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Separation, preconcentration, extraction and spectrophotometric determination of Mn(VII) from Acidic Aqueous medium

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ABSTRACT: Liquid ion exchange method as sensitive application method of solvent extraction used for separation and determination Mn(VII) as MnO_4^- from aqueous solution by used P-amino benzoic acid (P-ABA)in presence hydrochloric acid HCl at exact concentration. Spectrophotometric study show wave length for maximum absorbance of ion pair association complex extracted was λ_{Max} = 286nm as well as the study about pinpoint the optimum conditions for higher extraction efficiency shows this method need 0.6 MHCl in presence 60µg/5ml of Mn(VII) as MnO_4^- and shaking time equal to (10min), the study shows extraction method was endothermic and thermodynamic data, was ΔH_{ex} = 0.1374 kJmol^{-1} ΔG_{ex}= -60.89 KJ mol^{-1} ΔS_{ex} = 194.926 Jmol^{-1} as well as the study involved electrolytes effect, interference effect, organic solvent effect so that spectrophotometric Determination of Mn(VII) in different samples

KEYWORDS: Ion change extraction, Mn(VII), solvent extraction, p-amino benzoic acid, electrolyte effect, spectrophotometric.

1. INTRODUCTION

Liquid ion exchange method consider as an application for solvent extraction ,so that it is characterized as sensitive and accuracy method for separation and determination metal anion species after formation ion- pair association complexes with organic high molecular volume molecules behave as ion exchanger in hydrochloric acid medium after joined cloud point extraction method CPL with liquid ion exchange solvent extraction as sensitive accurate methods for separation , preconcentration and extraction with spectrophotometric Determination of different metal cation and anion(Shawket&Munar,2017),(Shawket&Noor, 2017),(Shawke&Nadia,2015),(Valentina,et,al,2018),(Shawket&Ebaa,2015)(Shawket,et,al,2018),(Shawke&,Ebaa, 2014) . Extraction Ni(II) as chloro anion complex $[NiCl_4]^-$ and Mn(II) as $[MnO4]^-$ as ion - pair association complex extractacted into organic phase by un- organic complexing reagent [α-NADPI(Fatimah, 2017). Extraction Co(II) by complexing reagent [PAN] after formation ion- pair association and study effective parameters such as pH ,the concentration of metal, concentration of complexing reagent , thermodynamic parameter and synergism study(Shawket,et,al, 2016). With important study involved separation of Ir(II) and Rh(III) between $SnCl_2$ extraction with Cyanex 301 and Cyanex 921 was investigated in the HCl concentration rang from over Rh(I) in the presence of $SnCl_2$. The extraction percentage of rhodamine by Cyanex 921in the presence of ascorbic acid was mush smaller than that in the presence of SnCl(Miuh,et,al,2018) Coupling two sensitive method which onium method and cloud point extraction (CPL) for separation and determination Fe(III) and Hg(II) by using BAEE from acidic hydrochloric acid(HCl) aqueous solution in the presence TritonX-100(Shawket,et,al, 2017). Extraction Fe(III) ion from hydrochloric media by using crown ether DB18C6 and format association complex and extracted by cloud point extraction method(shwket&Luay, 2015). By using NaCl media and the crown ether 15C5 as complexing agent extracted Al(III) as $[AlCl_4]^-$ and study all parameters effect on extraction methods such as concentration NaCl and Al(III) ions, shaking time, organic solvent effect , carting size effect with thermodynamic study(safa,et,al 2015). Extraction and separation Ni(II) and Co(II) from acetate medium and complexing reagent (Nadimi,et,al, 2015).

2-1:Experimental

For spectrophotometric studies and absorbance measurement, used Bio chrome double beam spectrophotometer mod(Biochrumlibra 560) (A Harvard Bio science company Cambridge UK), so for heating used water bath with regulator (Hamburg 90) England and electrical balance company limited, Dool, CE, HR200, Japan, stock solution $KMnO_4$ 1mg/L in 10mL distilled water in volumetric flack and another solution prepared by dilution with distilled water.

