

## EXTRACTION PRECONCENTRATION AND DETERMINATION OF COBALT (II) VIA CLOUD POINT METHOD

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### ABSTRACT

Extracted  $\text{Co}^{2+}$  ions according to CPE methodology as ion pair complex by Junnas green (JG) from acidic aqueous solution of HCl. The method appears 0.5M HCl was the suitable for extracted  $50 \mu\text{g Co}^{2+}$  in presence.  $1 \times 10^{-4}$  M JG and 0.5 ml 1% Triton X-100 with heating on electrostatic water bath at  $85^\circ\text{C}$  for 15 minutes. As well as the study involved thermodynamic study electrolyte effect and interferences in addition to spectrophotometric determination of  $\text{Co}^{2+}$ .

**KEYWORDS:** Cobalt, Cloud Point Extraction, Liquid Ion Exchange

### INTRODUCTION

Through possessing cloud point extraction. method a wide spread of application with high efficiency for separation quantitatively the analytes to perform for sensitive determination, used this method in wide range applications for determination metals in aqueous samples as ions, one of this application included extraction and preconcentration of  $\text{Mg}^{2+}$  ions via solvation method by used of 2,4-dimethyl-3-pentanone as extractant to form solvated species which is showed maximum absorbance of  $\lambda_{\text{max}} = 249\text{nm}$  with 0.5M  $\text{KNO}_3$  was necessary for prepared extracted solvated species [1] Separation, preconcentration and sensitive determination for nickel (II) as anion from acidic HCl media by Crown ether DB18C6 [2]. By focusing more on the cloud point extraction methodology extracted molybdenum (VI) as molybdate  $\text{MoO}_4^{2-}$  with 2-[Benzene thiozolyaso]-4-Benzene naphthol (BTABN) as extractant from acidic HCl media via liquid ion exchange extraction method, with limitation all optimum condition [3]. There is different application via cloud point extraction. methods for different goals of separation, extraction and determination of different analytes [4-7]. Via cloud point extraction methodology extracted cobalt (II) by used complexing agent 4-Benzyl m-piperidinedithiocarbamate [8]. Other sensitive application via cloud point extraction for separation preconcentration as well as determination different analytes [9-12]

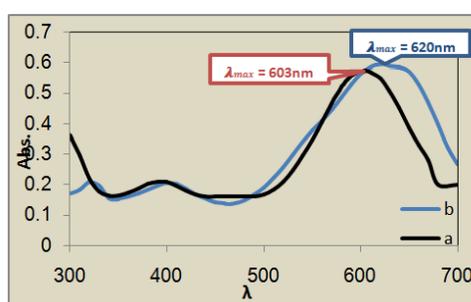
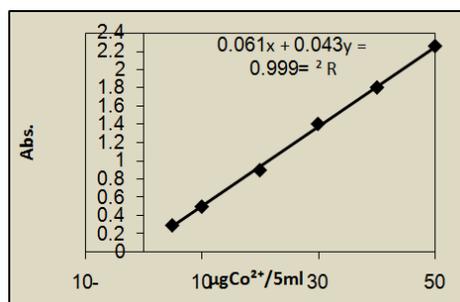
### EXPERIMENTAL

Biochrom model (80-7000-11) Libra 560 Cambridge CB40FJ spectrophotometer with 1cm quartz cell used to perform spectrophotometric studies and absorbance measurements as well as for maintain temperature used electrostatic water bath (WNB7-45 England). All chemicals used as received without further more purification, all solutions prepared by double distilled water. Stock solution of  $\text{Co}^{2+}$  (1mg/ml) prepared by dissolved 4.78gm of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  in 1 liter distilled water contain 2ml of concentration sulfuric acid  $\text{H}_2\text{SO}_4$  other working solution prepared by dilution with distilled water stock solution  $1 \times 10^{-2}$  M of Junnas green (JG) prepared by dissolved 0.05111gm in 100 ml distilled water in volumetric flask. Aqueous solution 10 ml in volume contain  $50 \mu\text{g Co}^{2+}$  and 1M hydrochloric acid HCl so as  $1 \times 10^{-4}$  M

