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Cloud Point Extraction with Liquid Ion Exchange For Separation And Determination Of Zinc (Ii)

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Abstract

For extraction Zinc (II) as ion pair association complex,used Cinchonine as organic reagent to performed this extraction method,spectrophotometric studies for ion pair association complex for Cinchonine and Zn^{2+} in acidic HCl medium, shows the wave length of maximum absorbance wasλ_{max}=290nm,as well as optimum conditions for higher extraction efficiency according to liquid ion exchange coupled with cloud point extraction method where,0.3MHCl ,in presence 50 µg Zn^{2+} in 10 mL aqueoussolution,0.5 mLsurfactant Triton X- 100 , with heating at 85^0C for 15 min. The stoichiometry shows up the composition of ion pair association compiles extracted was H Cinchonine$^+$; $HZnCl_2^-$, in addition to other studies such as effect ofelectrolyte, interferences, and else.

Keyword: Zinc (II), Cloud, point extraction method, liquid ion exchange, Cinchonine

Introduction

Cloud point Extraction method is applied for extract of Zn(II)as chloro anion complex from HCl media by using 3-[(pyridylazo)]-1-nitroso-2-naphthol (PANN) in presence 1% Triton X- 100 after spectrophotometricstudies for PANN and Zn (II) complex and this method is for separation and determination of Zn(II) in different sample[1].Zinc was separated from SCN^- by N-N- hexylaniline dissolved in xylene and H_2SO_4 media, studying several variables effecting on separation method as solvent, extractant, acid concentration and other studies[2].Cloud point extraction method used for determination of Cadmium , Copper , Lead and Zinc in water samples coupled with FAAS and formed complex with 1-(2- thiazolyazo)-2- naphthol and triton X-114 , LOD =(0.095, 1.1 , 0.270 , 0.009)µg $mL^{-1}$for (Cd , Cu, Pb, Zn)[3].Application of CPE technology to extract Cobalt ,Nickel, and Copper ions from water , urine and blood samples by farming complexes with (DHBPHC) and using an effective surface Triton X-100[4].Spectrophotometric study of Zn (II) and Co(II) extracted according to onium systems from acidic HCl Solution by (2,4-dimethyl pentan-3-one) as onium complex[5].The liquidion Exchange application for micro amount separation and determination for

elements[6,7].Cloud pointextraction joined with liquid ion exchange to separate and extraction some ions from acidic HCl media as ions pair association complexes[8]. Several studies have applied the cloud point extraction (CPE) technique in combination with the spectroscopic method, to separate and determination a number of elements is different environmental models, and results were characterized by accuracy and high sensitivity[9-17].Using a sensitive technique for the determination of Copper, Iron ,Nickel , and Zinc ions to form chelated complexes with (((3-indolin-3yl)(phenyl)methyl))indoline using Triton X-114in different samples [18].Application of liquid ion exchange technology with cloud point extraction technology to extract and determination the ions of Pt(II) and Mo (VI) by using Triton X-100 and study the factors affecting the acidic medium ofHCl and determination the ions inform of$PtCl_3^-$, $MoO_4^=$[19,20].

Experimental

A. Reagents

Distilled water was used in all experiments of this study in order to prepared solutions, all chemicals are obtained from certified companies, stock solution of Zn (II) in concentration 1mg/mL was proposed by dissolved 0.1g of Zn metal in 25 mL of dilute hydrochloric acid, and after complete the solubility complete the solution to 100mL with distilled water in volumetric flask, other solution of Zinc (II) prepared by dilution with distilled water in suitable volumetric flasks, as well as prepared Cinchonas solation in $1x10^{-3}$M by dissolved 0.0294 g of Cinchonine in 100 mL distilled water, and other solutions proposed by dilutionwith distilled water.

B. Instrumentation

All spectrophotometric studies performed by a Biochrom type (80-700-11- Libra s60) spectrophotometer from Japan was used, for heating the solutions used Water Bath, (Hamburg - 90), England with regular temperature, balance A&D (DOOl,CE, HR 200) japan.

