Cloud Point Extraction for Separation and Microamounts Determination of Copper (II) and Cobalt (II)

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Abstract

Copper(II) and Cobalt(II) preconcentrated and separated in different samples after complexation by 2-[4-Nitro phenylazo]-4,5-diphenyl imidazole (NPADPI) was presented with cloud point extraction method, are quantitatively extracted in TritonX-100 following separation. 5ml of ethanol was added to surfactant-rich phase prior to its analysis by UV-Vis spectrophotometry, All experimented conditions limited such as pH, concentration of TritonX-100, temperature, time of heating, stoichiometry for complex extracted ,as well as applications about determination quantity of Copper(II)and Cobalt(II) in different samples.

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

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application of surfactant in analytical chemistry [1,2]. Cloud Point extraction has been used for preconcentration of pb (II) and Cd(II) after complexation with 2-[(3-Bromophenyl)azo]-4,5-diphenyl imidazole(BPADPI) with Cd(II) and 2-[Benzothiazolyl azo]-4-benzylphenol (BTABP) with pb (II),then determination the steady elements by UV-Vis spectrophotometer and the complexes extracted to TritonX-100 [3] .The cloud Point extration (CPE) used for separation and preconcentration of nickel (II) with determination by graphite furnace atomic absorption 8-hydroxy quinoline used as liqand and TritonX-100 as surfactant and study all factors affecting the cloud point extraction[4] . Heavy metal ions Cd^{+2},Co^{+2},Ni^{+2},Pb^{+2},$Zn^{+2}$and Cu^{+2} separated from water samples with Cloud Point extration after forming complexes of metal ions with 8-hydroxy quinoline with determination by inductively coupled plasma optical emission spectrometry [5].Water soluble chelating agent p-sulfonatocalix[4]arene used for separation copper and lanthanoid ions according to Cloud Point extraction by use TritonX-100 as well as studies all the factors affecting the extraction efficiency and this method demonstrate Cu(II) can be separated from Ln(II) under weakly acidic conditions[6]. Lipophilic Schiff base N,N$^\backslash$ -bis(2-hydroxyacetophenone)-1,2-propane dimine used for separation copper from water samples according to cloud point extraction and determination by flame atomic absorption spectrometry and used TritonX-114 as surfactant .This method demonstrate detection limit was $0.06ngml^{-1}$ [7].Cloud Point extraction used for preconcentration of copper,nickel and cobalt ions in different samples after complextion with methyl-2-pyridylketone oxime in basic medium by used TritonX-114 as surfactant and studied all factors affecting [8].Extraction and determination of copper and nickel in food samples according to cloud point extraction by used complexing agent 2-(2$^\backslash$-benzothiazolylazo)-5-(N,N-diethyl) aminophenol and TritonX-114,with determination by flame atomic absorption spectrometry with limit of detection $0.1\mu g$ g^{-1}[9].Cloud point extraction procedure was presented for the preconcentration of copper (II) ion in various samples ,after complexation by 4-(phenyl diazenyl) benzene-1,3-diamine copper(II) ions were

quantitatively recorered in TritonX-114 and determination by flame atomic absorption spectrometry with detection limit 0.6ng ml^{-1}[10]. Asimple rapid and selective cloud point extraction method developed for preconcentration of trace Cu and Ag followed by flame atomic absorption spectrometion measurement by used TritonX-114 with detection limit 0.5μgl^{-1} [11]. 4-Ethyl-1-(pyridin-2-yl)thiosemicarbazide has been used as a new complexing agent in cloud point extraction (CPE) for preconcentration and determination of trace amounts of copper in saturated saline medium.The chemical variables affecting the separation and determination processes were optimized by using TritonX-114 [12] .

Experimental

Used analytical grade were obtained from international companies without more purification,organic   reagent   2-[4-Nitrophenyl   azo]-4,5-diphenyl   imidazole   (NPADPI) synthesized   according   to   general   procedure   [13],for   spectrophotometric   absorption measurements used shimadzu double beam UV-Vis spectrophotometer UV-1700 Japan and shimadzu   single   beam   UV-Vis   spectrophotometer   UV-1000-02   Japan   as   well   as pHmeterWTW,E163694 CE Germany .

