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Sensitive Cloud Point Extraction Methodology for Separation Preconcentration of Co(II) Followed by Spectrophotometric Determination in Different Samples

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Abstract
With application CPE methodology to separation preconcentration and extraction Co^{2+}ion used 2-[4-antybyren zolylazo]-1,2-dihydroxy-9,10-anthracene-dione (AADAD) as complexing agent to form ion pair complex as well as used non-ionic surfactant 1% Tritonx-100 at PH=8 , also this research involved limitation optimum conditions as well as thermodynamic study , Synergism effect and spectrophotometric determination of Co(II) in different samples with detection limit(D.L) =(1.6559×10^{-5}µg.mL^{-1}) and Sandell's sensitivity =(7.99×10^{-5}mg.cm^{-2}) and ε =(7374.12L.mol^{-1}.cm^{-1})and RSD% =(%0.0065).
Keywords: Cobalt(II) , Cloud point layer ,TritonX-100.

Introduction

Though the previous applications about separation and extraction different metal elements from samples having different nature and properties , one of this studies was involved application Cloud Point extraction methodology for separation and preconcentration trace amount of Co(II) by formation complex with 2-[(2-mercaptophenylimino)methyl] phenol (MPMP) and extracted this complex into surfactant Tritonx-114 after heating for 50°C and 10 minutes and pH=8 and determined the trace amount of Co(II) by flame atomic absorption spectrometry (FAAS) with detection limit 2.1 µgL^{-1}[1].Developed Cloud Point extraction method for the separation and preconcentration trace amount of Cobalt combined with atomic absorption for determination trace amount of Cobalt in water and food samples. The method depend on produce a complex between Cobalt(II) and 4-methoxy-2-sulfobenzene diazo amino azo benzene (MOSAAA) and extracted into mono ionic surfactant Tritonx-114 , with detection limit 0.47 ngml^{-1}[2].used flame atomic absorption spectrometry for determination Ni^{2+}, Cu^{2+} and Co^{2+} ions in real samples after Cloud Point extraction methodology for extraction. After complex formation with complexing agent N-(2-thiophenyl)-1-(2-hydroxy phenyl) imine(NTPHPI) in presence nonionic surfactant Tritonx-114 with detection limit 1,5 and 6 ngml^{-1} respectively[3]. Used successfully CPE methodology separation and preconcentration of trace amounts of palladium fallowed determination by FAAS or Visual spectrophotometry. The method involve complex formation between Pd(II) and 2-Hydroxyimino-3-(2-hydrazonopyridyl)-butane(HHB) in presence Tritonx-100 for separation complex[4]. In sensitive method used CPE methodology for separation and determination trace amount of Ni^{2+} by used DMG as complexing agent with monoionic surfactant Tritonx-100 , under optimum conditions this method giving detection limit 4 ngmL^{-1}[5].A thermospray flame furnace atomic absorption spectrometer (TS-FF-AAs)was employed for Co determination in biological materials. Cobalt presents a high atomization temperature and Consequently poor sensitivity is obtained without changing its thermo chemical behavior . The effect of different complexing agents on sensitivity was evaluated based on the formation of Cobalt Volatile Compounds. A Cloud Point procedure was optimized for Co preconcentration for further improvement of sensitivity. Samples were treated with 1 molL^{-1}hydrochromic acid solution for quantitative extraction of Co without simultaneous extraction of Fe with detection limit 2.1 µgL^{-1}[6]. The Cloud Point extraction methodology used for extraction Nickel(II) as chloro anion by use crown ether DB18C6, The ion pair complex extracted has maximum absorbance at λ_{max}=295nm in presence 0.5M HCl , 0.25M NaCl , 1×10^{-4}M DB18C6 and 0.6 mol of Triton x-100 with ΔH_{ex}=0.2897KJmol^{-1}, ΔG_{ex}=-63.92 KJmol^{-1}and ΔS_{ex}=176.861Jmol^{-1}k^{-1}[7]separation and microamount determination of Lead(II) and Cadmium(II) by CPE methodology by used Complexing agent 2-[(Benzothiazolyl)azo]-4,5-diphenyl imidazole for Cadmium in presence 0.5ml of Non-ionic Surfactant Tritonx-100 , after separation CPL from aqueous solution dissolved in 5ml 1,2DCE for Lead(II) and 5ml ethanol for Cadmium(II) , studied all optimum parameters and other parameters effective on extraction efficiency as well as stoichiometry and thermodynamic study [8]. Extracted Zinc(II) as chloroanion from aqueous solution as ion pair complex by Cloud Point extraction methodology this research show maximum absorbance of complex was at λ_{max}=414nm by use new Laboratory made azo dye 3-[2-pyridylazo]-1-nitrozo-2-naphthol(PANN) in 1M HCl and 1×10^{-4}M PANN , 0.6ml Tritonx-100 with D.L=0.0292ppm ε=70583Lmol^{-1}cm^{-1}Sandells sensitivity=63×10^{-4}µg.cm^{-2}[9].Dual detection of drug norfloxacin (NOR) and iron(II) ion in biological and pharmaceutical samples , by coupling CPE method with spectrophotometric method , the drug (NOR) react with Fe(III) ion is dilute acidic media to form hydrophobic complex (Fe(III)-NOR) extracted to CPL of Tritonx-114 ,The maximum absorbance at λ_{max}= 432nm with detection limit 0.692 µg.mL^{-1} for NOR and 3.42 µg.mL^{-1} for Fe(III) as well as RSD% at range 0.04-0.68% for

NOR and at range 0.59-0.97% for Fe(III)[10].

