Journal of Kufa for Chemical Science Vol.(1) No. (10) ………………….November 2015

Cloud Point Extraction Method for Separation, Extraction and Spectrophotometric Determination of Zn(II) and Ni(II) as Chloro Anion Complex by use of Crystal Violet

Jihan R. Muslim

Chemistry department, College of education for girls, Kufa university-Iraq

Email: jihanr2012@yahoo.com

الخلاصة

استخدمت طريقة استخلاص نقطة الغيمة لفصل واستخلاص وتقدير ايونات الخارصين الثنائي والنيكل الثنائي طيفياً بهيئة معقدات الكلور السالبة بوسط حامضي بعد تكوينها معقدات ترابطية مع صبغة البلورة البنفسجية وتم بعد ذلك دراسة وتحديد الظروف المثلى لعملية الاستخلاص مثل تأثير تركيز حامض الهيدروكلوريك ,تأثير تركيز الفلز ,تأثير حجم السطح المستخدم, تأثير درجة الحرارة وزمن التسخين وتضمن العمل ايضاً دراسة تأثير المتداخلات والمحاليل الالكتروليتية على عملية الاستخلاص بالاضافة الى تطبيقات تقدير العناصر في نماذج مختلفة.

Abstract

Sensitive extraction method is used for separation preconcentration coupled with spectrophotometric determination of Zinc(II) and Nickel(II) as chloro anions from acidic HCl media by using crystal violet after formation ion pair association complex after studied the optimum condition for extraction demonstrated 1.5M HCl for $Zn^{+2}$and 1M HCl for Ni^{2+}, with 50 µg Zn^{2+} and Ni^{2+}, 0.7mL 1% TritonX-100 for extraction ion pair association of Zn^{2+} as well as 0.9mL with Ni^{2+} and 80^0C suitable for formation CPL and extraction ion pair complex for both metal ions ,with 10 minutes of heating in thermostatic water bath for Zn^{2+} and 15 minutes for Ni^{2+} then study involved effect of interferences and electrolyte with spectrophotometric determination in different samples. The wave length for maximum absorbance of ion pair complex extracted was λ_{max}=590nm for $Zn^{2+}$and 595nm for Ni^{2+}complexes.

Introduction

Cloud point extraction CPE is depending on phase behavior of surfactants in aqueous solution and exhibit phase separation after an increase in temperature. Separation and preconcentration according to (CPE) are becoming an important and practical application of surfactant in analytical chemistry [1,2]. Acloud point extraction procedure was presented for the preconcentration of copper , nickel , zinc and iron in various samples, aftercomplexation by 2-(6-(1H benzo [d] imidazol-2-yl) pyridin -2-yl)-1H-benzo[d] imidazole -(BIYPYBI)[3]

.Heavy metal ions Cd^{2+},Co^{2+},Ni^{2+},Pb^{2+},$Zn^{2+}$and Cu^{2+} separated from water samples with cloud point extraction after forming complexes of metal ions with 8-hydroxy quinoline with determination by inductively coupled plasma optical emission spectrometry [4]. Recently, the cloud point methodology has been used for the preconcentration of Cd, Ni and Zn, Ag and Au and Cr separation as an initial step in the determination of these metals by flame atomic absorption spectrometry FAAS [5-7] .In metals analysis, this necessitates the complexation of the target metal ions with suitable ligands, producing water-insoluble complexes which are then preconcentrated in a condensed surfactant-rich phase [8]. This method, referred to as cloud point extraction (CPE), or micelle mediated extraction, has been widely exploited over the past years owing to its distinct advantages like the analysis of many samples, increased flexibility, enhanced recoveries and reproducibility [9,10]. The CPE of metals, with spectrophotometric detection, was first reported by Watanabeand co-workers, who studied the preconcentration of Ni with 1-(2-thiazolylazo)-2-naphthol in Triton X-100micellar solution [11]. Above the cloud point temperature, the micellar solution separates into a small, surfactant rich phase and a larger diluted aqueous phase. In the aqueous phase, the surfactant concentration remains near the critical micelle concentration. Any analyte solubilized in the hydrophobic core of the micelle in the unheated solution, will be concentrated in the surfactant rich phase following the cloud point extraction [12, 13]. Cloud-point extraction is based on the propertythat a solute present in aqueous solution of non-ionic surfactant is distributed between two phases. Recently great attention has been attracted for its great potential in separation of toxic solutes from several matrixes [14–17]. A simple rapid and selective cloud point extraction method developed for preconcentration of trace Cu and Ag followed by flame atomic absorption spectrophotometric measurement by using TritonX-114 with detection limit 0.5$\mu g L^{-1}$[18]. The chemical variables affecting the separation and determination processes were optimized by using TritonX-114 [19].

Experimental

For spectrophotometric studies used Shimadzu double beam UV-Vis spectrophotometer UV-1700 (Japan) and for absorbance measurements used single beam UV-Vis spectrophotometer UV-1000-02 (Japan) as well as thermostatic water bath Hamburg - 90 (England) .

Materials and solutions

All materials received from commercial and used as received without more purifications Zinc (II) solution of 1mg /mL solution prepared by dissolving (0.1000g) of Zn metal in 1:1 HCl and diluted with distilled water to 100mL in volumetric flask and for Nickel(II) (4.0530g) of $NiCl_2.6H_2O$ (purity 99%)there solutions prepared by dilution .with distilled water, organiccrystalviolet prepared by dissolved (0.0040g) in water of $1x10^{-3}$M and other solutions prepared by dilution with distilled water.