General procedure

Aqueous solution 10ml in volume containing analyte ion ,$1*10^{-4}$M(NPADPI) and fixed concentration of TritonX-100 with optimum PH for each ion,the mixture heating in water path for temperature of cloud point formation,then decanted the bulk aqueous solution.Miceller phase was dissolved in 5ml ethanol and evaluated the ion content by UV-Vis spectrophotometer at λ_{Max} =536nm for $Cu^{+2}$and λ_{Max} =480nm for Co^{+2},in addition to calculated distribution ratio D by following   suitable spectrophotometric method for determination each analytical metal in this study [14],with dependence on calibration curve Fig(1).
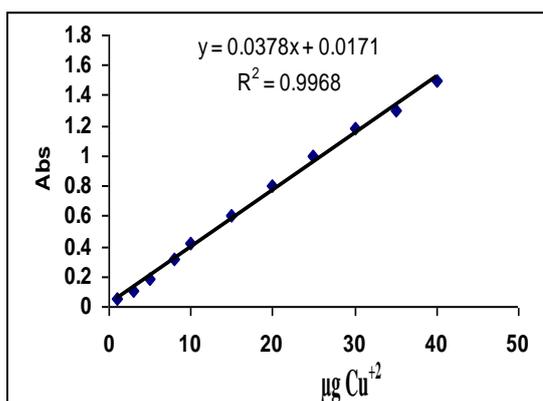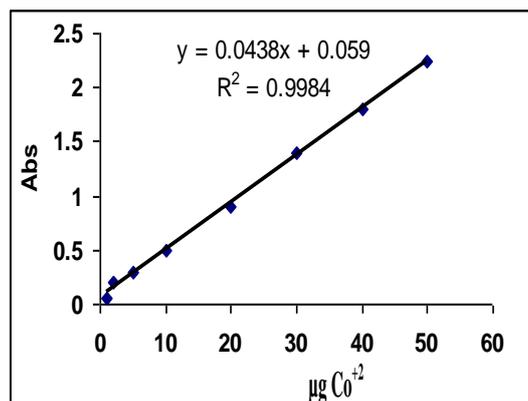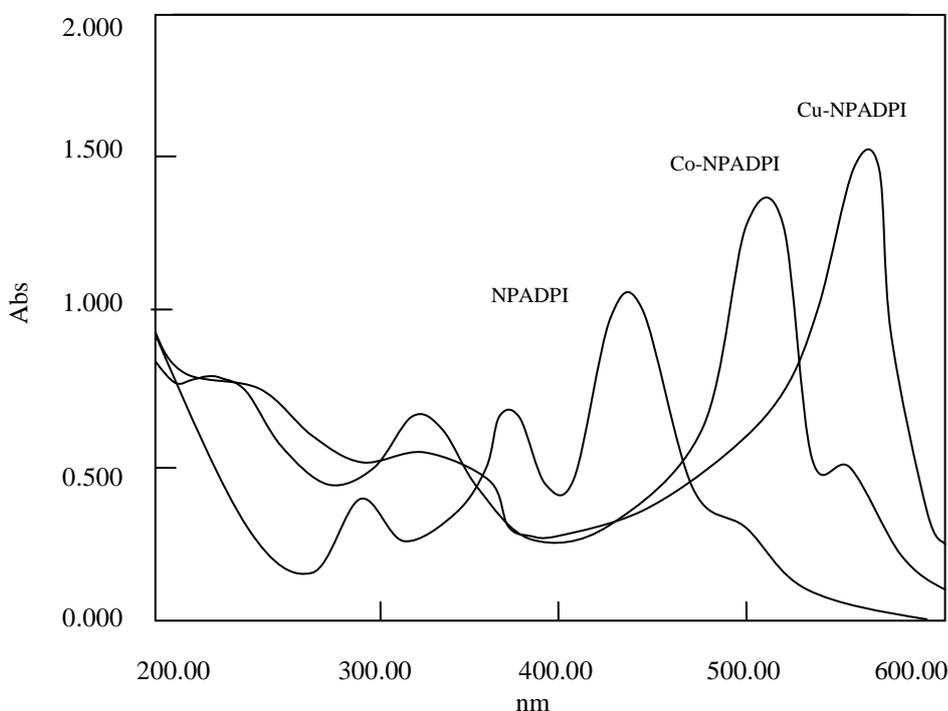
(a)   (b)

Fig(1): calibration curve by suitable spectrophotometric method
a/for Cu^{+2}
b/for Co^{+2}

Fig(2):Uv-Vis spectrum for organic reagent
and its complex with Cu(II)and Co(II)
Organic reagent NPADPI λ_{max}=424nm
**Complex Cu-NPADPI λ_{max}=536nm**
**Complex Co-NPADPI λ_{max}=480nm**

Results and Discussion

Effect of PH

Extracted analyte ions according to cloud point extraction depends on the PH at

which Complex formation ,where are PH effect as optimum condition for metal- complex