Experimental

Apparatus

Biochrome model (80-7000-11) Libra s60 Cambridge CB4 0FJ (England) UV-VIS spectrophotometer with 1cm quartz cell was used for recording the absorbance spectrum and absorbance measurements ,and water bath (WNB7-45) (England), and for the pH measurement used pH meter (HANNA Germany) .

Reagents and solutions

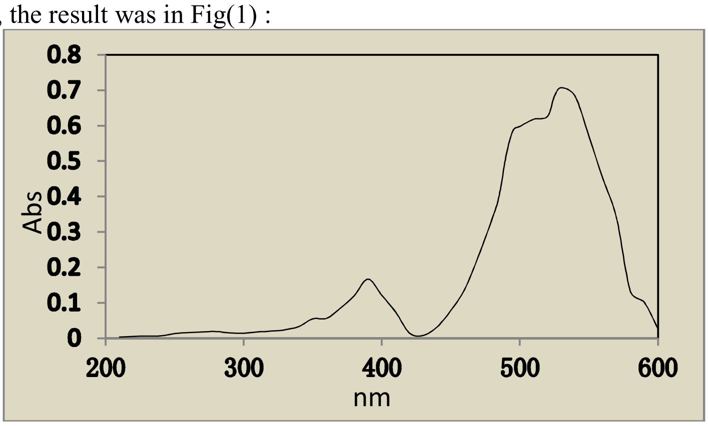
All chemical incoming from international companies with high purity and were used as received without more purification. Stock solution of 1mg/ml for Cobalt(II) was prepared by dissolved 0.3092gm of cobalt nitrate $Co(NO_3)_2$ in 100ml distilled water contain 1ml concentration HNO_3 in volumetric flask and other working solution prepared from stock solution by dilution with distilled water , as well as for determination remainder quantity of Cobalt(II) in aqueous solution after extraction used 1-nitroso-2-naphthol at 0.5% concentration in spectrophotometric method after prepared by dissolved 0.5gm in 100ml glacial acetic acid as well as before used shaking with 1gm of activated carbon.

Reference method

10ml aqueous solution contain optimum concentration of Co(II) at fixed pH value and suitable concentration of Non-ionic surfactant TritonX-100 as well as optimum concentration of 2-[4-antybyren zolylazo]-1,2-dihydroxy-9,10-anthracene dion (AADAD), then heating this solution electric water bath for suitable temperature until formation cloud point layer (CPL) after that separate (CPL) from aqueous solution and dissolved (CPL) in 5ml of ethanol and measure the absorbance of ethanolic solution at λ_{max} for ion pair complex extracted to (CPL) , but aqueous solution treated according to 1-nitroso-2-naphthol spectrophotometric method and return to calibration curve in order to determine remainder quantity of Co^{2+}in aqueous phase as well subtraction this quantity from original quantity of Co^{2+}in aqueous solution before extraction to determine partition quantity of Co^{2+} ionic CPL at rather calculate distribution ratio (D).

Results and Discussion

Spectrophotometric studies to determine wave length for maximum absorbance of complex involve taken 10ml aqueous solution contain 50mg Co^{2+} at pH=8 and 1×10^{-4}M complexing agent 2-[4-antibyren zolylazo]-1,2-dihydroxy-9,10-anthracenedion(AADAD) ,in presence 0.5ml from 1% Tritonx-100 as Non-ionic surfactant heated the solution to suitable temperature and time until formation. Cloud Point layer (CPL) and then separated CPL and dissolved in 5 ml ethanol and taken the spectrum for it against blank prepared at the same manner absence metal ion Co^{2+}, the result was in Fig(1) :

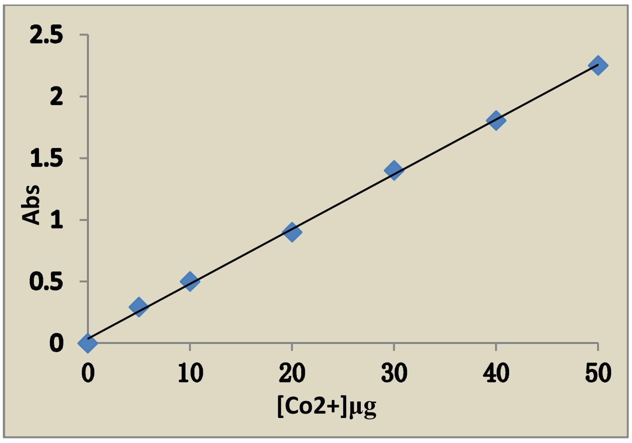


Fig(1) : UV-VIS absorption spectrum of complex.