Junnas green with 0.5 ml of 1% Triton X-100 , heating this solution in electrostatic water bath at 85 °C for 15 minutes until complete formation cloud point layer CPL , separated this layer and dissolved in 5 ml ethanol , measure the absorbance of alcoholic solution at  $\lambda_{\max}$  of ion pair complex extracted as well aqueous solution after separation treated according to spectrophotometric method (1-nitroso-2-naphthol) [13] , and return to calibration curve fig[1] to determined remainder quantity of  $\text{Co}^{2+}$  ions in aqueous solution and subtraction this quantity from 50  $\mu\text{g}$  of  $\text{Co}^{2+}$  to determine the transfer quantity of  $\text{Co}^{2+}$  to CPL as ion pair complex and then dividing transfer quantity on remain quantity to calculate Distribution ratio  $D = \frac{[\text{Co}^{2+}]_{\text{CPL}}}{[\text{Co}^{2+}]_{\text{w}}}$

## RESULTS AND DISCUSSIONS

10ml aqueous solution contain 50 $\mu\text{g}$   $\text{Co}^{2+}$  ion and 1M HCl with 0.5ml of 1%TritonX-100 so  $1 \times 10^{-4}$  M (JG) heating the solution in electrostatic water bath at 85 °C for 15 minutes until complete formation cloud point layer CPL with higher density and smaller volume separate this layer from aqueous solution and dissolved in 5ml ethanol afterward taken UV-Vis absorption spectrum for ethanolic solution against blank prepared at the same manner without  $\text{Co}^{2+}$  ion , the result as in fig[2].



**Figure 1: Calibration Curve for Determination Remainder  $\text{Co}^{2+}$  in Aqueous Solution 1-Nitroso-2-Naphthol/ Junnas Green ,** **Figure 2: UV-Vis Absorption Spectrum of: b/ Ion Pair Complex Extracted. Spectrophotometric Method.**

The spectrum show maximum absorbance for ion pair complex extracted to  $\text{Co}^{2+}$  ion with Junnas green (JG) was at  $\lambda_{\max} = 620\text{nm}$

### Effect of HCL Concentration

10 ml aqueous solution contain 50  $\mu\text{g}$   $\text{Co}^{2+}$  ions with different concentration of hydrochloric acid HCl and  $1 \times 10^{-4}$  M from Junnas green (JG) and 0.5 ml 1% Triton X-100 , heating these solution at 85°C for 15 minutes to formation cloud point layer. Then separate CPL from aqueous solution and dissolved CPL in 5 ml ethanol hence measure the absorbance of alcoholic solution at  $\lambda_{\max}=620\text{nm}$  against blank prepared at the same manner with out  $\text{Co}^{2+}$  ions , but aqueous solution treated according to the spectrophotometric determination method (1-nitroso-2-naphthol) [13] and return to the calibration curve figure1, the results was in figure3, 4.

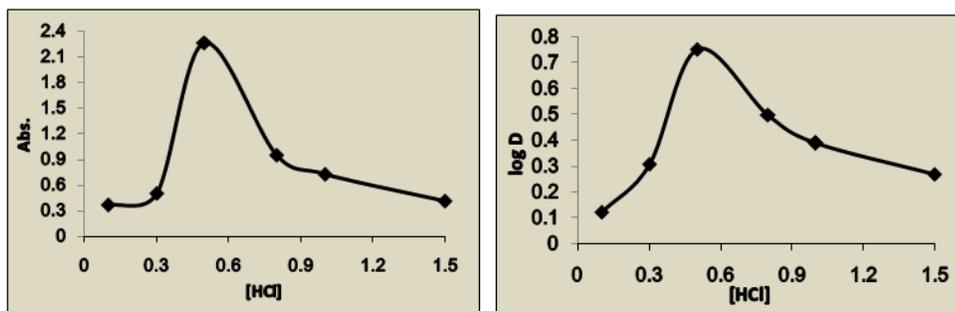
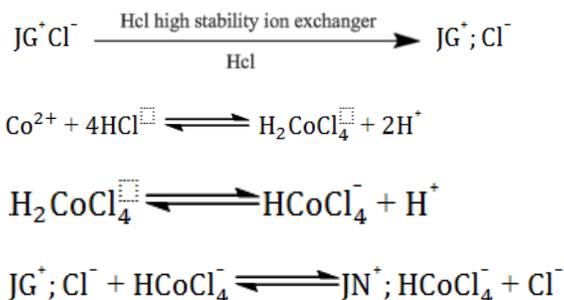