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formation and subsequent extraction when we are extracted Cu^{+2} and Co^{+2} in cloud point extraction methodology at PH ranging from 4 -12 giving the results as in Fig 3 (a,b)
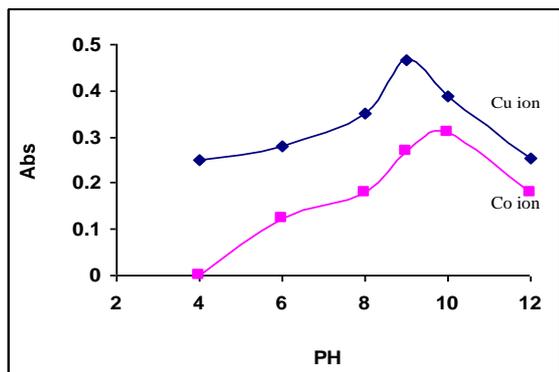
**Fig (3 a) Effect of PH on micelles formed**
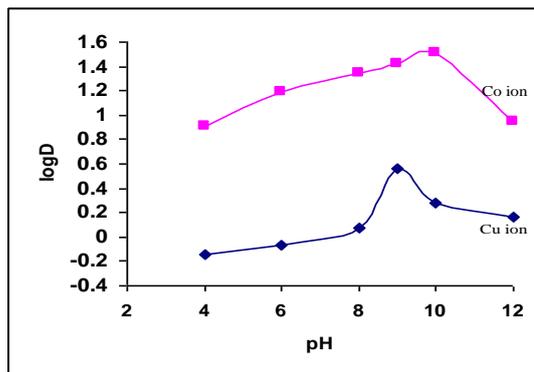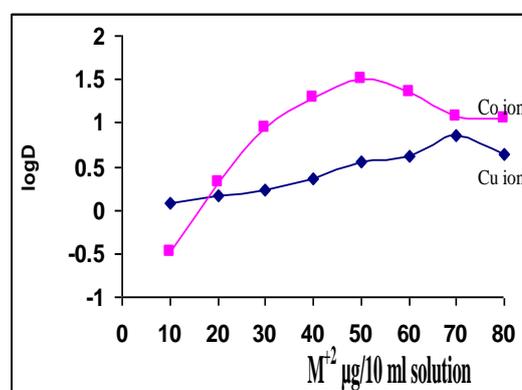

Fig (3 b) Effect of PH on distribution ratio D

The results shows there is an effect for PH on absorbance and sensitivity of method also distribution ratio D values, maximum extraction of Cu^{+2} at PH=9 and Co^{+2} at PH=10, with decrease complex formation extracted to cloud point at lower and higher PH

Effect of ion concentration

Thermodynamic behavior of cloud point extraction demonstrate metal ion concentration play important major parameter on formation and stability of complex and micelles .CPE of Cu^{+2} and Co^{+2} ions were studied for solutions contain range of concentration for each ion from 10µg to 80 µg in 10ml solution as in Fig 4(a,b).
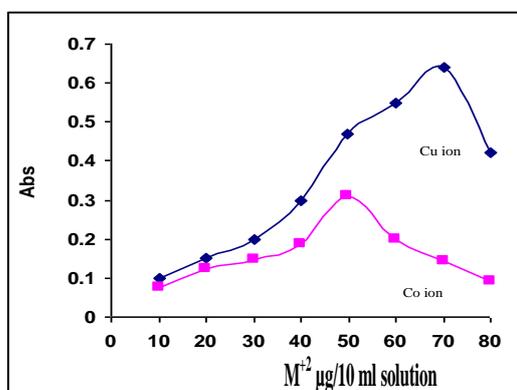
Fig(4 a) Effect of metal ion concentration on complex formation by CPE

**Fig(4b) Effect of metal ion concentration on distribution**

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Th results shows more sensitive with CPE at 70μg Cu^{+2} and 50μg Co^{+2},Thermodynamic equilibrium not allow to reaching at less concentration of metal ion,as well as concentration more than optimum effect to inverse equilibrium to dissociation of complex and increases ionic form according to mass action law and Lechatlier principle.

Effect of temperature

Thermodynamic behavior   of cloud point formation illustrate there is an optimum temperature for cloud point extraction CPE, Extraction   performed with temperature ranging from 60C^{0} to 90C^{0} as the resultes in Fig 5 (a,b).
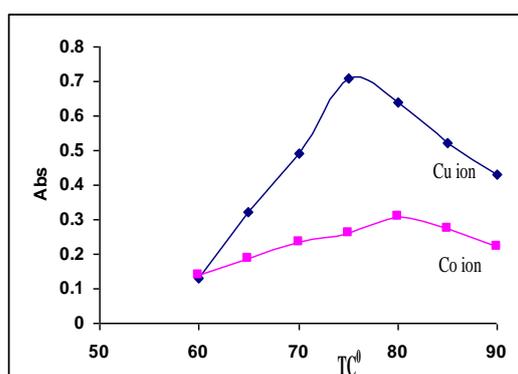
Fig (5 a) Effect of temperature on cloud point formation and complex extraction
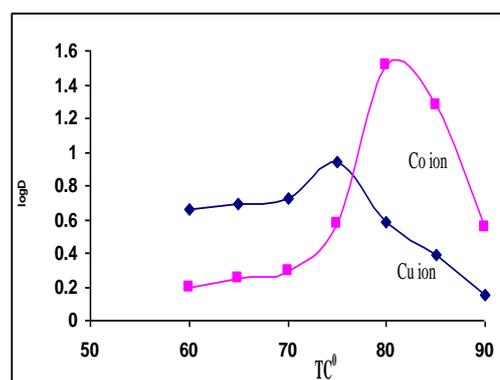
Fig(5b)Effect of temperature on distribution ratio D for extraction Cu(II)and Co(II)

