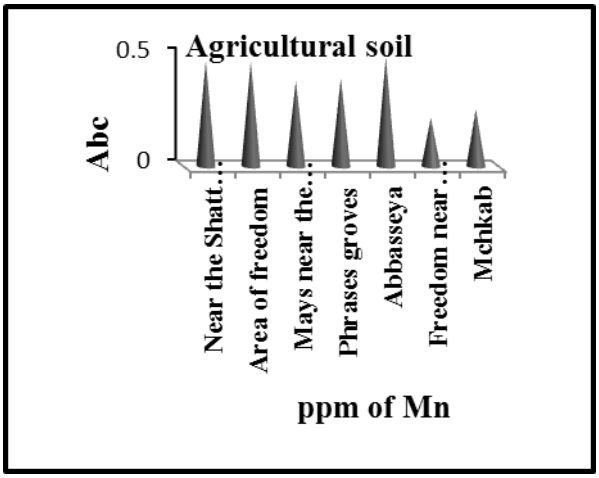
Fig(13) Calibration curve for spectrophotometric determination of Mn(VII) and Ni(II).

Determination of Mn(VII) and Ni(II) in different samples by liquid ion exchange method:

Application liquid ion exchange method determination quantities of Mn(VII) and Ni(II) in different vital and enviro of metal samples.

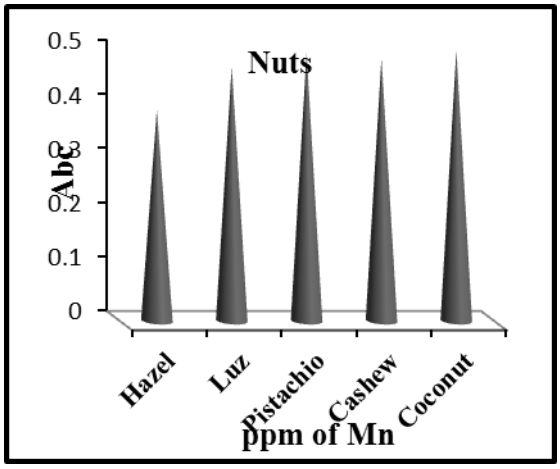
Table(5) and Fig(14): Manganese content in agricultural soil

sample		*ppm*
1	*Near the Shatt al-Kufa*	*450*
2	*Area of freedom*	*420*
3	*Mays near the street*	*280*
4	*Phrases groves*	*258*
5	*Abbasseya*	*382*
6	*Freedom near the street*	*365*
7	*Mchkab*	*250*



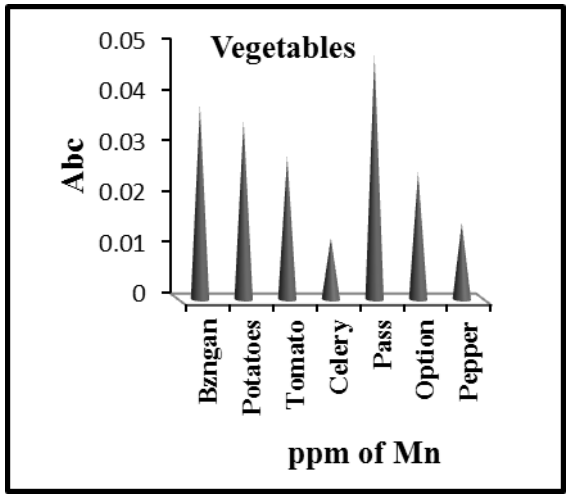
Tabel(6)and Fig(15): Manganese content in Nuts

samples		*Ppm*
1	*Hazel*	*390*
2	*Luz*	*425*
3	*Pistachio*	*490*
4	*Cashew*	*450*
5	*Coconut*	*500*



Table(12) and Fig(16); Manganese content in Vegetable

sample		*Ppm*
1	*Bungan*	*6.8*
2	*Potatoes*	*6.4*
3	*Tomato*	*5*
4	*Celery*	*4.6*
5	*Pass*	*9*
6	*Option*	*4.5*
7	*Pepper*	*3.7*



Table(7) and Fig(17): Manganese content in water

samples		ppm
1	Euphrates River	0.2
2	Shamiu Puncture	0.1
3	Indian River-Karbala	0.18
4	Umm Qasr-Bosrah	0.15
5	Zekh shatt	0.16
6	Abbasid Punctuncture	0.11
7	Watre liquefaction-Najaf	0.3
8	Baghdad Water	0.14

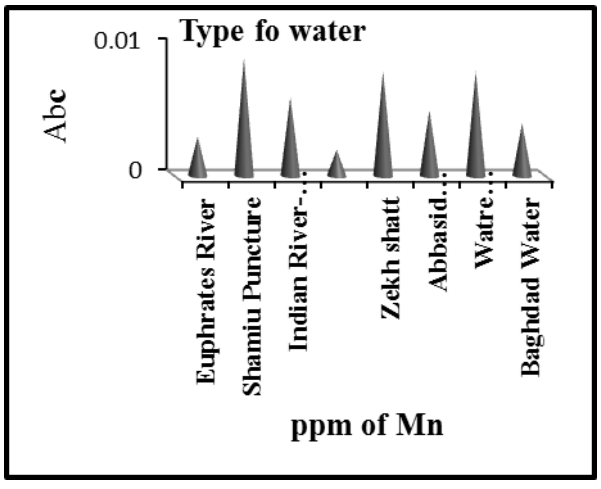
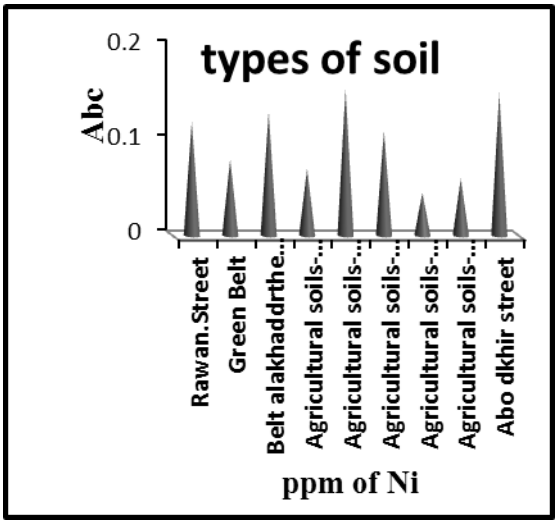