Figure 3: Effect of HCl Concentration on Complex Figure 4: D=F [HCl] Formation and Stability

The results show 0.5M HCl was the optimum concentration suitable for efficiency extraction of  $Co^{2+}$  ions as ion pair complex, this concentration for formation and stability of  $CoCl_4^{2-}$  as well as ion exchanger with (JG) as equilibrium below.



Any concentration less than optimum value decline extraction efficiency by decrease formation and stability of  $CoCl_4^{2-}$  so that ion exchanger of (JG) as well as any concentration more than optimum effect to decrease extraction efficiency by effect of dissociation according to mass action law and Le chatelier principle.

**Effect of  $Co^{2+}$  Concentration**

Extracted  $Co^{2+}$  ions via cloud point extraction method according to procedure detailed in experimental from 10 ml aqueous solution contain different concentration of  $Co^{2+}$  ion and 0.5M HCl,  $1 \times 10^{-4}$  M JG, 0.5 ml of 1% Triton X-100. The results was as in figure 5, 6

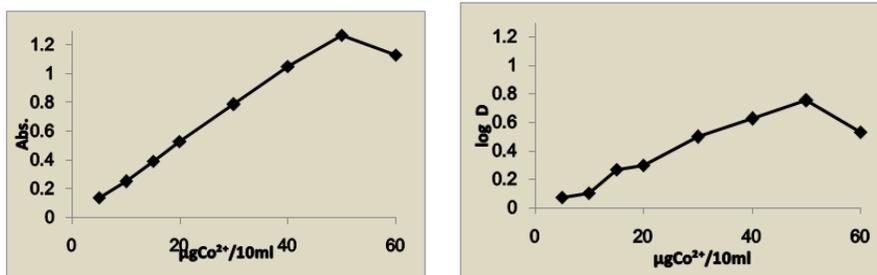


Figure 5: Complex Formation and Stability Depend Figure 6: Effect of  $Co^{2+}$  Concentration on Efficiency and D Value

The results show optimum concentration of  $\text{Co}^{2+}$  ions was  $50\mu\text{g}/10\text{ml}$  giving higher absorbance for ion pair complex extracted as well as D-value because this concentration giving higher concentration with higher stability of  $\text{CoCl}_4^{2-}$  need in thermodynamic equilibrium of ion complex formation and extraction, any concentration less than optimum not enough to reach thermodynamic equilibrium, so that any concentration of  $\text{Co}^{2+}$  ions more than optimum value effect to decrease extraction efficiency by reason of deviation the equilibrium into backward direction according to mass action law

### Effect of JG Concentration

According to procedure detailed in experimental part via CPE method extracted  $\text{Co}^{2+}$  at optimum condition with different concentration of JG, the results was as in fig[7,8].

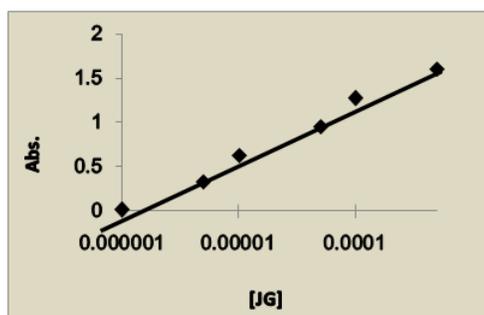


Figure 7: Ion Pair Complex Formation =F [JG]

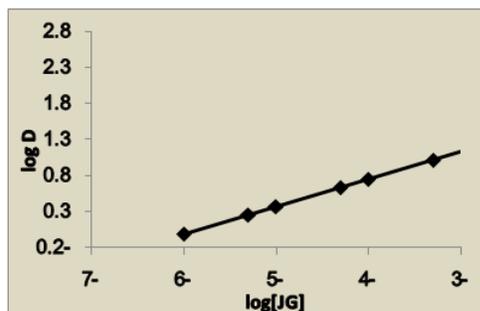
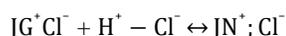
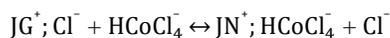