2-2:Experimental

Comprehensive method

Aqueous solution 5ml in volume contain optimum quantity of Mn(VII) with optimum concentration of hydrochloric acid HCl add to this solution 5mL of para-amino benzoic acid p-ABA dissolved in chloroform in 1x10^{-4}M concentration, shaking the solution for optimum shaking time , then separate organic phase from aqueous phase, then measure the Absorbance of

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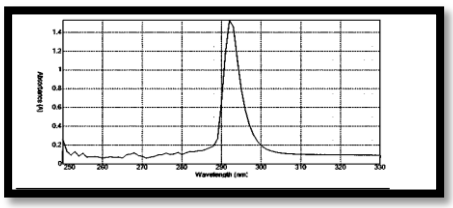
organic phase at wave length for maximum absorbance λ_{max} against blank prepared at the same manner in absence metal ion Mn(VII), as well as treated the aqueous phase according to spectrophotometric special solution method(Marczenko,1986) and after return to the calibration curve to determine the remainder quantity of Mn(VII) ion in aqueous solution after extraction, and abstraction this quantity from the basic quantity to determine the transferred quantity of Mn(VII) ion into organic phase to formation ion- pair association complex and then calculate the distribution ratio D as in the relation below[15];

$$D = \frac{[Mn(VII]org}{[Mn(VII)]aq.}$$

3-Results and Discussion

Spectrophotometric study involved 5mL aqueous solution contains 50µg of Mn(VII) ion as MnO^-_4 with 0.1 M hydrochloric acid HCl added to this solution 5mL of P-ABA solution dissolved in chloroform at $1x10^{-4}$M concentration shakes the solution to 10min. then separate organic phase from the aqueous phase and takes Uv-vis Absorption spectrum for organic phase against blank prepared in the same manner in absence Mn(VII) ion. The result demonstrates in fig(1)



Fig(1) UV-vis Absorption spectrum for ion- pair association complex of Mn(VII) with P-ABA.

The spectrum shows the wave length for maximum absorbance was λ_{max} = 286nm

4-Variation HCl concentration

Take 5mL aqueous solution to contain 50 µg of Mn(VII) ion as MnO_4^- with rising concentration of hydrochloric acid HCL added to each aqueous solution 5mL of P-ABA solution dissolved in chloroform at $1x10^{-4}$mol L^-, then shaking these solutions for 10 min. afterward separated the organic phase from the aqueous phase and complete the experiment as in comprehensive method the results were as in fig 2,3,4

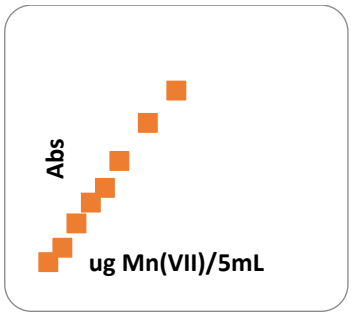
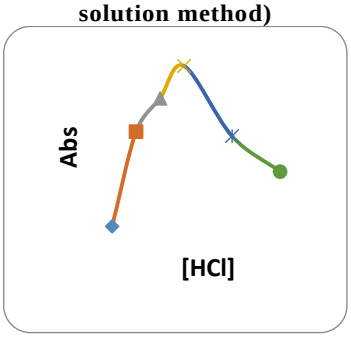


Fig (2)= calibration curve for determination Mn(VII) ion in aqueous solution (spectrophotometric special solution method)



Fig(3);effect of HCl concentration on formation efficiency of Mn(VII) ion and D- value with p-ABA

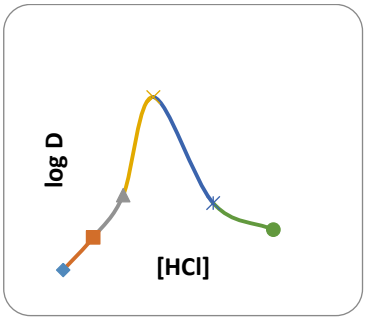


Fig (4); effect of HCl concentration on extraction ion- pair association complex of Mn(VII) ion

