

# Cloud Point Extraction Methodology for Separation and Extraction Platinum (II) as Chloro Complex Anion Coupled with Spectrophotometric Method for Determination in Different Samples

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## Abstract

Whereas the platinum is very important metal with several special properties to provide it as expensive metal with important using , for separation preconcentration and extraction platinum as Chloroanion  $PtCl_4^-$  according to cloud point extraction method used Triton X-100 at optimum conditions such as 1M HCl with  $1 \times 10^{-4} M$  Janus green (JG) and 0.5 mL of 1% Triton X-100 Cloud point layer Formation at 75°C of heating in electrostatic water bath for 15 minutes , The stoichiometric study show the more probable structure of ion association Complex extraction was  $[JG^+ ; HPtCl_4^-]$  , with thermodynamic data  $\Delta H_{ex} = 0.0814 KJ mol^{-1}$  ,  $\Delta G_{ex} = -61.42 KJ mol^{-1}$  and  $\Delta S_{ex} = 176.7 J mol^{-1} K^{-1}$  , the main method for extraction show D.L =  $6.8028 \times 10^{-6}$  S=0.003133  $\mu g cm^{-1}$  R.S.D= 0.00885 the maximum absorbance wave length was = 690 nm and  $\epsilon = 6227.861 L mol^{-1} cm^{-1}$

**Keywords:** platinum, cloud point extraction

## Introduction

In previous application there is many studies in CPE method about extraction and separation anions from aqueous solutions. One of these research include extraction of Nickel(II) as Chloro Complex anion after formation ion pair association complex with DB18C6crownether by CPE method by used Triton X-100 as surfactant in presence of favorite concentration of hydrochloric acid , the ion pair complex extracted has maximum absorbance at  $\lambda_{max} = 295 nm$  [1] . Anew and versatile procedure for the spectrophotometric determination of manganese using micelle – mediated extraction. The method involved the formation of an ion association complex between manganese oxyanion  $MnO_4^-$  and brilliant green in acidic solution and the complex extracted into the surfactant Tritonx – 100 at optimum condition and has maximum absorbance at  $\lambda_{max} = 657nm$  [2] . Anew trend in extraction and preconcentration of Chromium (VI) using laboratory-made azo dye reagent 2-[benzenethiozolyazo]-4- benzenenaphthol (BTABN) after Cloud- point extraction (CPE) and its determination spectrophotometrically. The method involved the reaction of  $Cr_2O_7^{2-}$  with BTABN in acidic medium to formation hydrophobic ion – association complex  $[HBTABN^+][HCr_2O_7^-]$  Which is entrapped into micelle-mediating solvent (Triton X-100) and the Cr(VI) detected spectrophotometrically at  $\lambda_{max} = 475nm$  [3] . A Cloud –point extraction procedure was presented for preconcentration of Lead (II) and Cadmium (II) ions in various samples after Complexation by 2-[benzenethiozolyazo]-4- benzyl phenol (BTABP)with Lead (II)and 2-[3- Bromophenylazo ]-4,5- diphenyl imidazole (BPADPI)with Cadmium ions are quantitatively extracted in Triton X-100 following separation [4]. Some worker used CPE methodology coupled with ICP-OES method for separation and spectrophotometric determination for heavy metals  $Cd^{+2}$  ,  $Co^{+2}$  ,  $Ni^{+2}$  ,  $Pb^{+2}$  ,  $Zn^{+2}$  ,  $Cu^{+2}$  by used 8- Hydroxyquinoline as complexing agent [5]. Another worker used CPE method for extraction and determination of  $Cu^{+2}$  and  $La^{3+}$  by used Complexation agent p-Sulfonatocalix [4] arene and surfactant Triton X-100 and studied all effective parameters on the CPE efficiency [6]. To rely on sensitivity of CPE method used for preconcentration of Cobalt from different samples of water with complexing agent 4-Benzyl – mpiperidinedithiocarbamate and Triton X-100 coupled with FAAS for determination [7]. By used CPE method for separation ,preconcentration and determination of Nickel(II) in presence 8- Hydroxyquinoline as complexing agent with surfactant Triton X-100 as well as studied all parameter effective on efficiency of the method [8]. By application of CPE method for separation , extraction and preconcentration of  $Cu^{+2}$  and  $Ag^+$  with used Triton X-100 , coupled with FAAS for determination Analyte elements with detection limit  $0.5 \mu g L^{-1}$  [9]. Sparation and preconcentration of Cadmium by use Cloud – point extraction method with surfactant Triton X-114 as well as used TAN as complexing agent coupled with FAAS for determination with limit of detection  $0.099 ng ML^{-1}$ [10]. Some worker implement Cloud – point extraction method for separation , extraction and preconcentration .Cadmium after Complexation with PAN by use surfactant Triton X-114 and used FAAS for determination in soft drinks with detection limit  $0.0018 ngml^{-1}$ [11]. In one research the worker used Amoniumpyrolidinedithiocarbamate as complexing agent for Cadmium(II) to extracted from foods by CPE method with surfactant Triton X-114 , and determination of Cadmium with Electro thermal atomic absorption ETAAS and the detection limit was  $0.004 ngml^{-1}$ [12]. There is an research involved Extraction Cr(VI)from water according to CPE method by used [(1-hydroxy naphthalene -2- yl) methylene amino]-2- Hydroxy benzoic acid