Comprehensive procedure

10 mL aqueous solution contain fixed quantity of metal cation Zn^{2+} or Ni^{2+} and optimum concentration of HCl in the presence of suitable concentration of organic reagent crystal violet and favorable mL of 1% TritonX-100,and heating the solution to 80^0C for suitable time until formation of cloud point layer ,afterward separate CPL from aqueous solution and dissolved CPL in 5mL ethanol and measure the absorbance at λ_{max} against blank prepared at the same manner in absence of metal ion, as well as aqueous solution treated according to spectrophotometric method for each metal ion and after return to calibration curve determine the remainder quantity and subtraction this value from original quantity to determine transferred quantity to CPL as ion pair association at later calculate distribution ratio of extraction by $D=C_0/C_W$, as well as performed reference procedure to determine transferred quantity by stripping method after shaking alcoholic solution of CPL with two portion of 5mL of 2M NaOH to dissociation ion pair complex and return metal ion to aqueous solution and determined the quantity of strippedmetalion by spectrophotometric determination [20].the experimental procedure illustrate the quantity of transferred metal ion determined by stripping method equal to the same quantity of metal ion determined by subtraction .then following the subtraction method became easier and faster.

Results and Discussion

Spectrophotometric studies

10 mL aqueous solutions contain 50µg of a metal ion Zn^{2+} or $Ni^{2+}$and 1M HCl, 0.5mL 1% TritonX-100 and $1x10^{-4}$M crystal violet heating the solutions in thermostatic water bath at 80^0C for 10minutes after separated CPL from aqueous solution and dissolved CPL in 5mL ethanol and taking spectrum against blank prepared at the same manner without metal ion, the results was as in **Figure 1,2**:

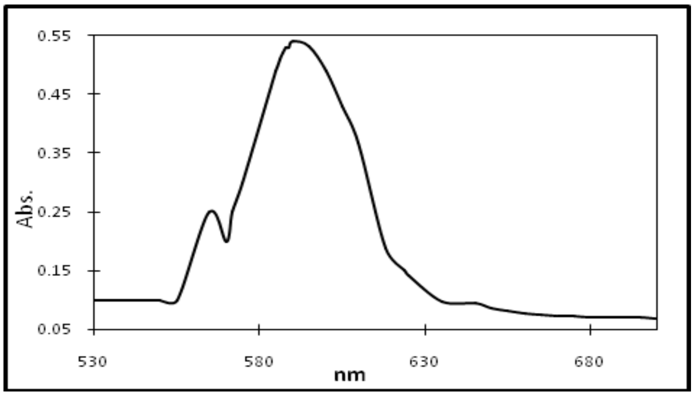


Fig. 1:UV-Vis Absorption spectrum for ion pair complex of Zn(II)

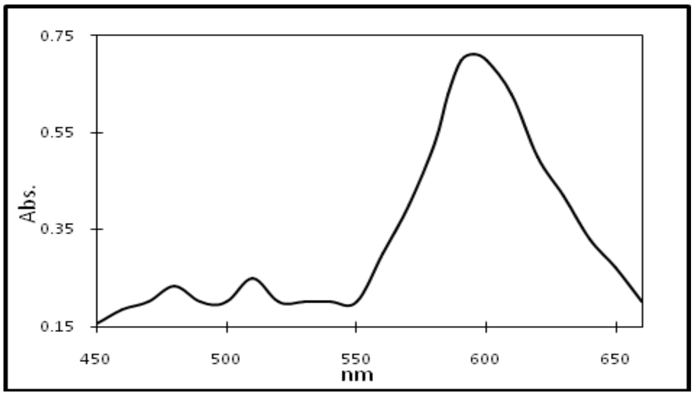


Fig. 2:UV-Vis Absorption spectrum for ion pair complex of Ni(II)

The spectrum in Figures above show λ_{max}=590 nm for ion pair complex of Zn^{2+} and λ_{max}=595 nm for ion pair complex of Ni^{2+}.

Effect of HCl concentration

Extracted 50µg of Zn (II) and Ni (II) from 10 mL aqueous solutions contain different concentrations of HCl and 0.5 mL 1% TritonX-100 and $1x10^{-4}$M crystal violet and heating these solutions at 80^{0}Cfor suitable time until formation CPL so separate CPL from aqueous solutions and determined absorbance of alcoholic solutions of CPL and calculate D-values after return to calibration curve **Figure 3 a and b** according to procedure detailed in comprehensive method. The results were as in **Figure 4, 5**:

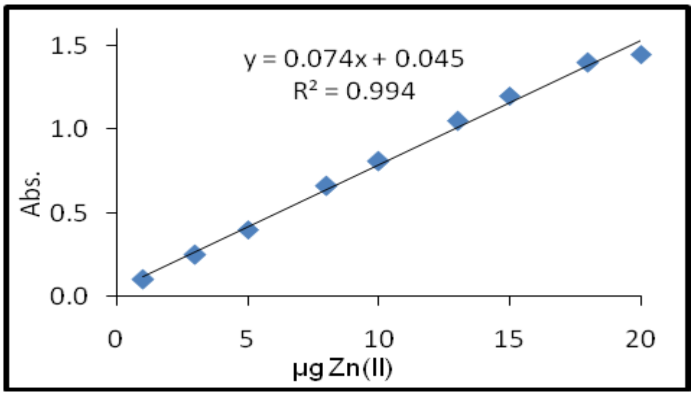


Fig. 3-a: calibration curve by dithizone method for Zn (II).