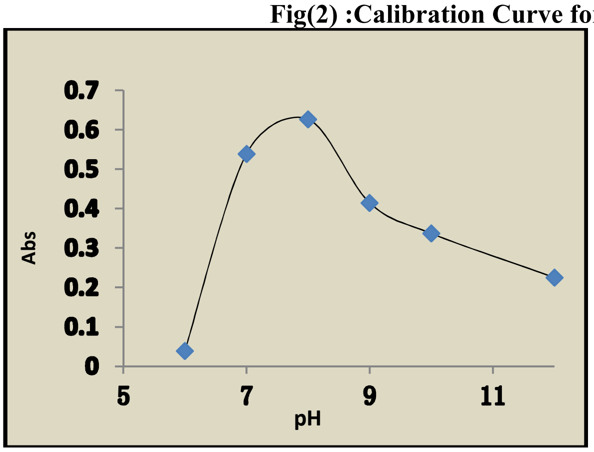
The spectrum show the wave length appear maximum absorbance to the complex extracted was λ_{max}=530nm.

Effect of pH

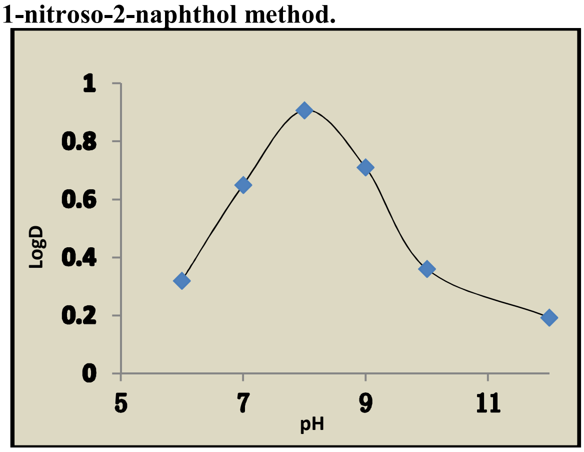
Extracted 50mg Co^{2+} in 10ml aqueous solution at different pH and 1×10^{-4}M (AADAD) so 0.5ml of Non-ionic surfactant 1% tritonx-100 then heating this solutions for optimum temperature and time until formation (CPL) after work determined absorbance of alcoholic solutions of CPL and D values such as procedure detailed in reference method the results was as in figures 3,4 :



Fig(2) :Calibration Curve for 1-nitroso-2-naphthol method.



Figure(3): Effect of pH on complex formation and extraction.



Figure(4): Effect of pH on extraction efficiency.

The results show pH=8 was the optimum value for best thermodynamic equilibrium complex formation and extraction and giving higher values of absorbance and distribution ratio D.

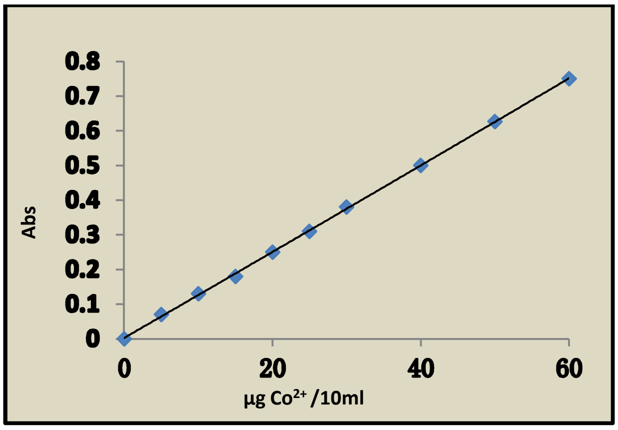
$$Co^{2+} + AADAD + NO_3^- \rightleftharpoons [Co - AADAD]^+ ; NO_3^-$$

$$\underset{\text{aqueous solution}}{[Co - AADAD]^+ ; NO_3^-} \rightleftharpoons \underset{\text{CPL}}{[Co - AADAD]^+ ; NO_3^-}$$

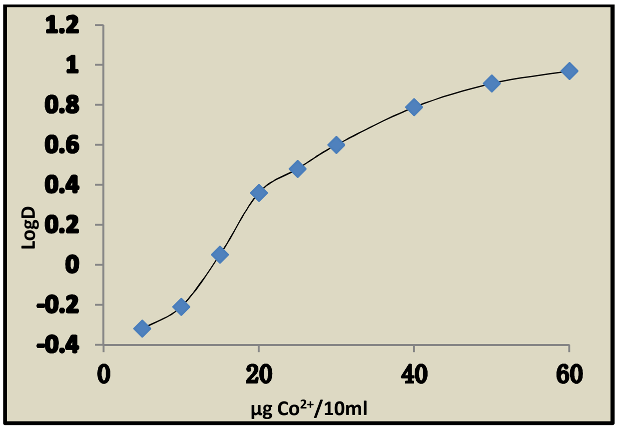
Any pH value less than optimum not suitable for thermodynamic equilibrium according to CPE methodology which as effect to decrease extraction efficiency in addition to protonation of electron donor position in complexing agent decline the ability to complex formation and this effect decrease absorbance and D-values as well as any pH value more the optimum effect to decrease extraction. Efficiency also because effect to formation stable compound of Co(II) with OH ions as well as participation of hydroxyl ion in the formation of ion pair association complex which is more hydrophilic and partition to the aqueous phase more than CPL.

Effect of metal ion concentration

Extracted $Co^{2+}$from 10ml aqueous solutions contain different quantity of ionCo^{2+} at pH=8 and presence 1×10^{-4}M (AADAD) and 0.5ml of 1% Tritonx-100 by fallowed the procedure detailed in reference method and The results was as in Figures(5,6).