General Method

Preparing 10 mL aqueous solution contain 50µg Zn^{2+}ion, 0.3 M hydrochloric and HCl, $1x10^{-4}$Cinchonine, and 0.5 mL of surfactant Triton X-100, heat the solution in electrostatic water bath at 85^{o}C for 15 minutes, until formation cloud points layer (CPL),then we are separate cloud point layer CPL from aqueous solution,and dissolved CPL in 5 mL ethanol, afterward measure the absorbance of alcoholic solution at λ_{max}= 290 nm vis blank prepared at the same manner without Zn^{2+} ion, but the aqueous solution treated with dithizone spectrophotometric method [21],then return to calibration curve in Fig (2), in order to determine remain quantity of Zn^{2+} ion in aqueous solution after

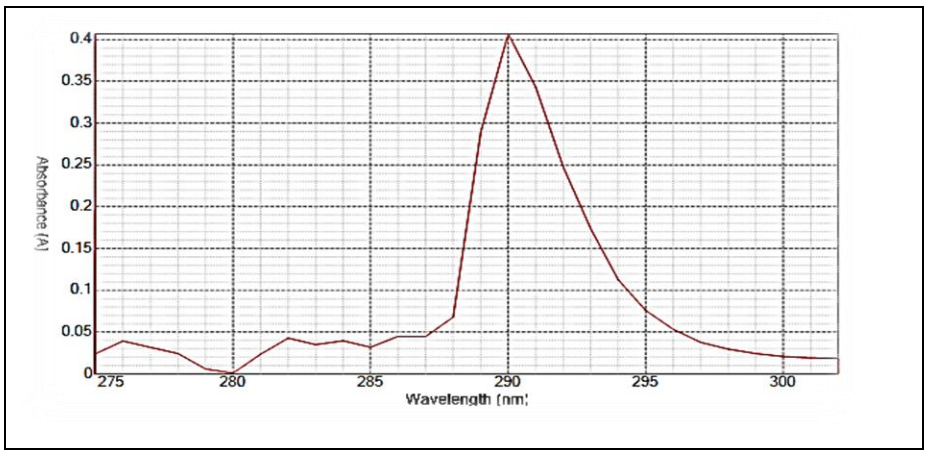
extraction, afterward we subtract this remain quantity of Zn^{2+} ion from the original value, in order to determine, the quantity transferred to cloud point layer an ion pair association complex, at latter calculate Distribution ratio D from this quantities as in relation below

$$D = \frac{[Zn^{2+}]_{cpl}}{[Zn^{2+}]_{aq}}$$

Results and Discussion

Spectrophotometric study

Prepared 10 mL aqueous solution contain 50 µg Zn^{2+} ion, 0.5 M hydrochloric acid HCl, $1x10^{-4}$M Cinchonine, and 0.5 mL surfactant Triton X-l00, heat this solution in electrostatic water bath at 85C^{o} for 15 minutes, until formation Cloud point layer CPL, then separation CPL from aqueous solution, and dissolved in 5 mL ethanol, afterward we took UV-Vis spectrum for alcoholic solution against blank prepared at the same manner without Zn^{2+} ion, the result demonstrate is Fig (1)



Fig(l)= UV-Vis absorption spectrum for ion pair association complex of Zn^{2+}will Cinchonas

The spectrum show up the wavelength for maximum absorbance was λ_{max}= 290 nm , used this wave length to measure the absorbance of alcoholic solutions in subsequent experiments.

Effect of HCl Concentration

Prepared 10 mL aqueous solution contain 50 µg Zn^{2+}ion,$1x10^{-4}$M Cinchonine, 0.5 mL surfactant Tritonx-l00, with exists different concentration of hydrochloric and HCl, heat these solutions in electric water bath at 85^{o}C for 15 min., until formation Cloud point layer CPL, then separation CPL from aqueous solution and dissolved in 5 mL ethanol, and complete the work as in general method, the results were as in Figs 3, 4.