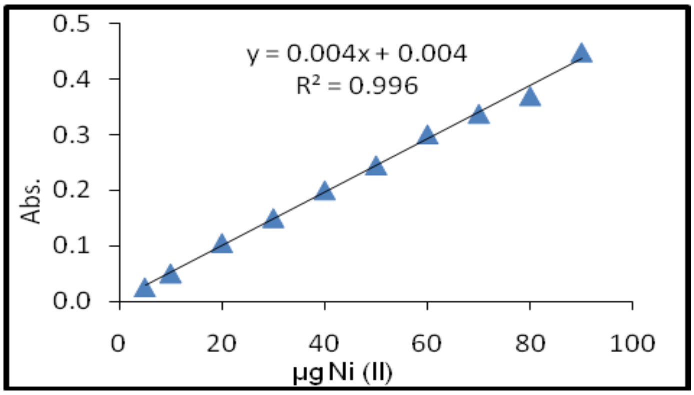


Fig. 3-b: calibration curve by DMG method for Ni (II)

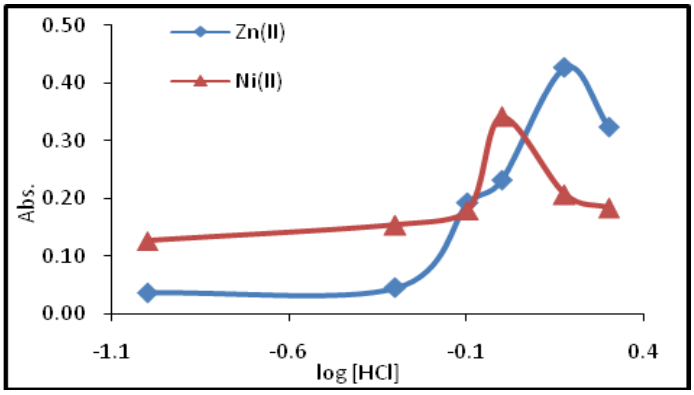


Fig. 4: Effect of HCl concentration on complex formation and extraction

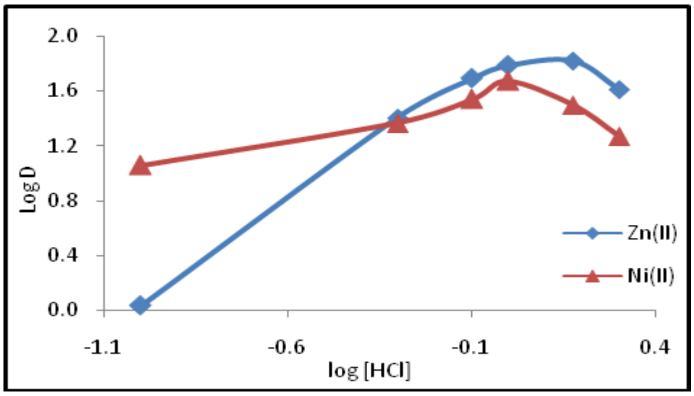


Fig. 5:D=F [HCl]

The results show optimum values for extraction Zn^{2+} was 1.5 M HCl and for Ni^{2+} was 1 M HCl and at these concentration reached favorable thermodynamic equilibrium for extraction to giving higher values of absorbance and D-values ,as well as any concentration of HCl less than optimum value not enough to reach thermodynamic equilibrium and giving decrease in absorbance and D-value .So that HCl more than optimum value concentration effect to decline extraction efficiency by reason of electrophoretic effect and formation of stable compounds of Zn^{2+} and Ni^{2+} in addition to formation ion pair association complex with Cl^- more stable than $ZnCl_4^=$ and $NiCl_4^=$.

Effect of metal ion concentration

Zn^{2+} and Ni^{2+} were extracted separately from 10 mL aqueous solutions contain increasing quantity of each ion and 1.5 M HCl for Zn^{2+} and 1M HCl for Ni^{2+} so $1x10^{-4}$M crystal violet and 0.5 mL of 1% TritonX-100,heating the solutions at 80^0C for 10 min afterward separate CPL from aqueous solutions and determined absorbance and D-values according to the comprehensive method .The results was as in **Figure 6, 7**:

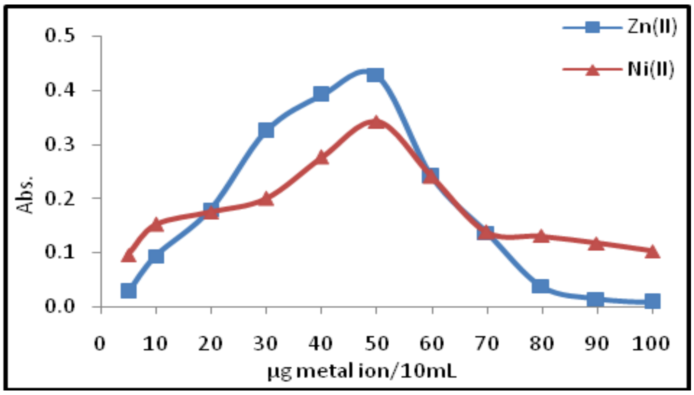


Fig. 6: Effect of metal ion concentration on complex formation and extraction

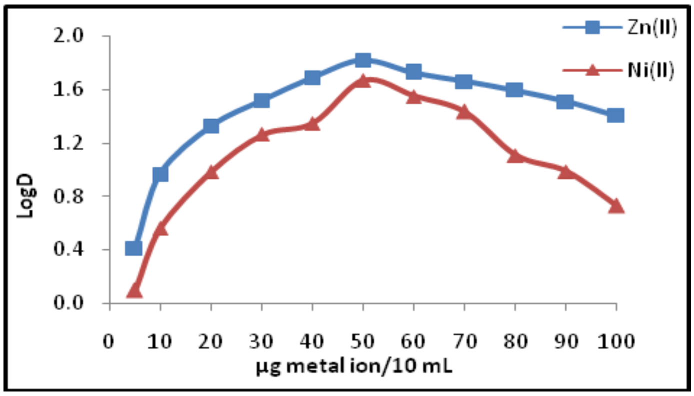


Fig. 7: D= F [metal ion]

The results show extraction efficiency change as a function of HCl concentration and giving a straight line relation to optimum value of metal ion which is 50µg /10 mL for both metal ion Zn^{2+} and Ni^{2+},this concentration effect to reach the favorable thermodynamic equilibrium and giving enhancement in the rate of forward direction of equilibrium. For that produced high concentration of ion pair complex extracted in CPL, but any concentration less than optimum value not enough to reach the best thermodynamic equilibrium and giving decline in the rate of forward direction and minimize absorbance and D-value, so that concentration more than optimum effect to decrease extraction efficiency by effect of mass action law and Le Chatlier principle .As in equilibrium below.

$M^{2+} + CV^{+};Cl^{-} + 3HCl \rightleftharpoons CV^{+};MCl_3^{-} + 3H^{+}$

Or$M^{2+} + CV^{+};Cl^{-} + 4HCl \rightleftharpoons CV^{+};HMCl_4^{-} + 3H^{+}$

Whereas $M^{2+} = Zn^{2+}, Ni^{2+}$

CV = Crystal Violet

Effect of surfactant volume

50µg of metal ion from 10 mL aqueous solutions contain 1.5 MHCl with Zn^{2+} and 1M HCl with Ni^{2+} in presence $1x10^{-4}$ M crystal violet and different volume of TritonX-100 were extracted, after heating the solutions to $80^{0}C$ for 10 min and separated CPL from aqueous solution .Afterward determined absorbance of alcoholic solution of CPL and calculated D-values according procedure detailed in comprehensive method were calculated .The results were as in **Figures 8,9**:

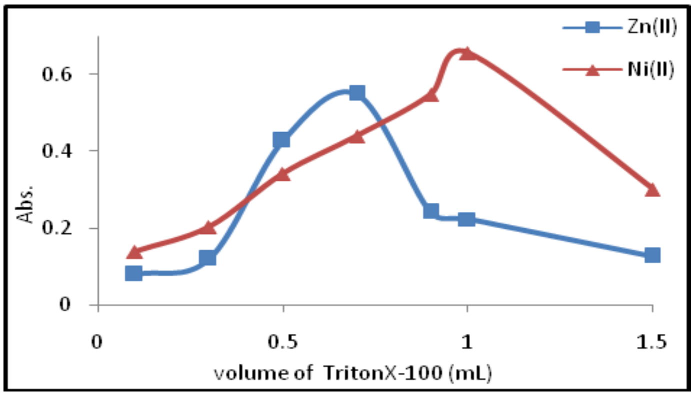


Fig. 8: Effect of surfactant volume on extraction efficiency of ion pair complex.

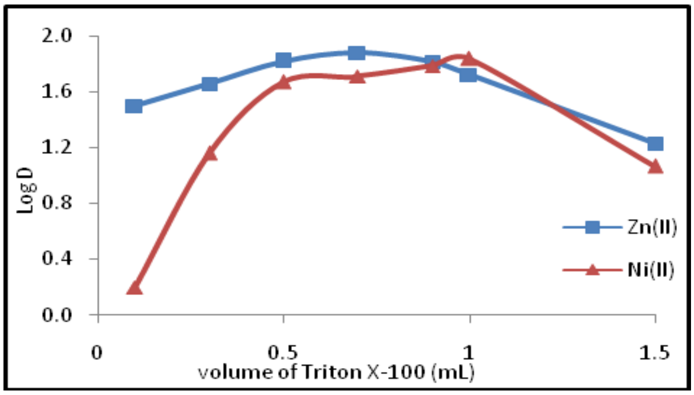


Fig. 9: Effect of surfactant volumeon D-values.

The results illustrated that 0.7 mL was the optimum volume for extracting $Zn^{2+}$and for Ni^{2+} was 1 mL these volumes of surfactant produced the critical micelles concentration (CMC) giving cloud point with smaller volume and higher density enough to give higher extraction efficiency. Any volume less than optimum volume is not suitable to form cloud point layer could extracted ion pair association complex with higher absorbance and D-values .As well as surfactant volume more than optimum effect to increase diffusion of micelles in aqueous solution by effect of hydration and appear minimization in (CMC) and decrease partition of ion pair complex to cloud point layer.