as complexing agent and surfactant Triton X-114 as well as FAAS method for determination Chromium (VI) with detection limit  $5.2 \text{ ngml}^{-1}$  [13].

### Experimental

For spectrophotometric measurement used A shimadzu double beam UV-Vis spectrophotometer model UV-1700(Japan) , also for absorbance measurements used single beam (UV-Vis) spectrophotometer TRIUP international Corp –TRUV , 74,5,(Italy).

### Chemicals and Solutions

All Chemicals used directly as received without any further purification , Stock solution of Platinum (II) 1mg/ml in concentration prepared by dissolving 0.1 g platinum in 100ml of aqua regia in volumetric flask ,other working solutions prepared by dilution with distilled water ,so as all other solutions prepared by used distilled water .

### Fundamental procedure

Aqueous solution 10 ml in volume contain  $100 \mu\text{g Pt}^{2+}$  , and 1 M HCl ,  $1 \times 10^{-4}$  Janus green , 0.5 ml of 1% Tritonx – 100 , heating this solution in electrostatic water bath to  $75^\circ\text{C}$  for 15 minute until formation cloud point layer , at latter separate cloud point layer (CPL) from aqueous solution and dissolved in 5 ml ethanol and measure the absorbance at  $\lambda_{\text{max}} = 690 \text{ nm}$  obtained from spectrum in fig (1) , against blank prepared at the same manner without platinum (II) . but aqueous solution treated according to spectrophotometric method ( $\text{SnCl}_2$  method) [14] , and after return to calibration curve fig (2) determine remainder quantity of platinum (II) in aqueous solution after extraction and transfered quantity of  $\text{Pt}^{2+}$  into CPL determine by subtraction The remainder from original quantity . Of stripping method shaken ethanolic CPL solution with two portion of 5ml Concentrated ammonium solution and determined  $\text{Pt}^{2+}$  stripped to aqueous ammonium solution by ( $\text{SnCl}_2$  method) . worth mentioning the transfered  $\text{Pt}^{2+}$  determined by stripping equal to The same quantity determined by subtraction then to relay on subtraction method in all experiment because easier and faster . afterward calculate Distribution ratio (D) .