The results shows the optimum concentration of hydrochloric acid give higher extraction efficiency was 0.2M HCl, at this concentration reach higher velocity of thermodynamic equilibrium for formation ion pair association complex with para-Amino benzoic acid P-ABA. Any concentration of HCl less than optimum value not allow to reach higher velocity of formation equilibrium of ion pair association complex.So any concentration of HCl more than optimum value give decrease in extraction efficiency of Mn(VII) also because increase the dissociation direction of thermodynamic equilibrium and decrease concentration of ion pair association complex formation according to mas action law

5-Variation Mn(VII) concentration

5ml aqueous solution contain rising quantity of Mn(VII) with 0.2M HCl add to each solution 5mL of P-ABA

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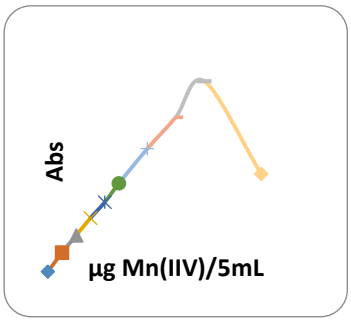
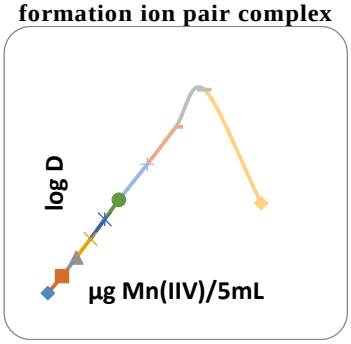
solution dissolved in chloroform at $1x10^{-4}$mol/L, shaked the solution for 10min. afterward separated organic phase from aqueous phase, then measure the absorbance of organic phase at λ_{max}=286nm against blank prepared at the same manner with out Mn(VII) ion, and the aqueous phase treated according to spectrophotometric special solution method as in comprehensive method the results were as in figures 5,6



Fig(5) effect of Mn(VII) concentrated ion on formation ion pair complex

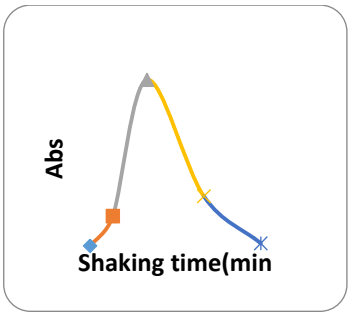


Fig(6) effect of Mn(VII) concentrate ion on extraction efficiency and D-value

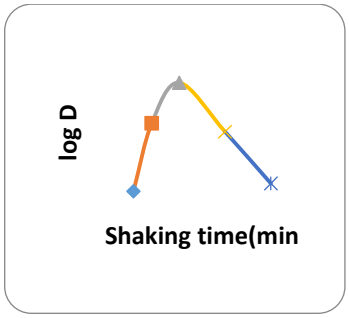
The results shows there is linear relation between metal ion concentration and extraction efficiency and the optimum concentration of Mn(VII) which is give higher extraction efficiency was 60µg, so the results confirm the concentration of metal ion is a thermodynamic factor effect on the equilibrium of ion pair association complex extracted. As well as any concentration of Mn(VII) more than optimum Mn(VII) concentration effect to decrease extraction efficiency according to mass action law.