Figure(5): Effect of Co^{2+}concentration on complex formation and extraction.

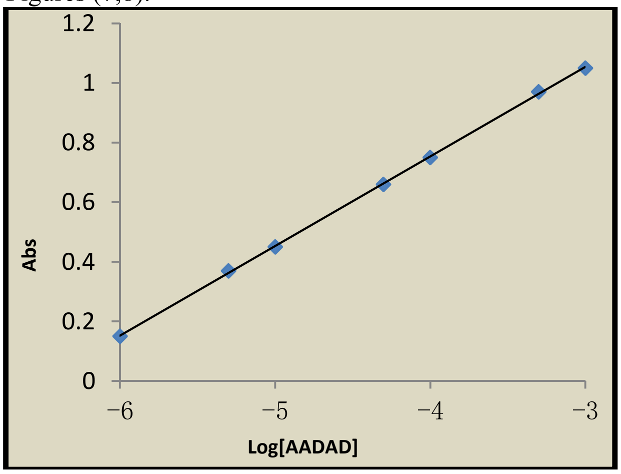


Figure(6): Effect of Co^{2+}concentration on extraction efficiency and D-value.

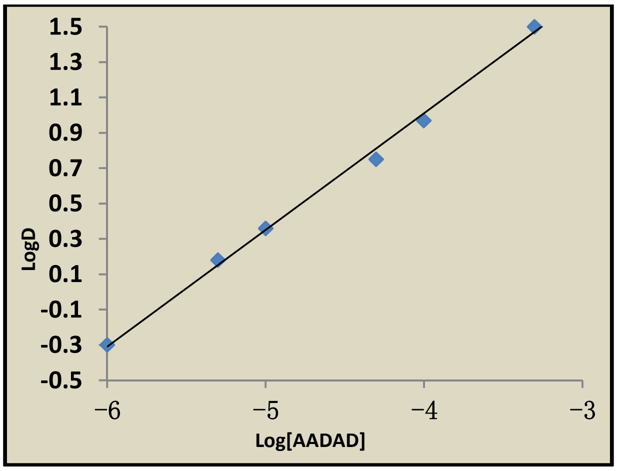
The results show there is a linear relation between absorbance and concentration of Co^{2+} ion as well as nearly straight line between distribution values and concentration of Co^{2+} ion. This relation proof the fact that metal ion concentration is thermodynamic data effect on the thermodynamic equilibrium of complex formation under all constant conditions.

Effect of complexing agent concentration

Extracted 60µg $Co^{2+}$from 10ml aqueous solution at pH=8 and in presence different concentrations of AADAD and 0.5ml of 1% TritonX-100 , according to the procedure detailed in reference method. The results was as in Figures (7,8).



Figure(7): Effect of complexing agent concentration on complex formation.



Figure(8): Effect of complexing agent concentration on extraction efficiency and D-values.

The results show there is regular gradualy inceasing in extraction efficieny as well as absorbance and D-values with increasing in concentration of complexing agent because complexing agent cocentration is a thermodynamic data effect on the thermodynamic equilibrium of extraction according to CPE methodology as well as the increasing in complexing agent concentration effect to increase the rate of forward reaction of complex formation ion addition to extraction.

Effect of surfactantconcentration

Extraction 60µg Co^{2+}in 10ml aqueous solution at pH=8 in presence 1×10^{-4}M AADAD and different volume of 1% TritonX-100 according to the procedure detailed in reference method previously the results was as in Figures (9,10).

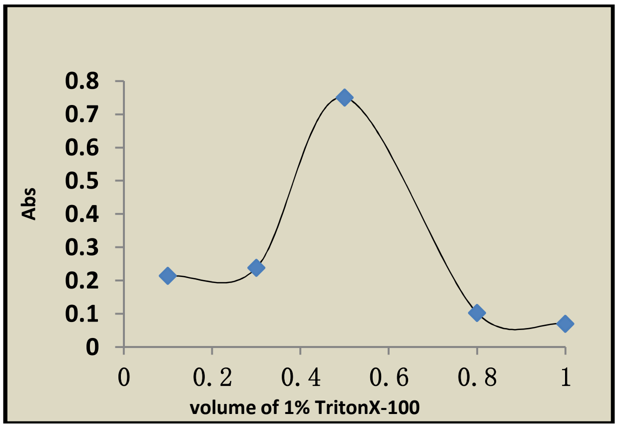
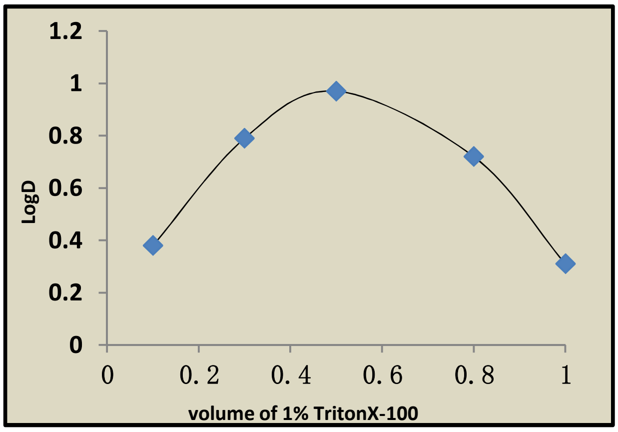


Figure (11): Effect of surfactant concentration on quantitatively complex extraction.