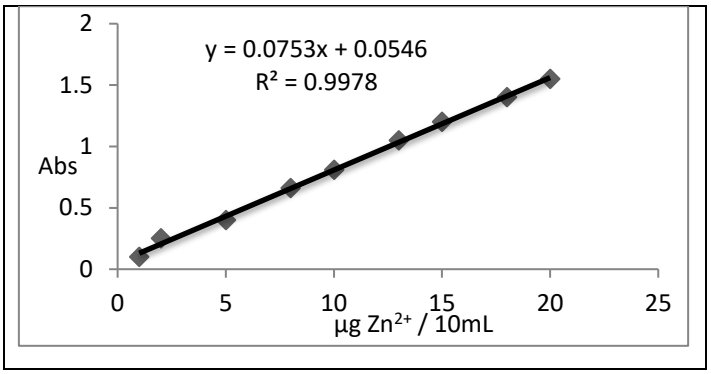


Fig (2): Calibration curve for determination Zn^{2+} ion in aqueous solution by dithizonespectrophotometric method

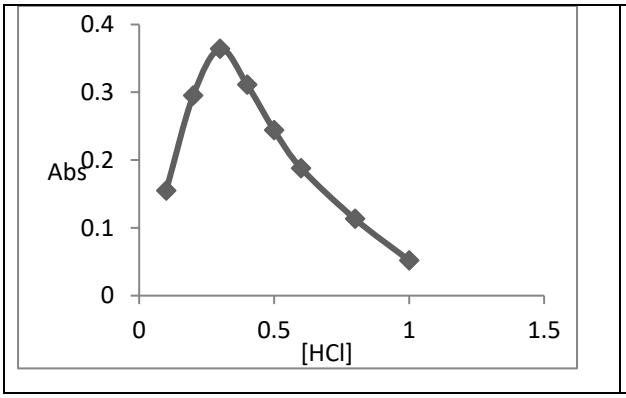


Fig (3). Effect of HCl concentration on formation and stability of ion pair association complex

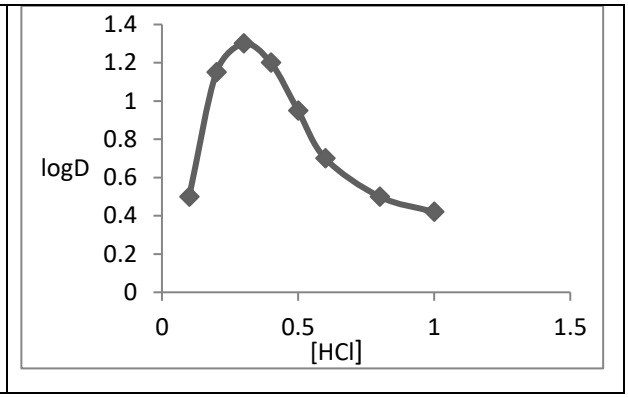


Fig (4): Effect of HClconcentration on extraction efficiency and D-values

The results appear 0.3M HCl was the optimum concentration, give higher extraction efficiency and D-value, become this concentration give best equilibrium to formation ion association complex and distribution to cloud point layer.

Effect of Zn^{+2} Concentration

A number of 10 mL aqueous solutions prepared,contain increased amount d Zn^{2+}ion, 0.3MHCl, $1x10^{-4}$ M Cinchonine, 0.5 mL non-ionic surfactant Triton X-100, heat the solutions in electrical water bath at 85^{o}C for 15 min, to formationcloud point layer CPL, we separated CPL from aqueous solutions and complete the experiment as in general method, the results were as in Fig 5, 6.

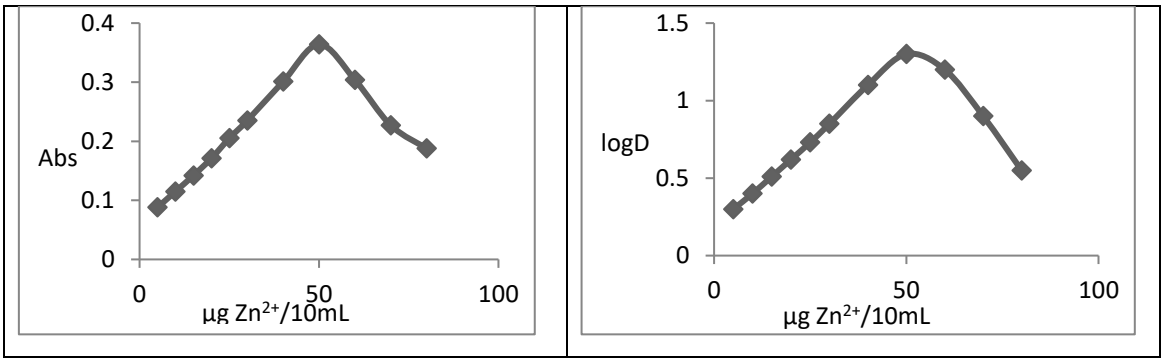


Fig (5): Effect of Zn^{2+} ion conc. on formationFig (6): Effect of Z^{2+} ion conc.