The results shows optimum temperature for extraction of Cu^{+2} in CPE was 75C^{0} but 80 C^{0} for Co^{+2}.The temperature less than optimum temperature not allow to cloud point formation with small volume and high density ,Higher temperature redused micelles agrigation to form cloud point ,after that calculate extraction contant K$_{ex}$ according to relation below

$$Kex = \frac{D}{[M^{2+}]_{aq}.[Ligand]_{org}}$$

The relation between logk$_{ex}$ and 1/T giving straight line and as in Fig (6)
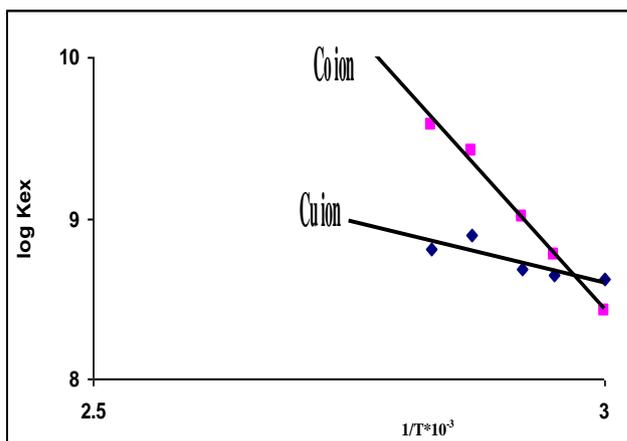
Fig (6) Effect of temperature on K_{ex} for extraction Cu(II) and Co(II)

for the slope of straight line

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

ΔG_{ex} = - R T ln K_{ex}

$\Delta G_{ex} = \Delta H_{ex}$ - TΔS_{ex}

The thermodynamic date was ΔH_{ex}=0.0112KJmol^{-1} for Cu^{+2} and 0.153 for Co^{+2} as well as ΔG_{ex} =-59.2789KJmol^{-1} for Cu^{+2},-64.74 for Co^{+2} but ΔS_{ex}=170.373Jmol^{-1}K^{-1} for Cu^{+2},183.8Jmol^{-1}K^{-1} for Co^{+2} .The complex formation and CPE was intropic in region.

Effect time of heating

Time for heating at optimum temperature was very necessary for cloud point formation and extraction,the experiment was performed at rang time of heating 5 min to 30 min giving the results as in Fig 7(a,b)
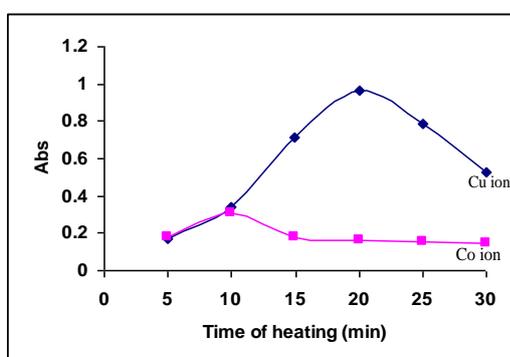
**Fig(7a) Effect time of heating on Extraction in CPE**
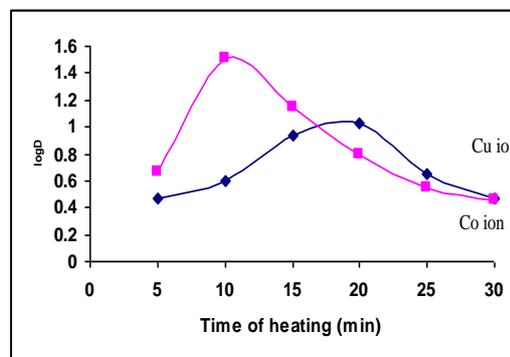

Fig(7b)Effect time of heating on distribution ratio D

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The results shows suitable time for cloud point formation at optimum heating time was 20 min for $Cu^{+2}$and   10 min for Co^{+2} the time less than optimum heating time not allow to complete cloud point formation with minimum volume and high density this effect to not allow to reach equilibrium of extraction with CPE. as well as longer time of heating decline absorbance and distribution ratio by reason of diffusion micelles of cloud point.