Effect of Temperature

50µg of metal ion Zn^{2+}, Ni^{2+} as chloro anion complex from 10 mL aqueous solution in presence $1x10^{-4}$ M CV and optimum concentration of HCl and optimum volume of TritonX-100 with each ion heating these solutions in water bath at different temperature, afterward determine absorbance and D-values at each temperature according to procedure detailed in comprehensive method. The results were as in **Figures 10, 11**:

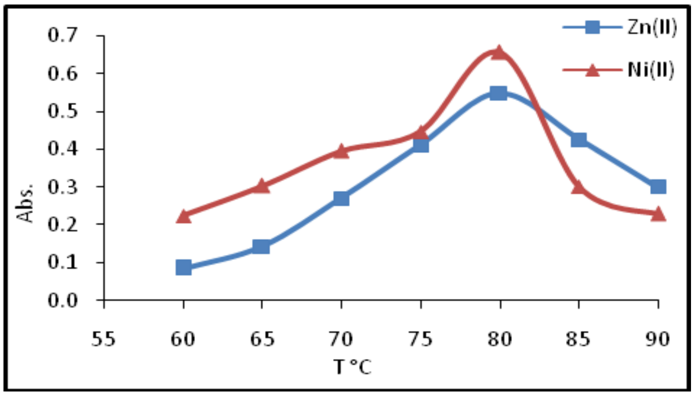


Fig. 10: Effect of temperature on separation activity

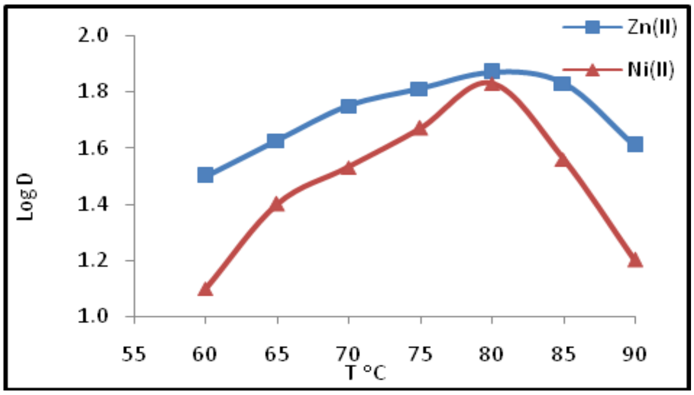


Fig. 11: Effect of temperature on D-values

So that calculated extraction constant K_{ex} at each temperature from the relation below:

$$\mathbf{Kex} = \frac{D}{[metalion].[CV]}$$

After that plotted log K_{ex} against 1/T K the results were appear in **Figure 12**:

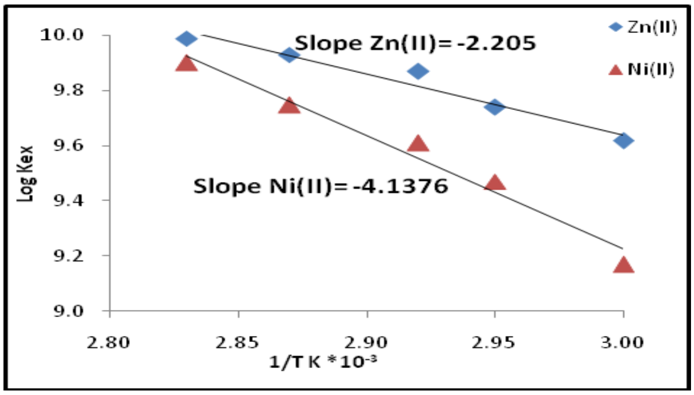


Fig. 12: Effect of temperature on K_{ex} for extraction Zn^{2+} and Ni^{2+}

From the slope of straight line relation above enthalpy of extraction is calculated

$$slope = \frac{-\Delta H_{ex}}{2.303R}$$

As well as calculate ΔG_{ex} and ΔS_{ex} from the relation below

$\Delta G_{ex} = - R\,T \ln K_{ex}$

$\Delta G_{ex} = \Delta H_{ex} - T\Delta S_{ex}$

The results were:

Zn^{2+}			***Ni^{2+}***		
ΔH $KJmol^{-1}$	**ΔG $KJmol^{-1}$**	**ΔS $Jmol^{-1}K^{-1}$**	**ΔH $KJmol^{-1}$**	**ΔG $KJmol^{-1}$**	**ΔS $Jmol^{-1}K^{-1}$**
49.7825	-67.5563	332.4045	116.7975	-66.9438	520.5135

Effect of heating time

Extracting 50 μg metal ion from 10 mL aqueous solutions in presence1x10^{-4}M CV, optimum HCl and volumes of TritonX-100 and heating these solutions in water bath at optimum temperature for different times later determine absorbance and D-values according to procedure detailed in comprehensive method was measured. The results were as in **Figure 13, 14**:

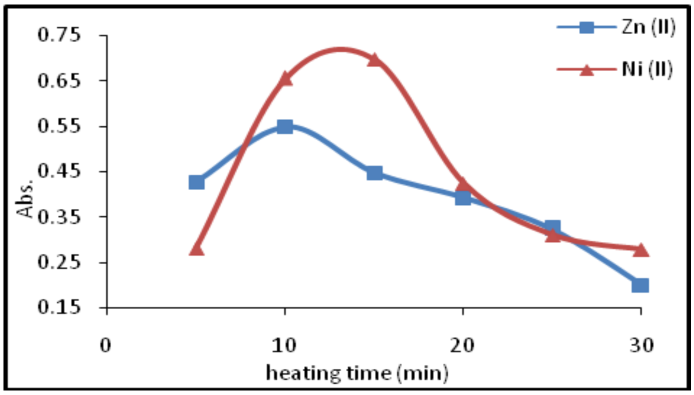


Fig. 13: Effect of heating time on separation activity and absorbance values.