and stability of ion pairs association complex on extraction efficiency and D-Value

The results appear maximum extraction efficiency and D-value obtained in exists 50 µg Zn^{2+} /10mL aqueous solution because metal is considering as thermodynamic value, effect on the thermodynamic equilibrium to formation ion pair association complex, whereas 50µg Zn^{2+}ion give best equilibrium state to formation in pair associationcomplex with higher stability.

Effect of Surfactant Volume

A series of 10mL aqueous solutions was prepares each one contain 50 µg Zn^{2+}, 0.3MHCl, $1x10^{-4}$ M in Cinchonine and different volume of surfactant Triton X-100, then heat all these solutions in electrostatic water bath at 85^{o}C for 15 min to formation cloud point layer CPL, and complete the work as in general method the results were as in Fig 7,8

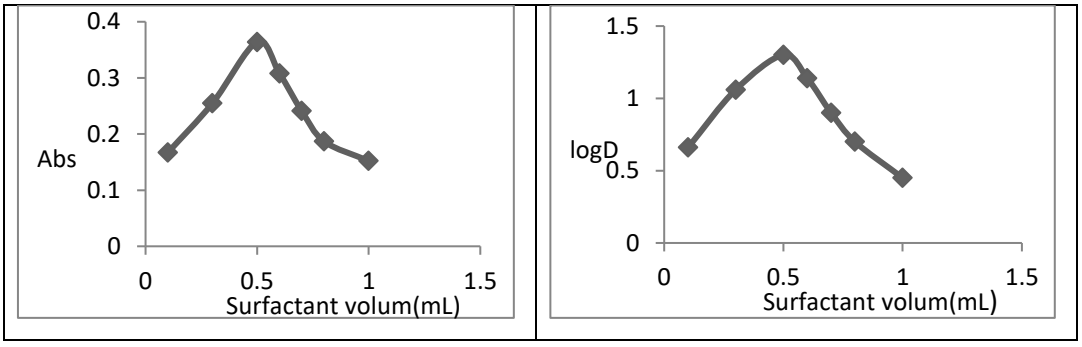


Fig (7) Effect of surfactant volume on Cloud point layer formationFig (8) Effect of surfactant volume on extraction efficiency and D-value

The results show up 0.5 mL of surfactant was the optimum volume gave higher extraction efficiency because this volume give best thermodynamic and kinetic equilibrium for aggregation micelles to

formation good Cloud point layer, with smaller volume and higher density, which is have large surface area to accommodating large amount ofion association complex extracted.

Temperature Effect

Many 10 mL aqueous solutions were prepared, contain 50 µg Zn^{2+} ion, 0.3 MHCl, $1x10^{-4}$ M Cinchonine, and 0.5 mL Triton X-100, then heat these solutions in electrostatic water bath at 85°C for 15min, until formation cloud point layer CPL, and complete the work as in general method, the results were as in Fig 9,3

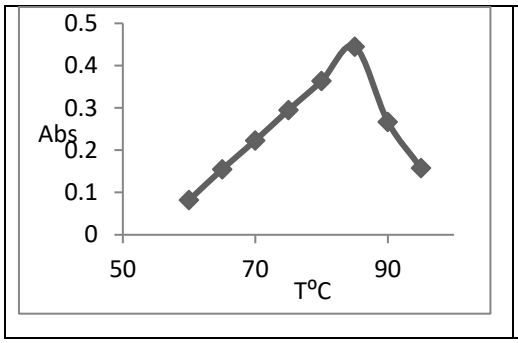


Fig (9): Effect of temperature on cloud point formation

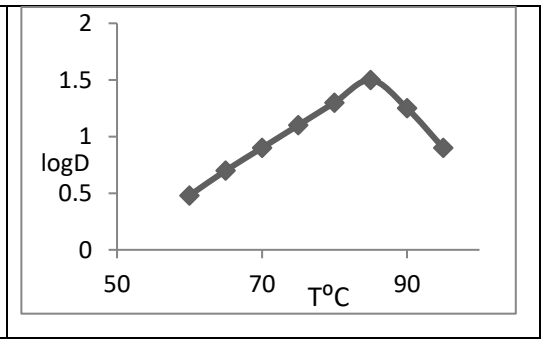


Fig (10): Effect of temperature on extraction efficiency and D-value

The results appear 85°C was the optimum temperature gave higher extraction efficiency. After calculated extraction constant $K_{ex}$from D-values by thermodynamic relation below the results clear in Fig (11).