Effect of TritonX-100 concentration

TritonX-100 which is non-ionic surfactant having many properties to make it suitable for CPE,commercial   availability in high purified homogeneous form .low toxicological properties,the high density of the surfactant rich phase easily separation, Additionally the cloud point of TritonX-100 permits its use in the extraction and lor

pre-concentration of alarge number of molecules and complex [15,16].To definition suitable concentration of TritonX-100 for CPE using ranging from o.1٪ to 1٪ (w/v),the results obtained as in Fig 8(a,b)
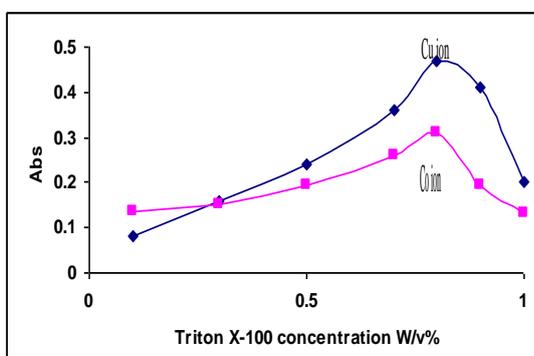
Fig(8a)Effect   of   TritonX-100 concentration on cloud point formation and extraction
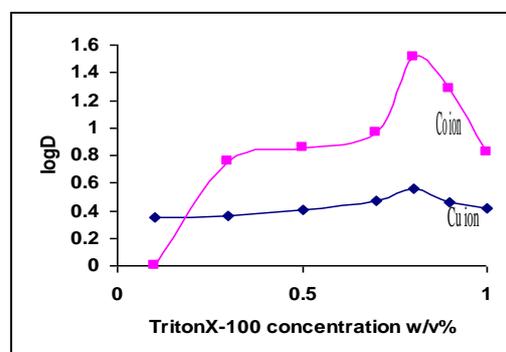
Fig(8b)Effect   of   TritonX-100 concentration on distribution ratio D

The results demonstrate suitable concentration   of TritonX-100 for extraction Cu^{+2}& Co^{+2} was 0.8 ٪   lower concentration TritonX-100 reduce the cloud point layer formation probably due to assemblies that were in adequate to quatitatively entrap the hydrophobic complex[17].

High concentration of TritonX-100 resulting in an increase in the volume of the surfactant rich- phase .In addition the viscosity of the surfactant rich- phase increase leading to poor sensitivily [18,19] .

Stoichiometry

slope ratio method

To demonstrate structure of complexes extracted Cu-NPADPI and Co-NPADPI, theprocedure include extracted metal cations with cloud point extraction with range of concentration forNPADPI $10^{-6}M$ to $5*10^{-4}M$ as well extraction with range of metal ions concentration for $10^{-6}M$ to $5*10^{-4}M$, obtained the results as in Fig 9(a,b)
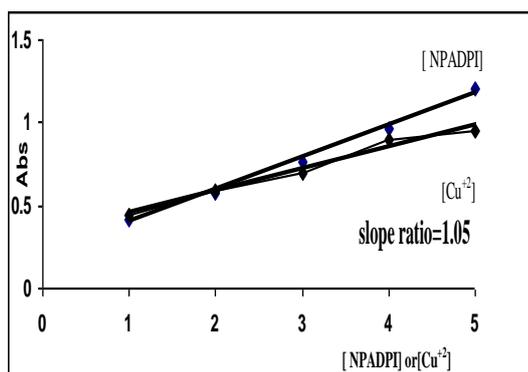
Fig (9a) slope ratio method for Cu^{+2} complex
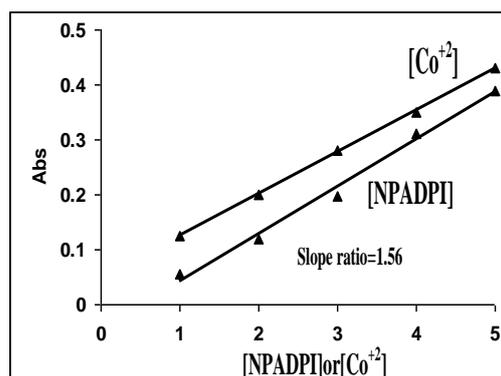
Fig(9b) slope ratio method for Co^{+2} complex