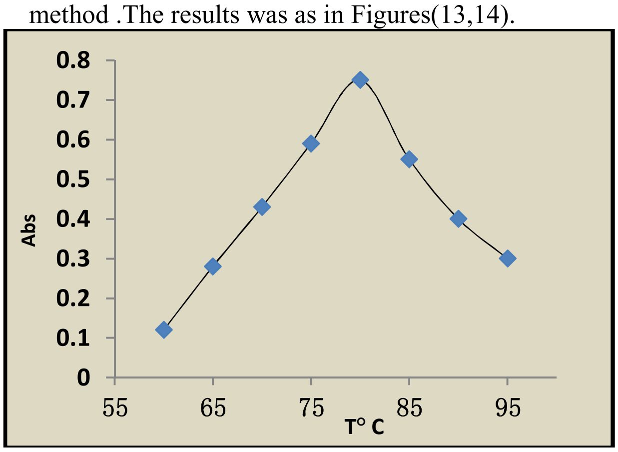


Figure(12): Effect of surfactant concentration on extraction efficiency and D-value.

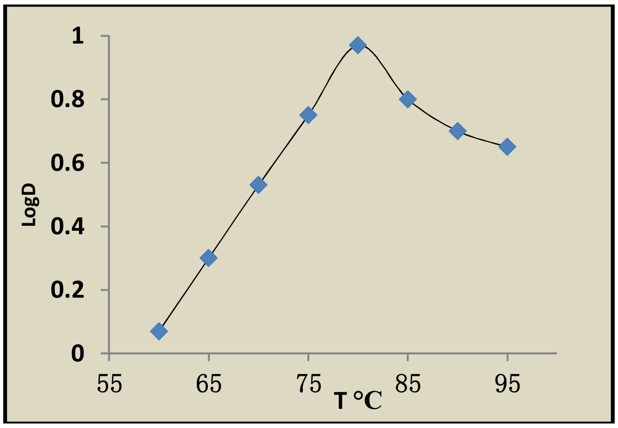
The results show 0.5ml of 1% TritonX-100 was more favourite for extraction ion pair complex quantitatively and giving higher absorbance and D-value because giving suitable CPL for extraction with high dehydration to formation CPL with smallest volume and higher density any volume of surfactant less than 0.5 not suitable for extraction effect to decline extraction efficiency as well as any volume more than 0.5 effect to decrease extraction efficiency too became increasing is volume of 1% Tritonx-100 effect to increase hydration and diffusion of micell's.

Effect of Temperature

Extracted 60µg Co^{2+}in 10 ml aqueous solution at pH=8 and in presence 1×10^{-4}M (AADAD) and 0.5ml of 1% TritonX-100, after heating the solutions for different temperature in electrostatic water bath for 15 minutes, determine absorbance of ethanolic solution of CPL and D-value according to procedure detailed in reference method .The results was as in Figures(13,14).



Fig(13): effect of Temperature on complex formation and extraction.

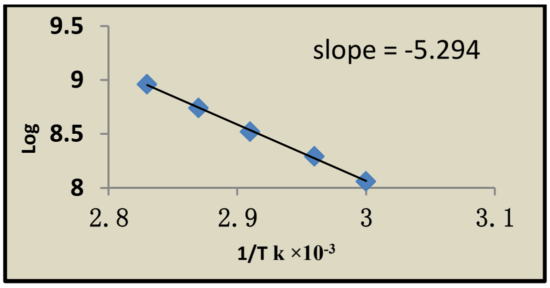


Fig(14): Effect of temperature on extraction efficiency and D-value.

Afterward calculated the extraction constant (k_{ex}) at each temperature through the straight by the equation below:

$$K_{ex}=\frac{D}{[Co^{2+}]aq[AADAD]org}$$

After plot Log K_{ex} against 1/Tk get straight line relation with slope equal to (-5.294) as in Fig(15) :



Figure(15) : The thermodynamic relation between$k_{ex}$and temperature.

Then from slope value of straight line calculate enthalpy of extraction by relation below:

$$\frac{\Delta logkex}{\Delta 1/T} = \text{slope} = \frac{-\Delta H}{2.303R}$$

As well as calculate ΔG_{ex} and ΔS_{ex} from relations :

$$\Delta Gex = -\text{RT LnKex}$$

$$\Delta Gex = \Delta \text{Hex} - \text{T}\Delta \text{Sex}$$

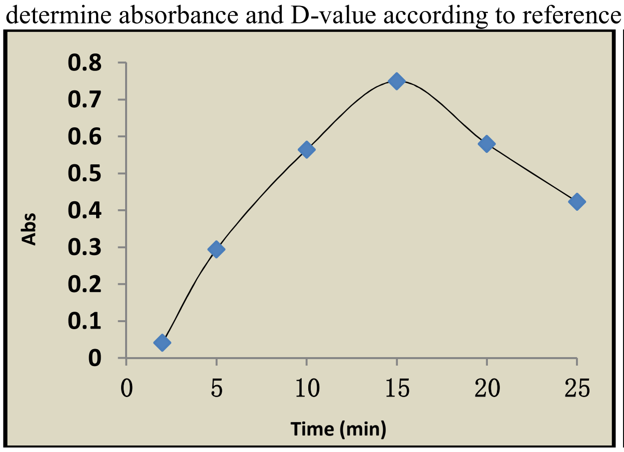
The results was :