6-Effect of shaking time

Prepared aqueous solutions 5mL in volume contain 60µg of Mn(VII) with 0.2M hydrochloric acid HCl adds to each solution 5mL of P-ABA dissolved in chloroform at $1x10^{-4}$mol/L shaking the solutions for different times and complete the work as in the comprehensive method, the results were as in fig7,8



Fig(7) : effect of shaking time on formation efficiency and D-value

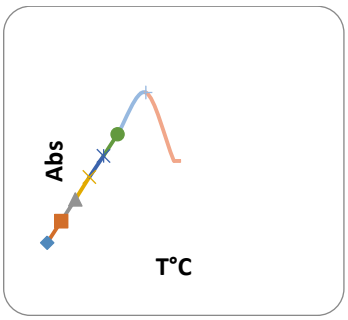


Fig(8) : effect of shaking time on extraction of ion pair complex

The results shows 10 minutes was the optimum shaking time which is help to reach maximum extraction efficiency because shaking time is the kinetic energy of indirect extraction method at this time we will achieve higher rate for thermodynamic equilibrium of formation ion pair complex and getting maximum concentration of complex attracted any less shaking time not allow to reach this rate and concentration of complex. So that shaking time. more than optimum value effect to decrease extraction efficiency

7-Effect of temperature

Prepared a series of aqueous solutions contain 60µg of Mn(VII) with 0.2M HCl, add to each solution 5mL of P-ABA dissolved in chloroform at $1x10^{-4}$mol/L, shaking these solution for 10 minutes at different temperature, then complete the work as in comprehensive method, the results were as in fig(9,10)



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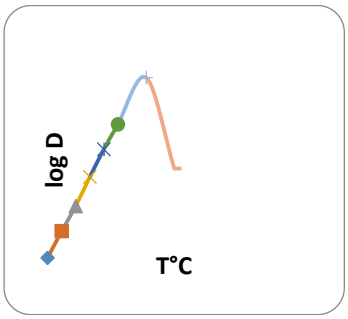
Fig(9) : effect of temperature on formation of ion pair complex



Fig(10) : effect of temperature on extraction efficiency and D-value

After calculate extraction constant Kex at each temperature according to relation below the results were as in fig(11).

$$Kex = \frac{D}{[Mn(VII)][p\text{-}ABA]}$$

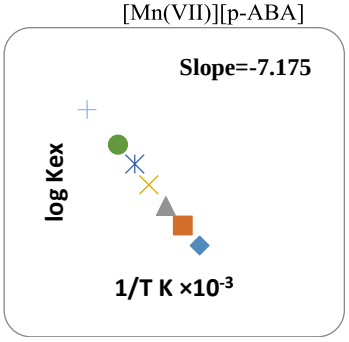


Fig (11) : effect of temperature on extraction constant

From the slope value of linear relation in fig(11) and thermodynamic relations calculate thermodynamic data the results were as in Table (1)

Table (1) thermodynamic data for extraction Mn(VII) according to comprehensive method.

ΔHex KJmol^{-1}	ΔGex KJmol^{-1}	Δsex Jmol^{1}K^{1}
0.1374	−60.89	194.976

The results shows the extraction technique was endothermic giving rising in extraction efficiency with increasing temperature to optimum temperature 40°c.

8-Effect of electrolytes

Prepared a series aqueous solutions 5mL in volume contain 60µg Mn(VII) as MnO_4^- and 0.2M HCl in existence 0.1M of different electrolytes each one alone, add to each solution 5mL of 1x10^{-4}M P-ABA dissolved in chloroform, shaking these solution in electrical shaker for 10 minutes, then separate the aqueous phase from aqueous phase. Afterward measure the absorbance of organic phase and treated the aqueous phase according to the comprehensive method, the results were as in Table (2).

Table (2) : ELECTROLTE EFFECT ON EXTRACTION EFFICIENCY OF Mn(VII)

Electrolyte	286nm	D
Licl	0.943	45.33
Nacl	0.785	32.65
Kcl	0.733	28.41
NH_4cl	0.695	24.82
$Mgcl_2$	0.824	36.17
$Cacl_2$	0.766	30.64
$Alcl_3$	0.722.	26.67

The results shows the presence of electrolyte in aqueous phase effect to rising extraction efficiency of Mn(VII), because the electrolyte effect to decrease Dielectric constant and polarity of aqueous phase that is effect to destroy hydration shell of Mn(VII) and increase the rate formation direction of ion pair association complex, the different electrolytes giving different effect because have different behavior in aqueous phase according to the cation kind in the electrolytes.