Figure 8: D=F [JG]

The results show there is a linear relation for complex formation and extraction efficiency with increasing concentration of extractant JG at other optimum condition as well as show extraction efficiency depend on thermodynamic equilibrium of ion pair complex formation and the rate of forward direction equilibrium increase with extractant increase by increasing concentration of ion exchanger with hydrochloric acid HCl



Increase concentration and stability effect to increase formation and stability of ion pair complex via liquid ion exchange as well extraction efficiency



### Effect of Volume Triton X-100

Extracted  $\text{Co}^{2+}$  ions from 10 ml aqueous solution via CPE methodology at optimum condition with different volume of 1% TritonX-100 according to procedure detailed in experimental part, the results was as in figure9, 10

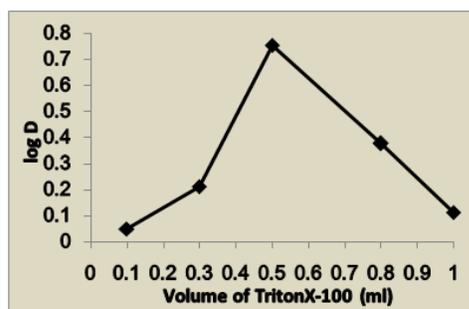
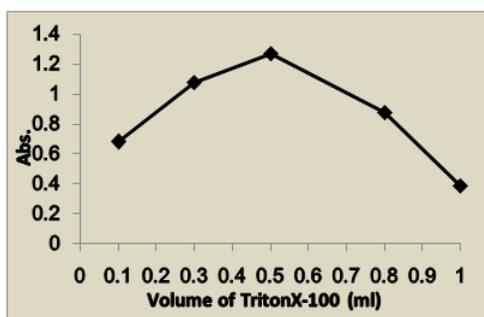


Figure 9: Effect of 1% Tritonx-100 Volume on Activity Figure 10: Effect of 1% Tritonx-100 Volume on of Extraction Thermodynamic

The results show 0.5 ml of 1% TritonX\_100 was the best volume to formation cloud point layer CPL which is sufficient to attainment higher extractability for  $\text{Co}^{2+}$  ions as ion pain complex  $\text{JN}^+; \text{HCoCl}_4^-$ , as well as the volume of surfactant is one of thermodynamic factors effect on extraction efficiency as well as this volume was effective formation CMC thermodynamically, any volume less than 0.5ml not suitable for extraction ,so that volume more than optimum value effect to increase diffusion micelles and decline extraction efficiency.

#### Effect of Temperature

Extracted  $\text{Co}^{2+}$  ions at optimum condition in different temperature via CPE methodology such as detailed previously, the results was as in figure11, 12

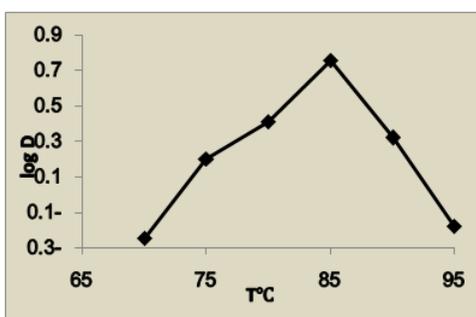
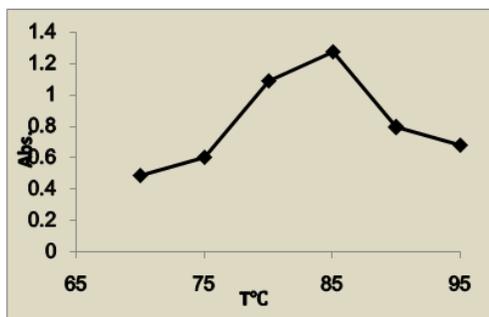


Figure 11: Effect of Temperature on Ion Pair Complex Transfer to CPL.