ΔH_{ex} = 0.1014 KJ.mol^{-1}
ΔG_{ex} = -60.565 KJ.mol^{-1}
ΔS_{ex} = 171.86 J.mol^{-1}.k^{-1}

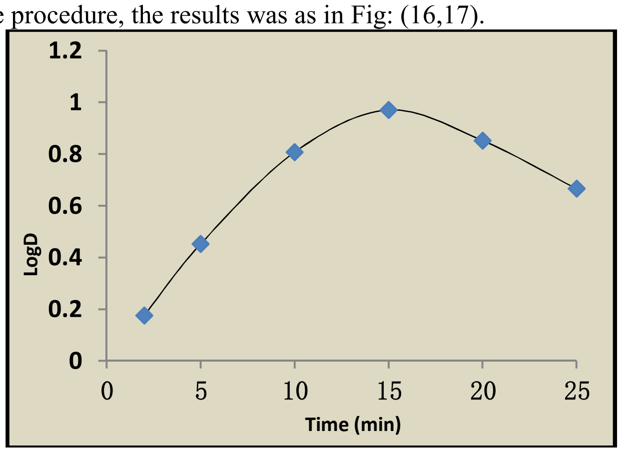
The result appear extraction method of Co^{2+}ion according to CPE methodology was endothermic and the law value of ΔH_{ex}reflect the high approach of ions in ion pair association complex extracted and high negative value of ΔG_{ex}illustrate the spontaneously of extraction method as well as high positive value of ΔS_{ex} mean the extraction method depend on the change from systematic to unsystematic by dehydration and destroy the hydration shell of ions as well as change in the hydrogen bonds lattice and called this method is (entropic region).

Effect of heating time

Extraction 60µg Co^{2+} from 10ml aqueous solution at pH=8 and in presence 0.5 ml of 1% TritonX-100 and 1×10^{-4}M(AADAD) and heating these solutions at 80°C in electrostatic water bath for different time at later determine absorbance and D-value according to reference procedure, the results was as in Fig: (16,17).



Fig(16): Effect of heating time on CPL formation and equilibrium of complex transition.

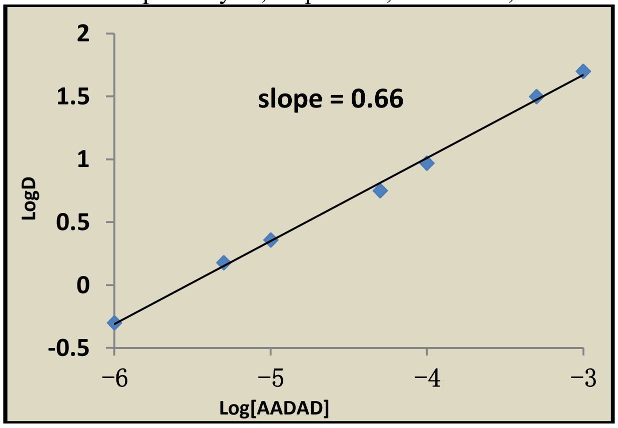


Fig(17) :Effect of heating time on extraction efficiency and D-Value.

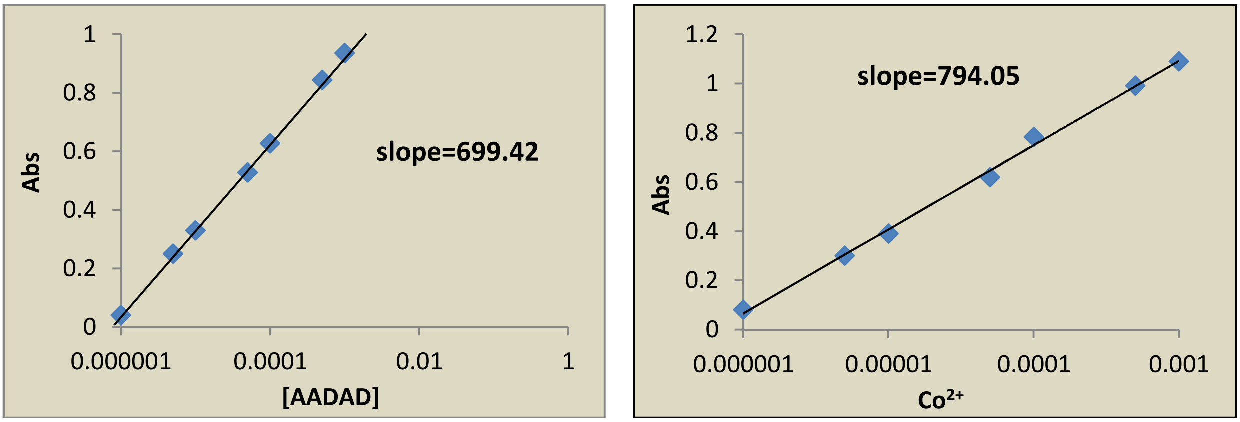
The results show 15 minutes was the optimum heating time suitable for reached thermodynamic equilibrium for extraction and any heating time less than 15 minutes not enough to reach equilibrium of extraction and effect to decline extraction efficiency also heating time more than optimum value effect to decrease extraction efficiency to too because the heating for excess time effect to increase quantity of heating in the solution and increase the diffusion of micell's and decrease CPL and extraction of ion pair complex.