$$K_{ex} = \frac{D}{[zn^{+2}]_{eq}[Cinchonine]_{eq}}$$

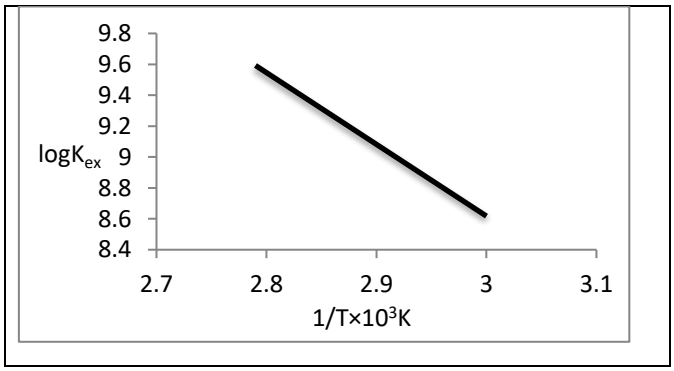


Fig (11): Effect of Temperature on extraction constant

From the slope of the straight line in Fig (11) the thermodynamic were calculated data

ΔH_{ex} = 32.763 k J mol^{-1}

ΔG_{ex}= - 65.77k J mol^{-1}

ΔS_{ex} = +275.23 J $mol^{-1}k^{-1}$

Effect of heating time

Prepared many 10 mL aqueous solution contains 50 µg Zn^{2+}ion, 0.3 MHCl, $1x10^{-4}$ M Cinchonine, and 0.5mL Triton X-100, heat these solutions in electrostatic water but at 85°C for different time, and complete as in general method, the results were as in Fig 12,13

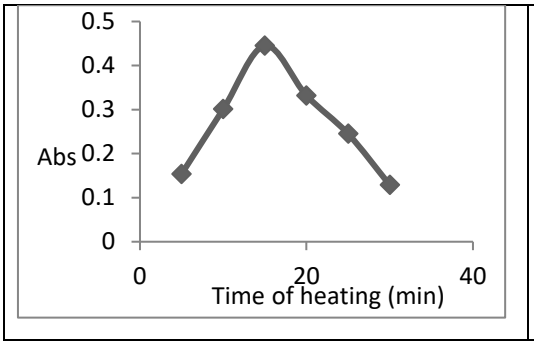


Fig (12) Effect of heating time on quality of cloud point layer

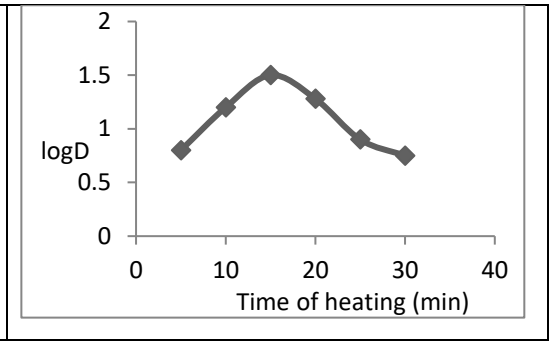


Fig (13): Effect of heating line on extraction efficiency and D-value

The results show up 15 min was the optimum timeof heating to give higher extraction efficiency. Because heating time represent the kinetic side of extraction method help to good aggregation micelles with complete dehydration to formation Cloud point layer with larger surface area to accommodating large amount of ion pair association complex extracted.

Stoichiometry

In order to determine the more probable structure of ion pair association complex extracted for Zn^{2+} ion with Cinchonine, used two spectrophotometric methods:Slope analysis metal and Slope ratio method the solutions treated according to general method, the results as in Figs 14,15,16.