Figure 12: Effect of Temperature on Extraction Efficiency and D-Values

The results show 85°C was the optimum temperature giving higher extraction efficiency at this temperature which is giving best aggregation of micelles to form critical could point CMC ,any temperature less than optimum effect to decline extractionefficiency because don't reach to CMC ,and temperature more than optimum decline extraction efficiency by effect of diffusion after calculate extraction constant  $K_{ex}$  according to relation.

$$K_{ex} = \frac{D}{[JG][\text{Co}^{2+}]}$$

And after plot  $\log K_{ex}$  against  $1/T$  °K giving straight line relation as in figure13

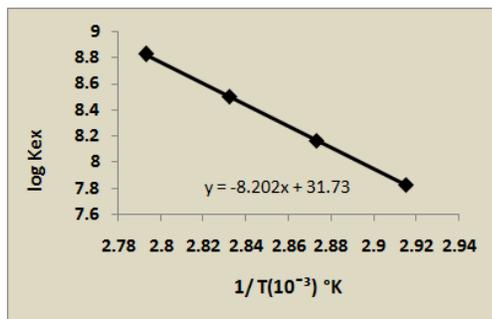


Figure 13:  $K_{Ex} = FT \text{ } ^\circ K$

And from slope of this straight line and thermodynamic relation calculated thermodynamic data

$$\Delta H_{ex} = 0.1570 \text{ KJ. mol}^{-1}$$

$$\Delta G_{ex} = -60.481 \text{ KJ. mol}^{-1}$$

$$\Delta S_{ex} = 169.379 \text{ J. mol}^{-1} \text{ K}^{-1}$$

The small value of  $\Delta H_{ex}$  effect the high approach each one to other for ion pair association complex which giving high attention about high stability of ion pair complex extracted so that high value  $\Delta S_{ex}$  giving a signal about the extraction according to CPE methodology was entropic in region

#### Effect of Heating Time

Extracted  $\text{Co}^{2+}$  ions according procedure detailed previously at optimum conditions but in different times of heating the results was as in figure 14, 15

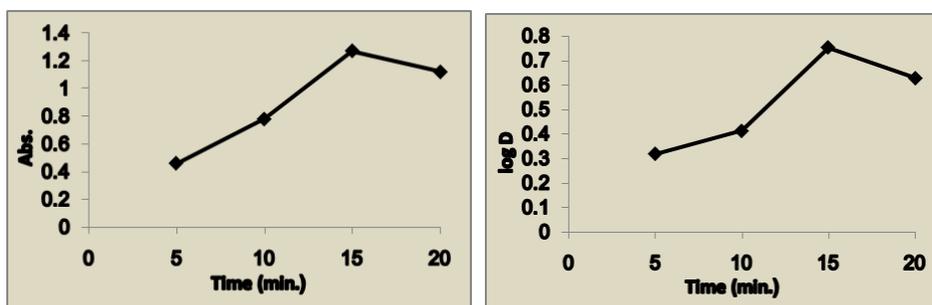


Figure 14: Effect of Heating Time on CPL Formation and Complex Transfer Figure 15: Effect of Heating Time on Extraction Efficiency and D-Values

The results show 15 minutes was the optimum heating time which is favorable heating time to formation CMC with high density and smaller volume to extracted quantitatively ion pair complex. any time Len than optimum not allow to reach thermodynamic and kinetic equilibrium for aggregation micelles to form CMC and decline extraction efficiency. as well as heating time more than optimum effect to increase quantity of heating more than need which in effect to increase diffusion of micelles. and decrease extraction efficiency also.