Stoichiometry

To limitation the more probable structure of ion pair complex extracted we are performed four spectrophotometric method which is slope analysis, slope ratio, mole ratio, Job method as in Figures(18-21).



Fig(18): slope analysismethod.

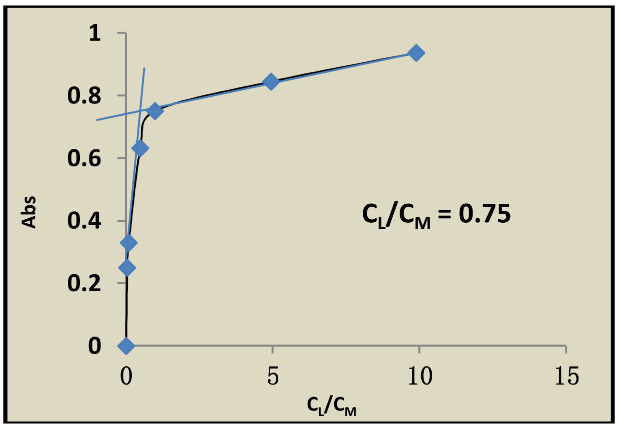


a/Effect of metal ion concentration on extraction ability.

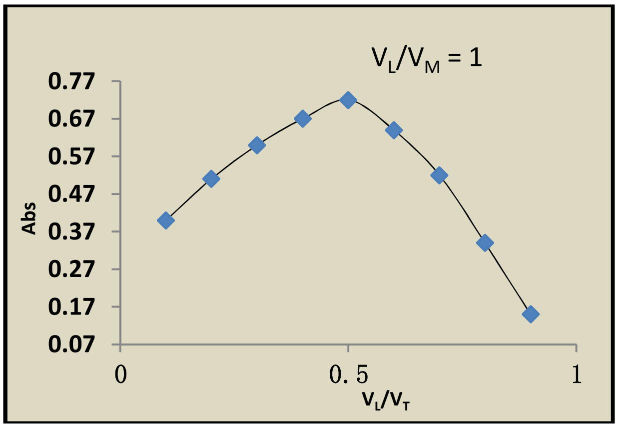
b/Effect of organic reagent concentration on extraction ability.

Figure(19) : slope ratio method.

$$\text{Slope ratio} = \frac{699.42}{794.05} = 0.88$$

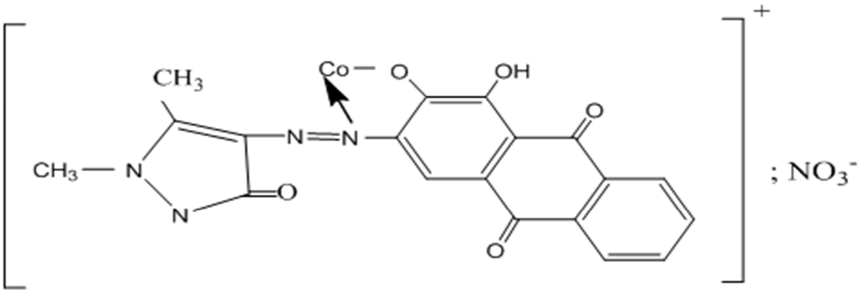


Fig(20) : Mole ratio method.



Fig(21) :Contiueos Variation method(Job method).

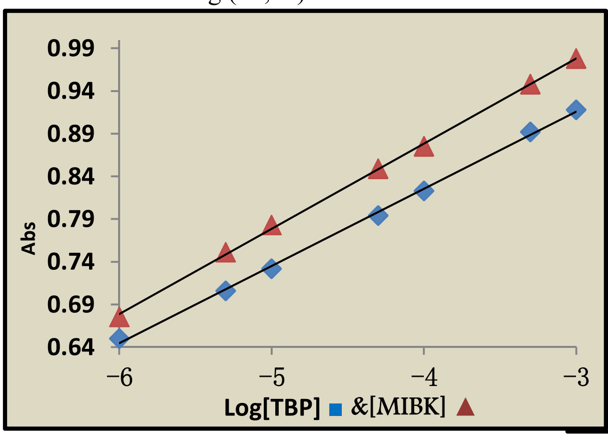
The results in these spectrophotometric method demonstrate the more probable structure of ion pair complex extracted was (1:1) [metal : ligand] as in figure (22) :



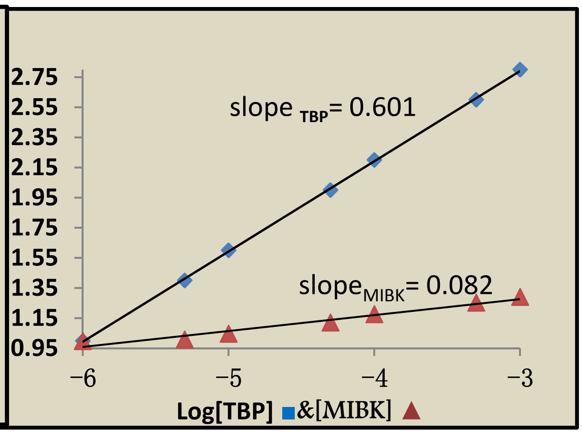
Fig(22) :The more probable structure of ion pair complex extracted.