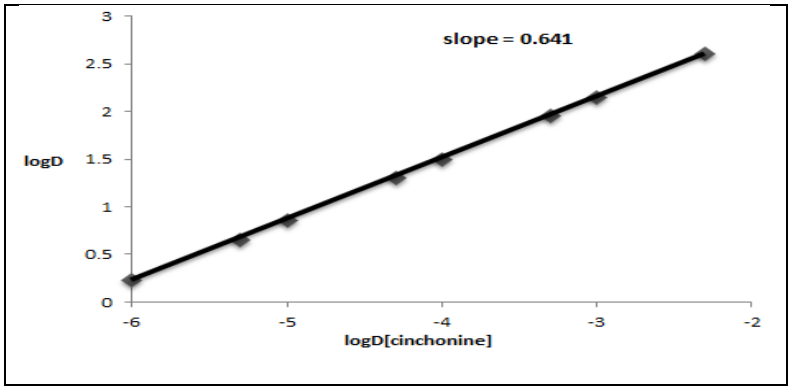


Fig (14) Effect of Cinchonas concentration of extraction efficiency and D-values

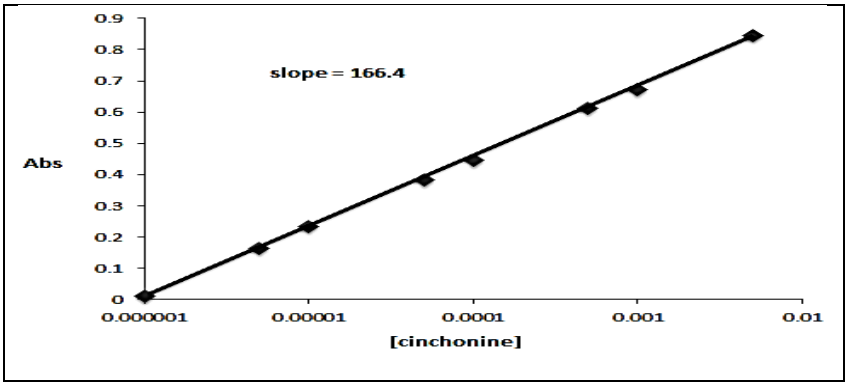


Figure (15) = Effect of Cinchonine Conc. On formation and stability of ion pair association complete

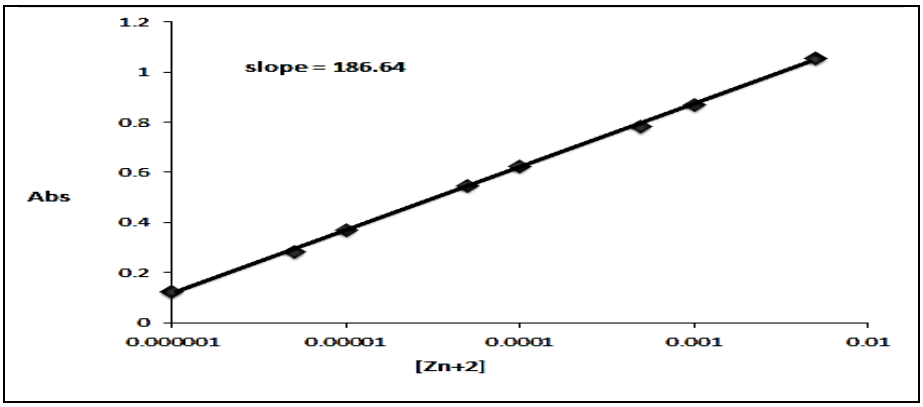


Fig (16): Effect of Zn^{2+}concentrations on formation and stability of ion pair association complete

slope ratio =$\frac{166.4}{186.64}$ = 0.892

The slope and slope ratio values lead to the structure of ion pair association complete extracted was 1:1 H- Cinchonine^{+}; $HZnCl_4^{-}$

Electrolyte Effect

According to general method and at optimum conditions extracted Zn^{2+} from 10mL aqueous solution in exists differentelectrolyte at different concentrations, the results were as in Figs 17,18