The results shows more probable structure of complex extracted was 1:1 metal:ligand for Cu^{+2} $[Cu(NPADPI)]^{+2}SO_4^{-2}$ and 1:2 metal:ligand for Co^{+2} $[Co(NPADPI)_2]^{+2}(NO_3)_2^{-}$.
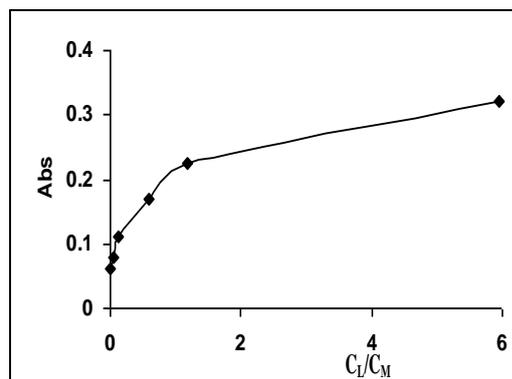
Mole ratio method

Extracted Cu^{+2} & Co^{+2} by CPE method with different concentration of NPADPI 10^{-6} M to $5*10^{-4}M$ the results in Fig 10(a,b) shows the structure of complexes extracted was

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1:1 metal : ligand for $Cu^{+2}[Cu(NPADPI)]^{+2}SO_4^{-2}$ and 1:2 metal : ligand for Co^{+2} $[Co(NPADPI)_2]^{+2} (NO_3)_2$.
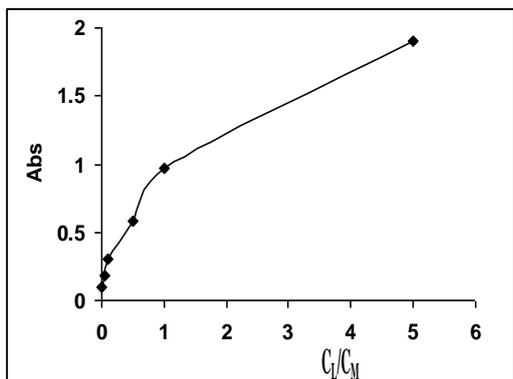
Fig(10a) Mole ratio method for Cu^{+2}

Fig(10b) Mole ratio method for Co^{+2}

Continueous variation method

Fig 11(a,b) give more evidence about the structure of complex extracted with CPE method, was 1:1 metal:ligand for Cu^{+2} $[Cu(NPADPI)]^{+2}SO_4^{-2}$ and 1:2 metal:ligand for Co^{+2} $[Co(NPADPI)_2]^{+2} (NO_3^-)_2$.
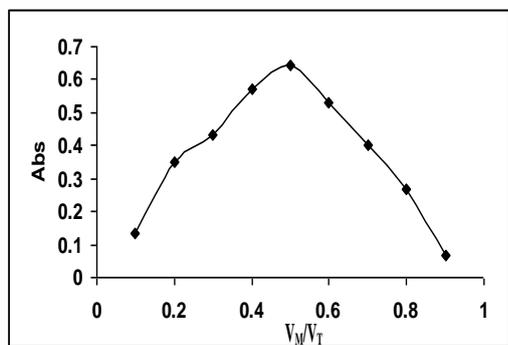
Fig(11 a) Continueous variation method for Cu^{+2}
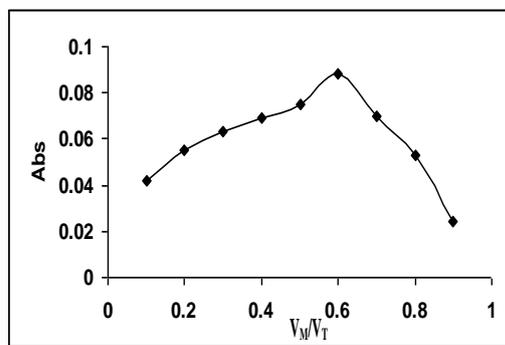
Fig(11b) Continueous variation method for Co^{+2}