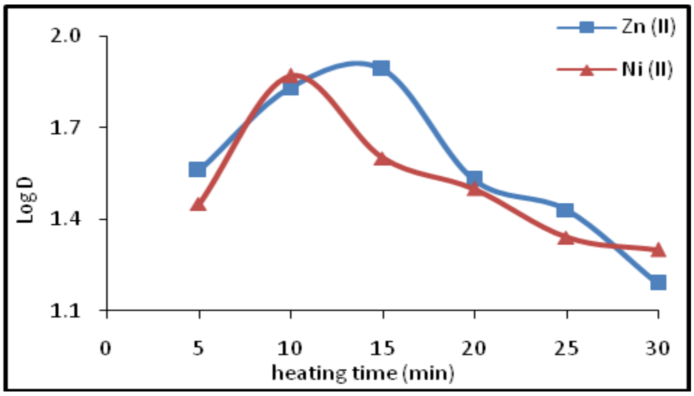


Fig. 14: Effect of heating time on extraction efficiency and D-values.

The results appear optimum heating time for extraction Zn^{2+} was15 minutes and forNi^{2+} was 10 minutes these time help to reached best thermodynamic equilibrium and giving optimum dehydration and produced favorable aggregation for CMC with smaller volume and higher density and giving higher absorbance and D-values .Whereas heating time less than optimum not enough to reached thermodynamic equilibrium and appear decline in extraction efficiency, but heating time longer than optimum value effect to increase diffusion of micelles by effect of increase potential kinetic energy and giving decrease in extraction efficiency also.

Stoichiometry

To know the more probable structure of ion pair complex extracted by use of cloud point extraction method (CPE) with application of two spectrophotometric method which is slope analysis method and slope ratio method ,the results was illustrated in Figures 15 and (16 a and b) (17 a and b):

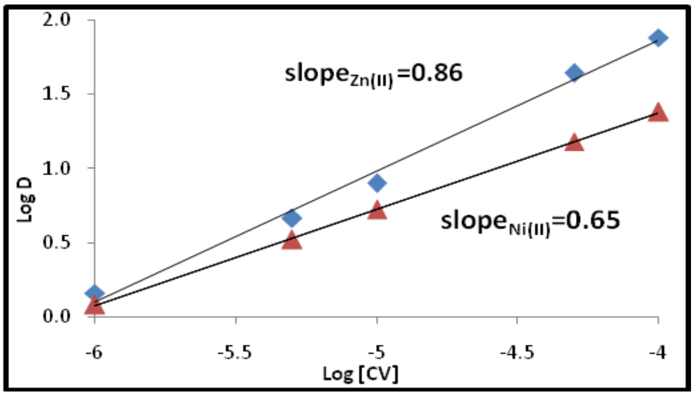
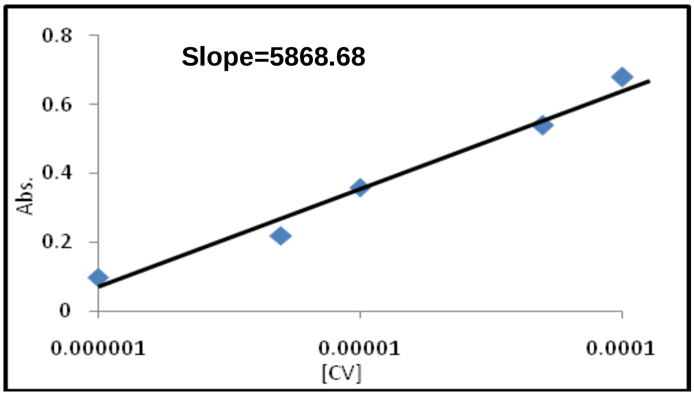
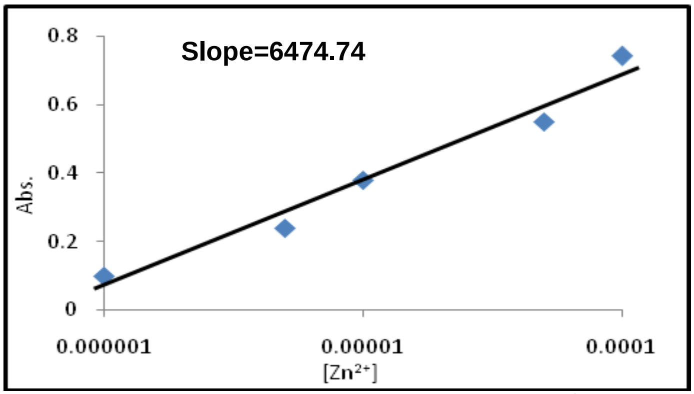