9-Effect of interferences

A series of aqueous solutions 5mL in volume prepared contain 60µg Mn(VII) as MnO_4^- and 0.2 M HCl in presence 0.1M NaCl electrolyte and 0.01M of different foreign ions, add to each solution 1x10^{-4}M P-ABA dissolved in chloroform according to comprehensive method. The result were as in Table (3)

Table (3) : effect to interferences on extraction efficiency of Mn(VII)

Interferences	Abs. 286nm	D
Cd^{2+}	0.333	10.17
Zn^{2+}	0.421	14.22
Ni^{2+}	0.542	16.43
Co^{2+}	0.286	7.23
Hg^{2+}	0.367	12.31
$Cr_2O_7^{=}$	0.125	2.55

The results shows these foreign metal cations give decline in extraction efficiency of Mn(VII), because the metal cation able to formation ion pair association complex extracted to organic phase after converted to anion chloro complex except $Cr_2O_7^{=}$ that is mean behave as interferences, and these behavior effect to consumption some of hydrochloric acid HCl and P-ABA and decrease its concentration from necessary concentration to formation ion pair association complex and this shows decline in extraction efficiency of Mn(VII).

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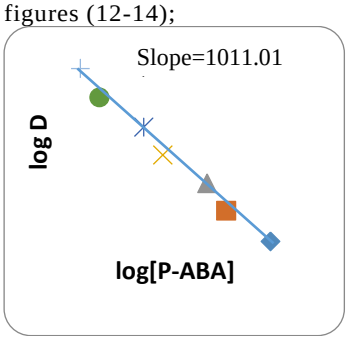
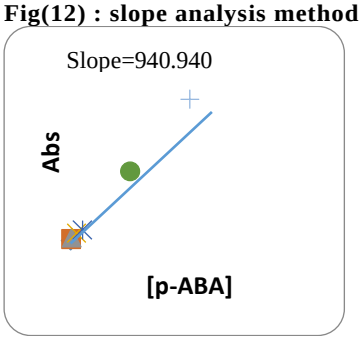
10–Stoichiometry

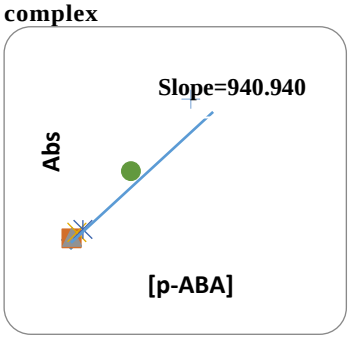
For determine the more probable structure of ion pair association complex of Mn(VII) extracted followed two spectrophotometric methods, slope analysis and slope ratio method. By application comprehensive method at optimum condition the results were as in figures (12-14);



Fig(12) : slope analysis method



Fig(13): effect of Mn(VII) concentration on formation and stability of ion pair association complex



Fig(14): effect of P-ABA concentration on formation and stability of ion pair association complex

$$slope\ ratio = \frac{940.940}{1011.011} = 0.931$$

The slope value and the slope ratio value demonstrate the more probable structure of ion pair association complex was (1:1) $[H\text{-}P - ABA]^+$; Mno_4^- according to mechanic extraction below

$$H^+ + Cl^- + p - ABA \leftrightarrow [H - PABA]^+;\ Cl^-$$

$$[H - PABA]^+;\ cl^- + MnO_4^- \leftrightarrow [H - PABA]^+ ; MnO_4^- + Cl^-$$

11-Spectrophotometer determination

By application the comprehensive method at optimum condition with preparing calibration curve for spectrophotometric determination of Mn(VII). Determined quantity of Mn(VII) in different samples the results were as in Table (4)

Table (4): The ppm quantity of Mn(VII) in deferent samples

Samples	Ppm Mn(VII)
Celery	125
Lettuce	212
Garlic	170
Beetroot	180
Watercress	225
Islands	200
Banana	153
Cucumber	153
Spinach	165

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