Synergism effect

Extraction of Cu^{+2} & Co^{+2} by CPE methodology at experimental conditions in the presence tributylphosphate (TBP) or methylisobutylketone (MIBK) in concentration ranging from $1*10^{-6}$ M to $1*10^{-3}$ M have shown in Fig(12,13)
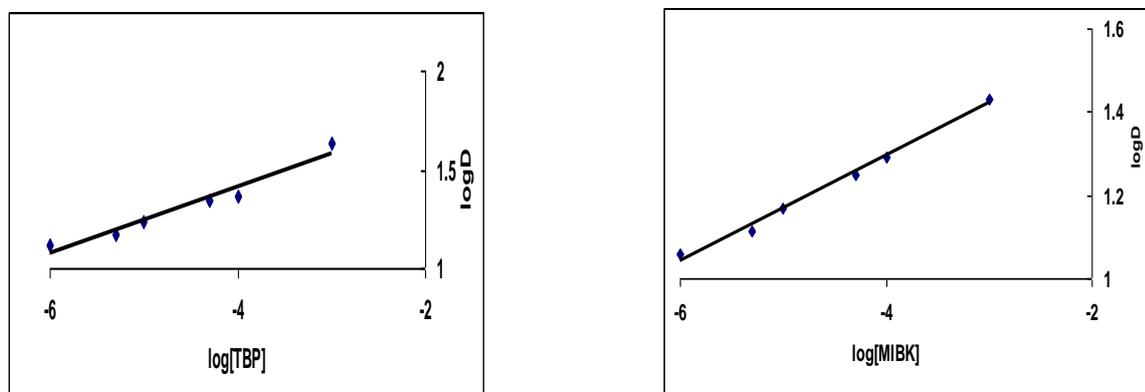
Fig(12) synergism effect on D values for Cu^{+2}
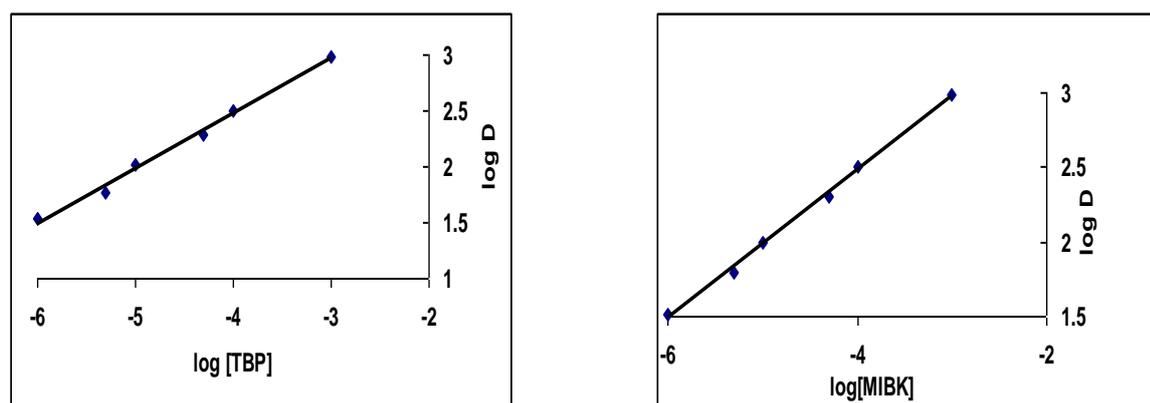
Fig(13) synergism effect on D values for Co^{+2}

The results shows the presence of TBP or MIBK effected to enhancement distribution values and giving straight line relation from the slope demonstrate there is one molecules of TBP or MIBK participate in the complex extracted to cloud point.

$[Cu(NPADPI)(TBP)]^{+2} SO_4^{-2}$, $[Cu(NPADPI)(MIPK)]^{+2} SO_4^{-2}$

$[Co(NPADPI)_2(TBP)]^{+2} (NO_3^-)_2$, $[Co(NPADPI)_2(MIPK)]^{+2} (NO_3^-)_2$
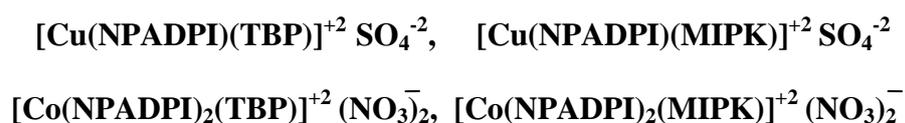
Salts effect

The electrolyte inorganic salts effect on the preconcentration and extraction according to CPE methodology. 10 ml solution contain analyte metal ions Cu^{+2} or Co^{+2} at fixed PH and 10^{-4} M NPADPI and TritonX-100 with 0.1M inorganic salt giving the results in Table (1)

Table (1): Effect of inorganic salts on complex extracted and D values

Inorganic Salts	Cu^{+2}		Co^{+2}	
	^{536}A	D	^{480}A	D
LiCl	1.38	42.75	0.545	64.2
NaCl	1.19	40.9	0.510	53.6
KCl	1.271	39.7	0.496	50
NH$_4$Cl	1.08	30.8	0.382	49.5
CaCl$_2$	1.17	35.88	0.528	58.1715
MgCl$_2$	1.26	38.5	0.515	54

The results shows presence electrolyte inorganic salts effect to increase extraction complex in cloud point as well as distribution ratio (D) by effect of increase dehydration with different inorganic salts.

Effect of anion

The complex extracted for Cu^{+2} and Co^{+2} was ion pair association complex with suitable anion associated with large cation produced from coordination linkage metal cation with complexation reagent. Extracted analyte metal cations by CPE method in presence different anions the result was an in Table (2).

| Anion	Cu^{+2}		Co^{+2}	
	^{536}A	D	^{480}A	D
ClO_4^-	0.978	11.5	0.186	52.4
$C_2O_4^=$	1.25	13.3	0.184	51.3
NO_3^-	0.989	11.7	0.321	69.3
I^-	1.18	13	0.191	56.6
$CrO_4^=$	1.36	25.9	0.219	60.5

The results shows more suitable anion giving more stable ion pair complex effect to increase extraction to cloud point .