#### Stoichiometry

To know the probable structure of ion pair complex extracted employed to spectrophotometric methods which is slope analysis method and slope ratio method. the results was an in fig[16,17,18]

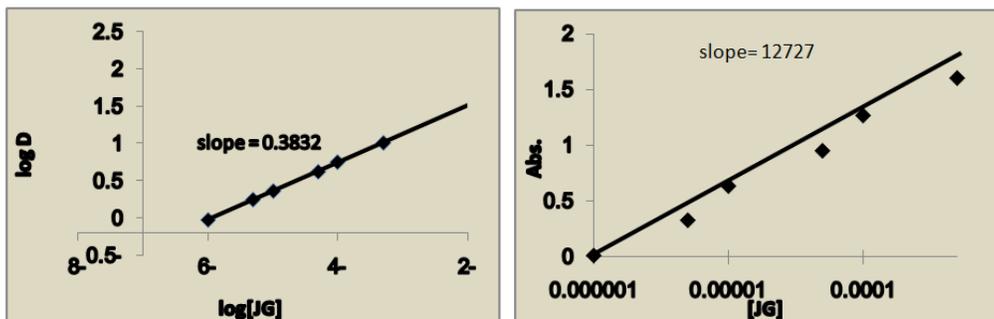


Figure 16: Slope Analyses Method. Figure Efficiency 17: Effect of JG Concentration on Extraction

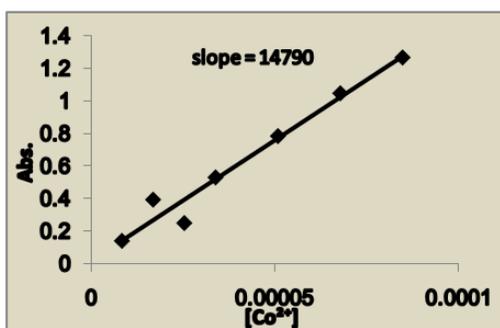


Figure 18: Effect of  $\text{Co}^{2+}$  Ion Concentration on Extraction Efficiency

From the slope value and slope ratio value suggest the more probable structure of ion pair complex extracted was 1:1  $\text{JG}^+$ ;  $\text{HCoCl}_4^-$

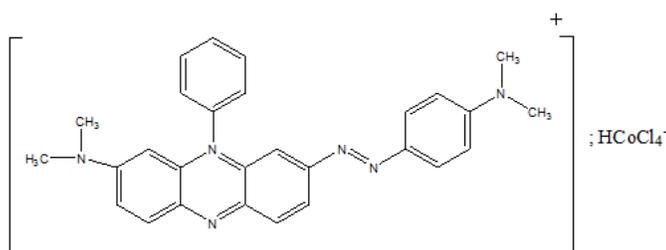


Figure 19

### Effect of Electrolytes

Extracted  $\text{Co}^{2+}$  ions from 10 ml aqueous solution contains  $50\mu\text{g Co}^{2+}$  ions , 0.5 M HCl,  $1 \times 10^{-4}$  M JG and 0.5 ml of 1% TritonX-100 in presence 0.1 M from electrolyte salts and follow the procedure detailed in experimental part , the results was demonstrated in Table (1).

Table 1: Effect of Electrolyte Salts

Electrolyte	Abs.620nm	D
LiCl	1.739	32.33
NaCl	1.652	15.67
KCl	1.402	13.29
NH <sub>4</sub> Cl	1.350	9.00
MgCl <sub>2</sub>	1.514	17.52
CaCl <sub>2</sub>	1.456	11.50
AlCl <sub>3</sub>	1.414	12.51

The results show presence electrolyte effect to increase extraction efficiency via CPE methodology because the electrolyte effect to increase dehydration and destroyed hydration shell of Co<sup>2+</sup> ions and effect to increase rate and stability CMC formation as well as quantitatively and stability of ion pair complex extracted, and this effect increase with decrease diameter metal cation in electrolyte salts and markedly LiCl giving higher extraction efficiency because Li<sup>+</sup> have smaller ionic diameter

### Effect of Interferences

Extracted Co<sup>2+</sup> ion from 10 ml aqueous solution contain 50 µg Co<sup>2+</sup> ion, 0.5M HCl, 1x10<sup>-4</sup> M JG, 0.5ml of 1% TritonX\_100, in presence 0.1M Ni<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, Cr<sub>2</sub>O<sub>4</sub><sup>2-</sup>, Mn<sub>4</sub>O<sub>4</sub><sup>-</sup> after flowed the procedure detailed in experimental part the results was demomtrated in Table (2).