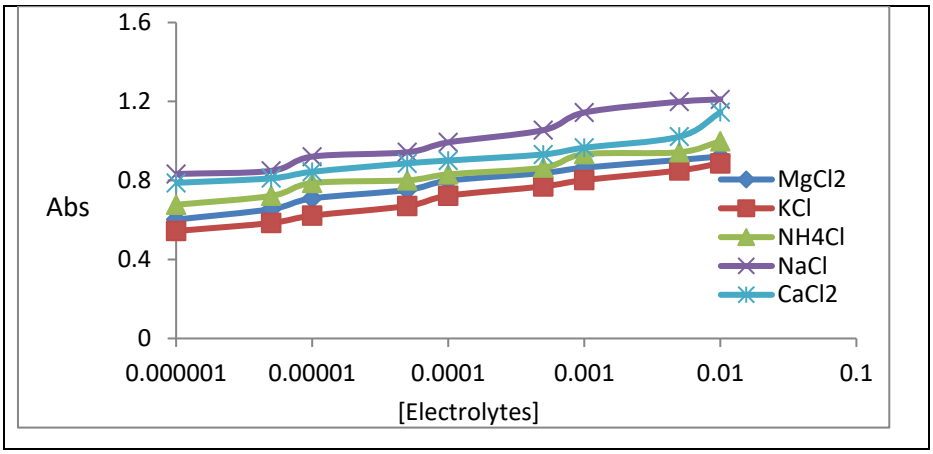


Fig (17): Effect of different conc. for different electrolytes on formations and stability of ion pair association complete extracted

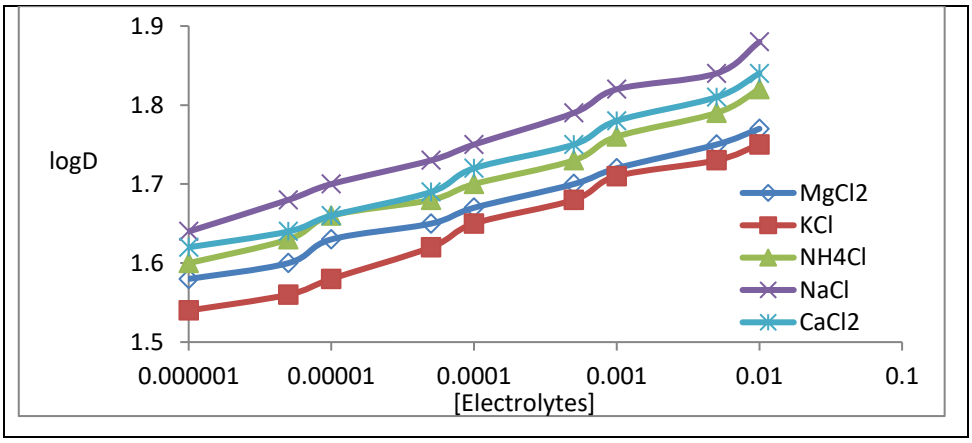


Fig (18): Effect or different conc. of different electrolytes on extracted efficiency and D-value

The results appear existence electrolyte in aqueous solution with Zn^{2+} ion effected to increase extraction efficiency and D-values, that is mean electrolyte increase chances of formation ion pair association complete, so that distribution it to CPL.

Effect of Interferences

By existence 0.01M of foreign ions in aqueous solution with Zn^{2+} ion, extracted the ion pair association complex formed for Zn^{2+} ion according to general method, the results were as in Table (1).

Table (1). Effect of interference on extraction efficiency0.01M

foreign ion	Absorbance at λ_{max}=290nm	D
Cd^{2+}	0.348	20.56
Ag^{+}	0.386	25.43

Hg^{2+}	0.331	16.67
Pb^{2+}	0.225	11.83
Ni^{2+}	0.285	14.51

The results show exists foreignion in aqueoussolution with Zn^{2+} ion effect to decrease extraction efficiency and D-values, so that this decreasingdiffers with different foreign ion.

Variations Surfactant Kind

According to the used extraction method and at optimum conditions by use 1×10^{-4}M Cinchonine with Different surfactant, extracted Zn^{2+} ion as ion pair association complex and results were as in Table 2.