Fig. 15:slope analysis method for both metal ions, Zn^{2+} and Ni^{2+}



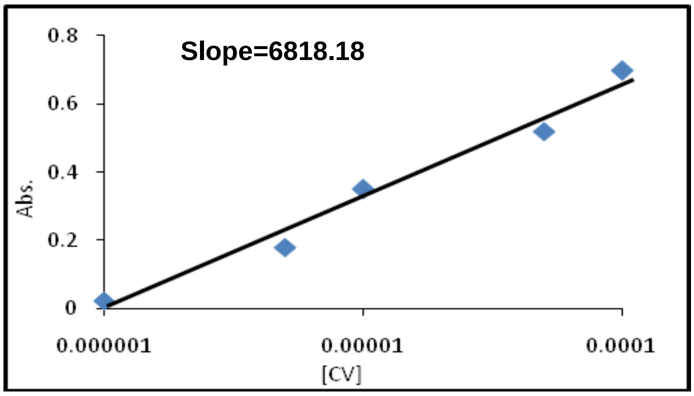
a- Effect of different concentration of organic reagent



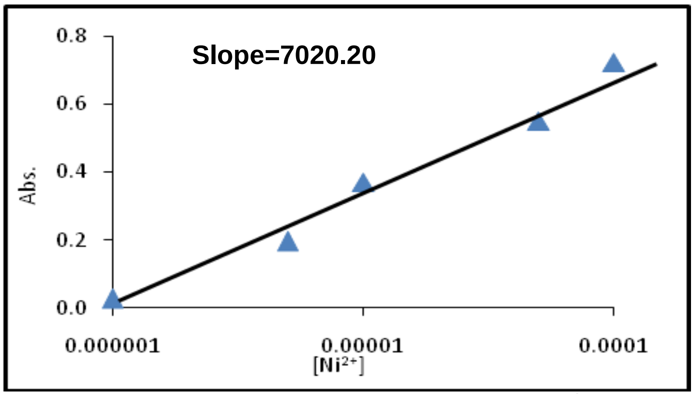
b-Effect of different concentration of Zn^{2+} ion

Fig. 16: Slope ratio

$$slope\ ratio = 5868.\frac{68}{6474}.74 = 0.9064$$



a-Effect of different concentration of organic reagent

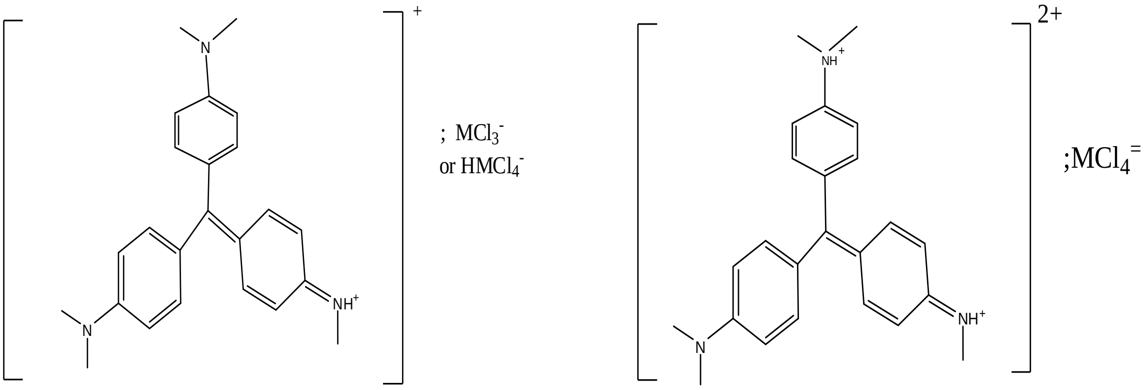


b- Effect of different concentration of Ni^{2+} ion

Fig. 17: Slope ratio

$$slope\ ratio = \frac{6818.18}{7020.20} = 0.971$$

The results appear the probable structure of ion pair complex extracted to CPL was 1:1 $[CV]^{+}$; $ZnCl^{-}_{3}$ or $[CV]^{+}$;$HZnCl^{-}_{4}$or $[CV]^{2+}$;$ZnCl_4^{-2}$, $[CV]^{2+}$;$NiCl_4^{-2}$



Whereas M=Zn^{2+} and Ni^{2+}

Effect of Interferences

Extracted 50µg from metal ion Zn^{2+} and Ni^{2+} from 10 mL aqueous solution contain optimum concentration of HCl for each ion and volume of TiritonX-100 in presence 0.1 M of different anion as oxy anions and chloro complexes anion heating these solutions at 80^{0}C for optimum time until produced cloud point layer with smaller volume and higher density at latter determined the absorbance and D-values according to procedure detailed in comprehensive method .The results was as in **Table 1**.

Table 1: Interferences effect of different anion on extraction efficiency.

Anion	*Zn^{2+}*		*Ni^{2+}*	
	^{590}A	D	^{595}A	D
MnO_4^-	0.432	63.10	0.129	7.47
$Cr_2O_7^=$	0.270	31.63	0.257	21.47
$HgCl_2$	0.405	52.31	0.181	17.46
$CdCl_2$	0.137	29.97	0.314	48.72
$WO_4^=$	0.397	44.55	0.297	31.52
$MoO_4^=$	0.440	63.93	0.301	42.60

The results of interferences experiment show there is an interference for the anions in the extraction of Zn^{2+} and Ni^{2+}, this interference reflect the participation of these anion in the formation of ion pair association complex with organic reagent crystal violet, but depend on the nature and behavior of each anion in the aqueous solution as well as each anion needing special optimum conditions and by the different interference with the metal ions Zn^{2+} and Ni^{2+}.