Table 2

Interferences	Abs.620nm	D
Ni <sup>2+</sup>	1.060	3.53
Cd <sup>2+</sup>	0.972	1.34
Hg <sup>2+</sup>	0.981	1.78
Cr <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	0.905	1.08
MnO <sub>4</sub> <sup>-</sup>	0.995	2.45

The results show all these ions participate Co<sup>2+</sup> ions in extraction as ion pair complex with different efficiency as well as when we are extracted Co<sup>2+</sup> ion must be use suitable masking agent for another ions can extracted.

### Spectrophotometric Determination of Co<sup>2+</sup> Ion

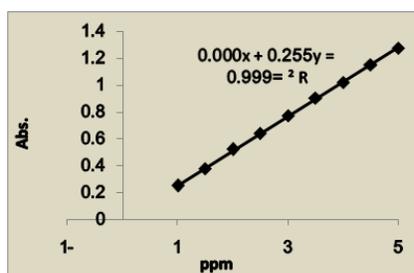


Figure 20

Table 3

<b>RSD %</b>	<b>0.0045</b>
<b>EL.mol<sup>-1</sup>.cm<sup>-1</sup></b>	150664
<b>D.L ppm</b>	6.971X10 <sup>-6</sup>
<b>S µg/cm<sup>2</sup></b>	3.911X10 <sup>-10</sup>

## REFERENCES

1. Shawket.K. Jawad and Faris H. Hayder.[ cloud point extraction, preconcentration and spectrophotometric determination of magnesium (II) by using 2,4-dimethylpentan-3-one ] Eur.chem. Bull 4(8), 360-363, (2015).
2. Shawket.K. Jawad and Ebaa A. Azooz.[cloud point extraction for separation , preconcentration and extraction of nickel (II)as chloroanion by use crown ether DB18C6 coupled with spectrophotometric determination ] international Journal for science and Technology.Vol.9,No.1, 17-23, (2014)
3. Shawket.K. Jawad and Mustafa N. MohamedSalih. [ sensitive separation , preconcentration molybdenum (VI) Via cloud point extraction methodology ] Journal of plastic and polymer Technology (JppT) Vol.1 , Issue.1 , 37-48 , (2015)
4. Zuhair A.A. khammas and noor S. Mubdir[ Cloud point extraction spectrophotometric method for mutual determination for morefloxacin and iron(III) in human serum and drug for formulations ] chemicalsciencetransaction4(1) (2015)
5. D. NagarjunaReddy [ extraction direct and derivative spectrophotometric determination of nickel (II) in medicinal leaves , soil and alloy samples by using pyridoxal -3- thio semi eabazom (ApT) ] Mater. Environ. Sci 5(4) , 1188-1199(2014)
6. Fazing Nekouei and shahramNekouei[simultaneouscloud point extraction and ion associate system for preconcentration of cadmium (II) in the presence of Zwiheveone surfactant 3-( cholamidopropylDimethylul ammonium)l.Propane sulphonateasachdating agent prior to itsspectrophotometric determination ] Indian J, sci.Res 8(1) , 130 -137 (2014)
7. Shawket K. Jawad and FarisH. Hayder[Optimization cloud point extraction methodology for separation , extraction and spectrophotometric determination of Zn(II) ] Chemistry and Materials Research Vol.7 , No.3 , 63-72 , (2015)
8. M.R. Jamali. M. Gholinezhad, S. Balarostaghi, R.Rahuama and S.H.A. RahimiJournal of chemistry 1(7) (2013)
9. BahramM, KhezriS. Curr. chem. left 2(1) , 49 -56 , (2013)
10. OKtariza, Y. Putra, O.D, Insann, M, Miftah, A.M, Int. J. pharm. Sci 5(4), 498-501, (2013)
11. Bahram M, Shahmoradi,S., Mozaffari,S. , Niko. A., Dilmaghani, K.A., Jordan J. chem. 8(1), 45-55, (2013)
12. Duran, c, ozdes, D, kaya, E.C, Kantelcin, H, Bulut, V.N, Tufekci, M. Turk J. chem. 36 (3), 445- 456 (2012)
13. Marczenko, Z, ((separation and spectrophotometric determination of element)) Allis HorwoodLtd, 1986