Table (2): Effect of surfactant kind on extraction efficiency of Zn^{+2} ion

Surfactant	**CPL** **Abs.λ_{max}=290nm**	**D**
Tween20	0.095	6.58
Tween40	0.221	10.63
Tween80	0.323	15.70

The results showed a decrease in the extraction efficiency of the Zn^{2+} ion as ion pair association complex whenusing Tweens as surfactants. These results indicate the Tweens are not suitablesurfactants on extraction of Zn^{2+}ion.

Variations of organic Reagent

By thegeneral method, different organic reagents were used with a concentration (1×10^{-4}M) to extract the Zn^{2+} ion at optimum conditions. The results are as in Table 3.

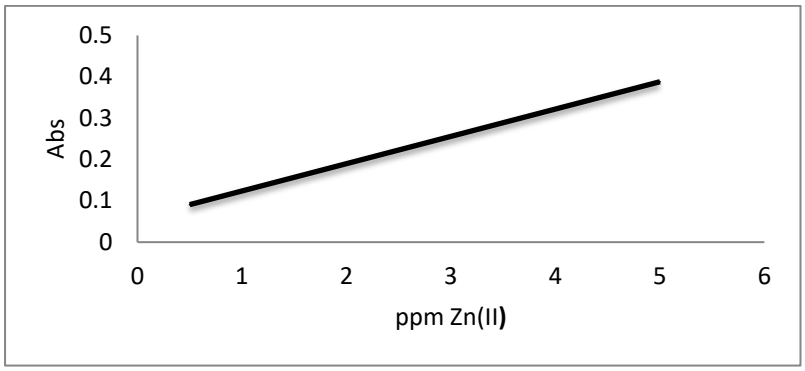
Table (3): Effect of organic reagent on extraction efficiency of Zn^{2+} ion

Organic reagent	**λ_{max}**	**CPL. Abs**	**D**
Ascorbic acid	292	0.372	36.04
Acetophenone	293	0.928	65.70
Salicylic acid	291	0.298	20.70

The results showed difference in the extraction efficiency of the Zn^{2+} ion by using different organic reagents,this differencebecause of the difference in behavior and structure, give variation in the sensitivity and extraction efficiency.

Spectrophotometric Determination Zinc(II)

Zinc(II) was determined spectrophotometrically in different environmental samples and using an appropriate masking agent , Calibration curve after setting the absorbance versus ppm for the zinc ion as in Fig. 19.



Analytical parameters for the calibration curve of the Zn(II) for the applied method are given in Table 4.

Table 4 : Analytical parameters of applied CPE with liquid ion exchange

λ_{max} (nm)	290
Parameter linearity (ppm)	0.5-5
Molar absorptivity(L.mol^{-1}.cm^{-1})	5.165×10^{3}
LOD(ppm)	0.3428
LOQ(ppm)	0.3673
Sandell's sensitivity (µg/cm^2)	1.27×10^{-2}

The samples were prepared according wet digestion method [22]and processed by the applied analytical method and at optimum conditions, then the absorption was measured, through the calibration curve, the zinc ion was determined in those samples. The results compared with FAAS, as standard method, and the results were shown in Table 5.

Table5: Zinc content (ppm) in different samples

No.	**Sample**	**Applied method (ppm)**	**FAAS Method(ppm)**
1	Agriculture Soil	2.84	2.81
2	Non-agriculture Soil	8.31	8.51
3	Soil from local market	2.64	2.91
4	Quince	1.16	1.20
5	Stump	1.88	2.00

6	Apples	0.61	0.59
7	Celery	2.36	2.27
8	Cress	2.48	2.35
9	Radish	0.55	0.58
10	Fish	2.96	3.21
11	Meat	9.11	9.02
12	Drinking water (Al-Ataba)	1.12	1.12
13	Drainage water	1.02	0.86
14	Water of Euphrates river	0.80	0.77
15	Human hair	2.30	2.28

Conclusion

1. Extraction efficiency according to ability of organic reagent to formation liquid on exchanger.

2. Extraction efficiency differ according the ability of metal cation to formation anion complex.

3. Acid concentration in aqueoussolution lead to different velocity for thermodynamic equilibrium to formation ion pairassociation complex.

4. when we are application this method to extraction and determination Zn^{2+} ion in different samples mint to med masking agent for the metal ions.

5. Heating time represented the kinetic side of extraction method lead to the quantity of heating in the solution to decide the velocity of micelles to aggregation.

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