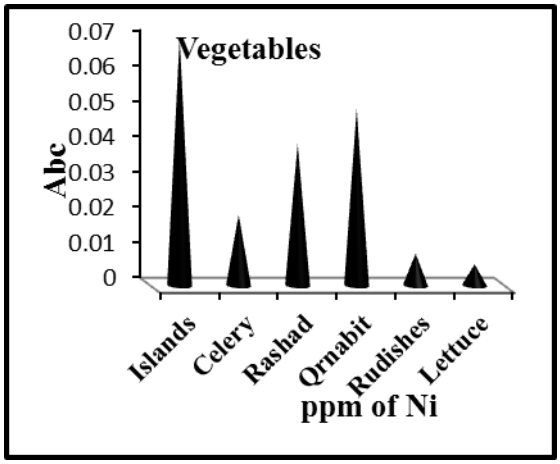
Table (8)and Fig(18):Nickel content in soil

Types of soil		*ppm*
1	*Rawan.Street*	*1.6*
2	*Green Belt*	*0.81*
3	*Belt alakhaddrthe Vs street/collage of eduction/kufa*	*1.7*
4	*Agricultural soils-shamia*	*0.7*
5	*Agricultural soils-Abbasseya*	*0.52*
6	*Agricultural soils-Mchkab*	*0.33*
7	*Agricultural soils-Zrkh*	*0.25*
8	*Abo dkhir street*	*1.5*



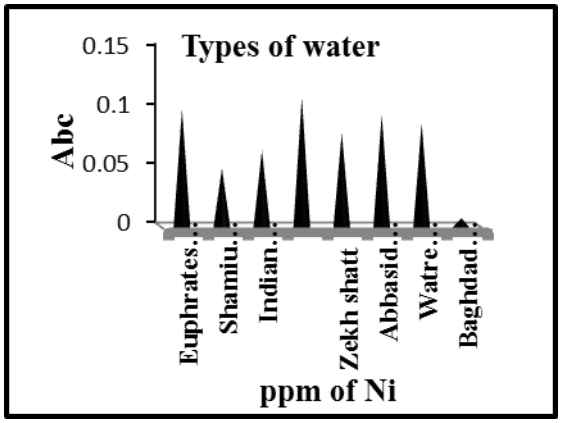
Table(9)and Fig(19): Nickel content in Vegetables

sample		*ppm*
1	*Islands*	*0.17*
2	*Celery*	*0.11*
3	*Rashad*	*0.31*
4	*Qrnabit*	*0.15*
5	*Rudishes*	*0.12*
6	*Lettuce*	*0.09*



Table(10) and Fig(20): Nickel content in water

Type of water		*ppm*
1	*Euphrates River*	*0.4*
2	*Shamiu Puncture*	*1.2*
3	*Indian River-Karbala*	*0.9*
4	*Umm Qasr-Bosrah*	*0.8*
5	*Zrekh shatt*	*0.6*
6	*Abbasid Punctuncture*	*1.3*
7	*Watre liquefactionNajaf*	*0.09*
8	*Baghdad Water*	*0.7*



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التقدير المايكروي واستخلاص المنغنيز (VII) والنيكل (II) على هيئة ايونات سالبة في نماذج حياتية وبيئية مختلفة بواسطة 2- [– الفا نفثول ازو] -5,4- ثنائي فنيل اميدازول

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الخلاصة

استخلص النيكل(II) على هيئة معقد كلورو سالب $NiCl_4^=$ والمنغنيز(II) على شكل معقدات ترابط ايوني تستخلص الى الطور العضوي باستعمال الكاشف العضوي 2-[α-نفثايل آزو] -4,5-ثنائي فنيل اميدازول كعامل تعقيدوقد تم تحديد كافة الظروف والعوامل المؤثرة على كفاءة الاستخلاص مثل تركيز حامض الهيدروكلوريك, تركيز الايون الفلزي, زمن الرج وكذلك دراسة تركيب المعقد المستخلص بينت ان للمعقد تركيب 1:1:1 [H-α-NADPI]$^+$$NiCl_3^-$,[H-α-NADPI]$^+$$HNiCl_4^-$, اضافة الى ان الدراسة الثرموديناميكية بينت ان عملية الاستخلاص وفق تقنية التبادل الايوني هي ماصة للحرارة endothermic بالاضافة الى استخدام هذه الطريقة في تقدير Ni(II) , Mn(VII) في نماذج بيئية وحياتية مختلفة.

الكلمات المفتاحية: التبادل الايوني السائل , الاستخلاص بالمذيب.

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