Characteristics of Method

Clibration Curve in Fig (14) were performed by extraction Cu^{+2} and Co^{+2} according CPE methodology at optimum conditions as well as this Calibration graph used for

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spectrophotometric determination of analyte metal in different environmental and vital sample.

ion	intercept	Correlation	Linearity	Sandal sensitivily ($\mu g\ cm^2$)	Detection Limit ($\mu g\ l^{-1}$)
Cu^{+2}	0.0299	0.9935	y=0.0138x + 0.0299	0.0072	$3.9*10^{-6}$
Co^{+2}	0.0023	0.9998	y=0.0062x -0.0023	0.0165	$4.6*10^{-6}$
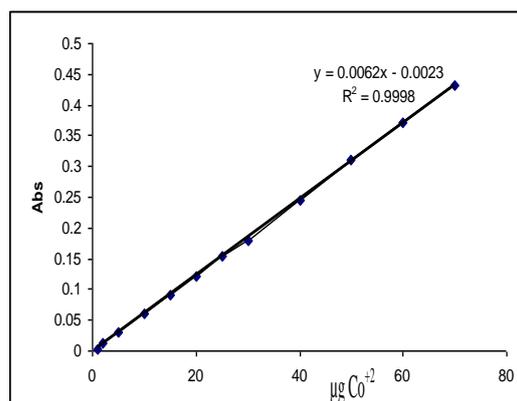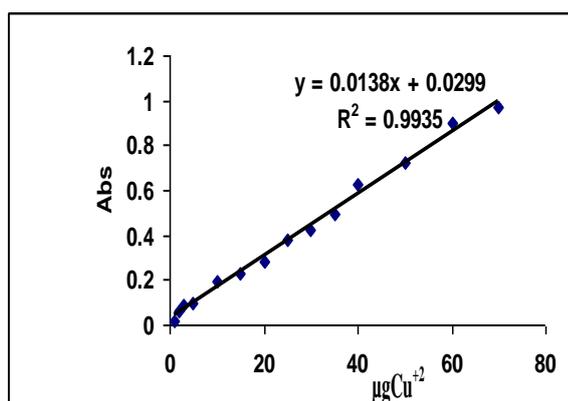
Fig(14): Calibration graph accordin to CPE methodology

Application

Table (3):determination microamount Cu^{+2} & Co^{+2} in different samples

Sample	Cu^{+2} $\mu g.g^{-1}$	Co^{+2} $\mu g.g^{-1}$
Un Agriculture soil Sample (Al-Kufa street)	6.80	16.5
Agriculture soil Sample (river of Najaf)	9.5	18.6
Water sample (Shatt al-shamiya)	1.274	0.31
Bean	9.52	0.006
Orange	10.78	0.005
Local Fish	1.791	0.007
Almond	1.729	0.092

Turkish chicken	1.718	0.007

Conclusion

Extraction of Cu^{+2} & Co^{+2} with NPADPI to micellar nonionic surfactant Tritonx-100 has been investigated .The sensitivity, metrological characteristics , ecological safty , simplicity and convenience of the suggested procedure are competitive have confirmed its applicability to the separation and preconcentration of copper and cobalt which due its high stability constant and high PH dependency with high selectivity loading and has been carried out .In aview glance to the results one can notice that present method is superior to those previously reported in term of some characteristics performance [25-27].

أستخلاص نقطة الغيمة لفصل والتقدير المايكروي للنحاس (II) والكوبلت (II)

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الخلاصة

أجريت عمليات الفصل والاغناء لأيونات النحاس (II) والكوبلت (II) من نماذج مختلفة بعد عملية التعقيد مع الكاشف العضوي2 -[4- نايتروفنيل ازو] -5,4- ثنائي فنيل اميدازول وبأتباع تقنية استخلاص نقطة الغيمة . وقدأجريت عملية الاستخلاص الكمي للعناصر قيد الدراسة الى TritonX-100 أعقبتها عملية فصل بأضافة 5 مل من الايثانول الى طبقة نقطة الغيمة تبعتها عملية تقدير طيفي لكل عنصربأستخدام مطيافية UV-Vis. وقد تم تحديد الظروف المثلى مثل PH وتركيز TritonX-100 ودرجة الحرارة وزمن التسخين مع دراسة تركيب المعقد المستخلص الى طبقة نقطة الغيمة. بالأضافة الى تطبيقات تقديرالعناصر قيد الدراسة في نماذج بيئية وحياتية مختلفة .

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