Synergism effect

Extracted 60µg Co^{2+} ion from 10ml aqueous solutionunder optimum conditions, and in presence different concentrations of TBP or MIBK , afterward determined absorbance and D-value such as the reference method. the results was as in Fig (23,24):



Fig(23) : synergistic effect on complex formation and extraction.



Fig(24) : synergistic effect on extraction efficiency and D-values.

The results shows presence TBP or MIBK in the aqueous solution of extraction effect to enhancement the extraction ability because TBP or MIBK substituted the water molecules binding coordinately to the complex to saturated the coordination shell of the metal ion and this substituted change the ion pair complex more hydrophobic and transfer quantitatively to the Cloud Point layer and increase absorbance and D-value as well as the slope of straight line relation of logD via log[TBP] or log[MIBK] appear there is one molecule of TBP or MIBK participate in the complex:

$[Co\text{-}(AADAD)^{-}(TBP)]^{+}; NO_3^{-}$ $[Co\text{-}(AADAD)^{-}(MIBK)]^{+}; NO_3^{-}$

Effect of interferences

Extracted 60µg Co^{2+}ion from 10ml aqueous solution at optimum conditions according to the procedure detailed in reference method in presence some cations0.1M concentration ,The results was as in Table (1).

Table(1) : Interferences effect.

Cations	CPL Absorbance	D
$Cd(NO_3)_2$	0.012	1.87
$Pb(NO_3)_2$	0.016	3.66
$Hg(NO_3)_2$	0.014	2.55
$Mg(NO_3)_2$	0.817	13.34
$AgNO_3$	0.193	5.79
$Ni(NO_3)_2$	0.098	4.11

The results show all metal cation appear interference seffect except Mg^{2+} ion all metal cation appear interferences and decline extraction deficiency because then ions formation complexes with AADAD , but in different abilities but Mg^{2+}not appear any interfere because not having any tendency to form complex and binding with AADAD but behave as electrolyte in aqueous solution and increase dehydration and extraction ability as well absorbance and D-value.

Electrolyte effect

Extracted 60µg Co^{2+}ion from 10mL aqueous solution at optimum conditions and in presence 0.1M of different electrolyte, the results was as in Table(2):

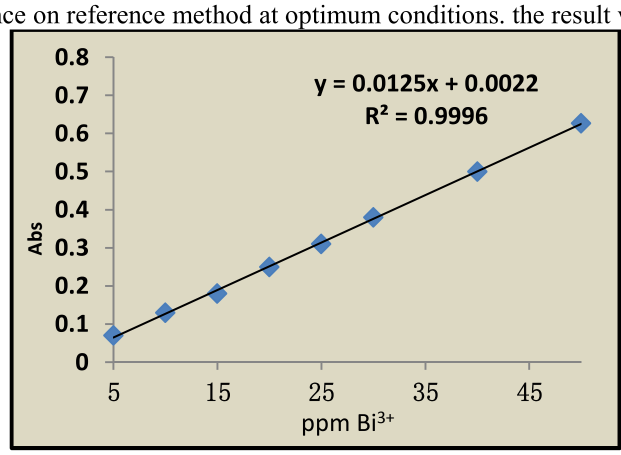
Table (2) : electrolyte effect.

Electrolytes	CPL Absorbance	D
$LiNO_3$	0.941	18.5
$Na\ NO_3$	0.885	16.28
$K\ NO_3$	0.755	14.61
$NH_4\ NO_3$	0.698	10.94
$Mg(NO_3)_2$	0.817	15.47
$Ca(NO_3)_2$	0.675	12.84
$Al(NO_3)_2$	0.811	13.41

The results show there is an enhancement in extraction efficiency as well as absorbance and D-value in presence electrolyte in aqueous solution because these electrolyte help to increase dehydration to forming CPL with smaller volume and higher density in addition to destroy the hydration shell of metal ion, and this behavior increase with change density increase as in the table.

Spectrophotometric determination:

For application this method for determination Cobalt(II) in different samplesspectrophotometricaly perform calibration curve dependence on reference method at optimum conditions. the result was as in Fig(25).



Figure(25) : Calibration curve for spectrophotometric Determination of Co^{2+}.

After application the reference method on different samples and return to the calibration curve determine cobalt(II) in these samples and the results was illustrated in the table(3).

Table(3) : determination of Cobalt(II) in different samples.

No.	*samples*	*ppm Cobalt(II)*
1	Nail Pulish ZNM	3.9
2	Skin cream BB 7 in 1	0.5
3	Electrical Fuse :cat.No.CE0C	6.4
4	Chicken liver	0.5
5	Chicken meat	0.09
6	Beef	0.08
7	Printer Ink	1.4
8	Mobile cell	0.8
9	Microprocessor	0.23
10	Bord connections	0.7

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