Effect of electrolyte

Extracted 50μg of metal ion (Zn^{2+}, Ni^{2+}) from 10 mL aqueous solution contain optimum concentration of HCl for each ion and optimum volume of TiritonX-100 in presence 0.1 M concentration of electrolyte salts, Heating these solutions at 80^0C at optimum time for each ion until formation cloud point layer and complete separation of ion association complex .Afterward determined absorbance and D-values in presence each electrolyte salts. Theresults were as in **Table 2**.

Table 2: Effect of electrolyte salts on extraction efficiency of Zn^{2+} and Ni^{2+}

Electrolyte Salts	***Zn^{2+}***		***Ni^{2+}***	
	^{590}A	**D**	**^{595}A**	**D**
LiCl	0.752	98.43	0.824	96.35
NaCl	0.711	91.63	0.760	87.45
KCl	0.665	82.52	0.731	84.40
NH_4Cl	0.608	78.46	0.708	79.77
$CaCl_2$	0.573	81.29	0.773	81.39
$MgCl_2$	0.689	88.57	0.809	85.62
$AlCl_3$	0.771	94.41	0.810	86.62

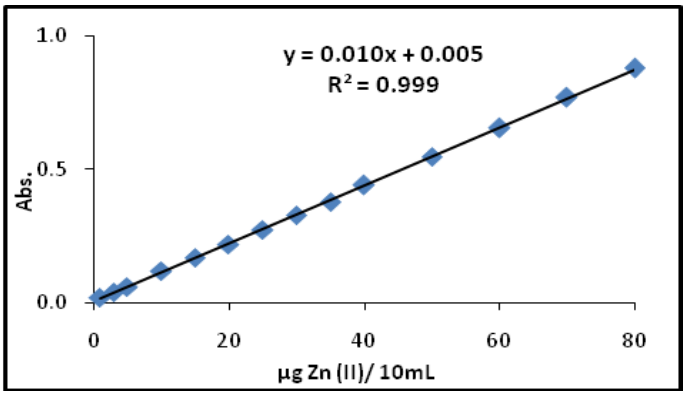
The results show that presence of electrolyte salts in the aqueous solution appear general effect by increase the extraction efficiency with enhancement in absorbance and D-values due to increase in the ionic strength of the aqueous solution and help to increase dehydration of

CMC layer ,as well as increasing destroyed of hydration shell for anion and help to increase the chances of formation ion pair association complex and good aggregation of micelles to form suitable layer of cloud point with smaller volume and higher density. As well as the results show this relation behavior appears as a function for ionic diameter of cation in electrolyte salt and behavior of this electrolyte salt in aqueous solution.

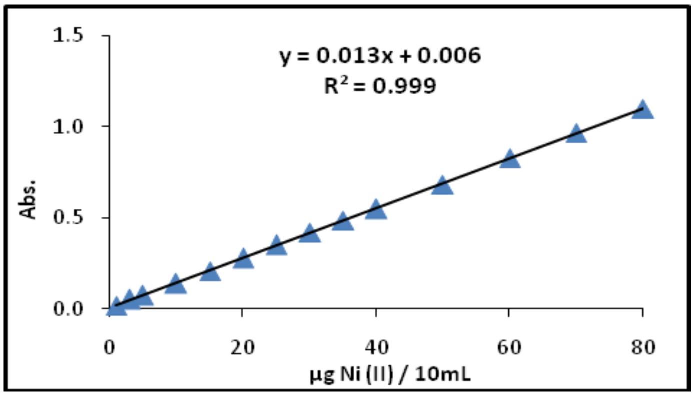
Characteristics of Method

Calibration Curve in **Figure 18** were performed by extraction Zn^{2+} and Ni^{2+} according CPE methodology at optimum conditions as well as this Calibration graph used for spectrophotometric determination of analyte metal in different environmental and vital sample.

ion	**Ɛ** **L $mol^{-1}cm^{-1}$**	**R.S.D**	**Sandell's sensitivity ($\mu g\ cm^{2}$)**	*D.L* *($\mu g\ mL^{-1}$)*
Zn^{2+}	7110.68	0.00789	$9.19*10^{-9}$	$3.7*10^{-6}$
Ni^{2+}	8038.86	0.00792	$7.3*10^{-9}$	$4.05*10^{-6}$



a-Calibration curve of Zn (II)



b-Calibration curve of Ni (II)

Fig. 18: Calibration graph according to CPE methodology

Table 3: determination micro amount Zn^{2+}& Ni^{2+} in different samples.

Sample	Zn^{2+}ppm	Ni^{2+}ppm
Nonagriculture soil (Al-Mishikhab)	**20**	**16**
Old city soil	**60**	**36**
Cabbage	**12**	**20**
Chicken liver	**62**	**32**
Fish farms	**38**	28

Conclusion

Extraction of Zn^{+2}& $Ni^{+2}$with crystal violet to micellar nonionic surfactant Tritonx-100 has been investigated .The sensitivity, ecological safety , simplicity and convenience of the suggested procedure are competitive have confirmed its applicability to the separation and preconcentration of Zinc and Nickel which due its high stability constant and high selectivity loading and has been carried out .In a view glance to the results one can notice that present method is superior to those previously reported in term of some characteristics performance[21-23].

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