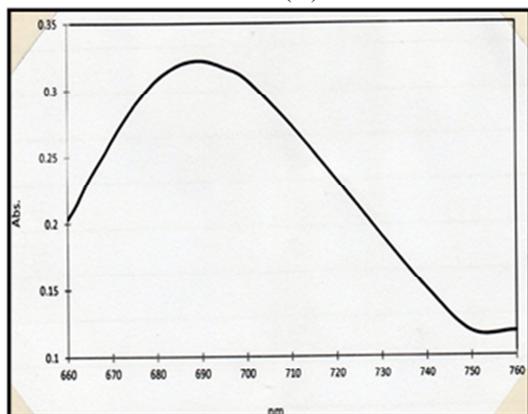


Fig (1) :UV-Vis- absorption

*Spectrum for ion pair complex*

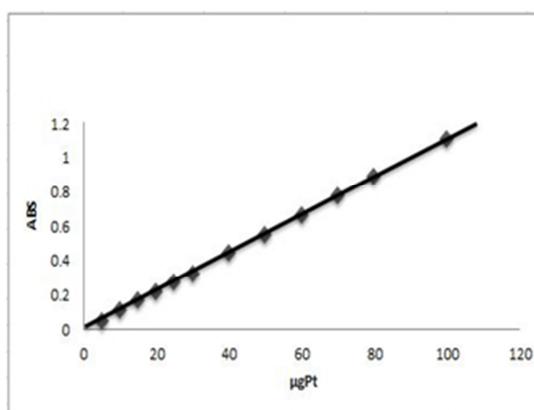


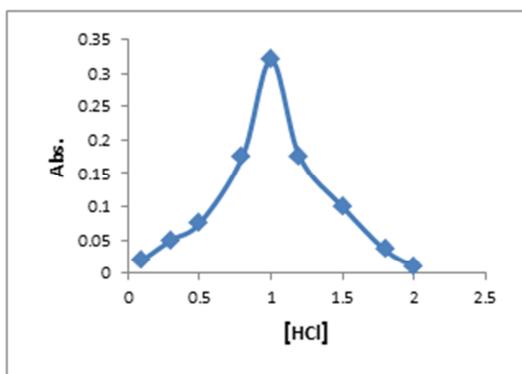
Fig (2):Calibration Curve / for determination

*Pt<sup>2+</sup> in aqueous Solution (SnCl<sub>2</sub> method)*

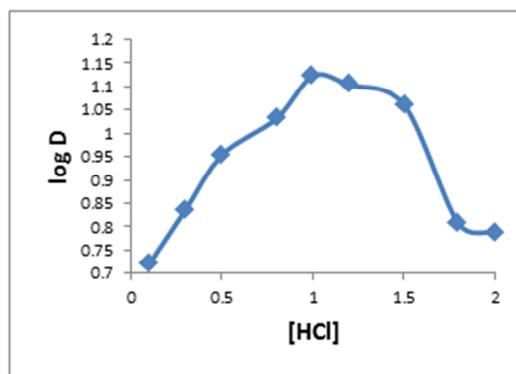
### Results and Discussion

#### Effect of hydrochloric acid concentration

Aqueous solution 10 ml in volume contain  $100 \mu\text{g}$  of platinum (II) and different concentrations of hydrochloric acid HCl at range (0.1 – 2) M and  $1 \times 10^{-4}$  M Janus green , 0.5ml of 1% Tritonx – 100 , then heating the solution in electrostatic water bath for suitable temperature and time until form cloud point layer , separate cloud point layer from aqueous solution and dissolved in 5ml ethanol and measure the absorbance at  $\lambda_{\text{max}} = 690$  against blank prepared at the same manner without  $\text{Pt}^{2+}$  and the aqueous solution treated with  $\text{SnCl}_2$  spectrophotometric method [14] and calculate D- values - . The results was as in fig 3,4

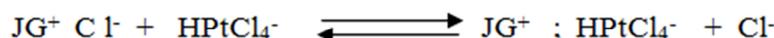


**Figure3:** effect HCl concentration on ion pair complex formation and efficiency of extraction



**Figure4:**  $D=f[HCL]$

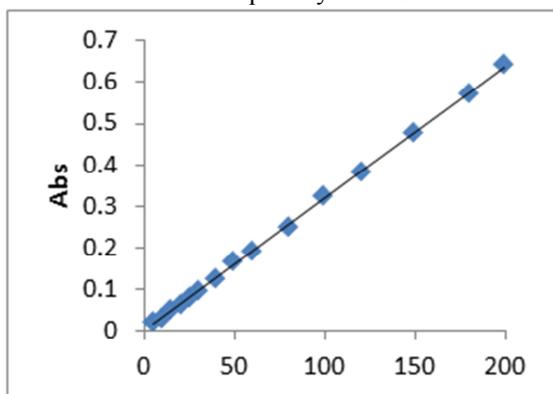
The results show hydrochloric acid do to high formation of  $PtCl_4^-$  and increased stability of this anion as well as help to change Janus green into stable ion exchanger can be exchange with  $HptCl_4^-$  in aqueous solution to produce ion association complex extracted to cloud point layer and this behaviour need suitable concentration of HCl which was 1M as optimum concentration giving higher absorbance for ethanolic CPL and D-value . as in equilibrium below .



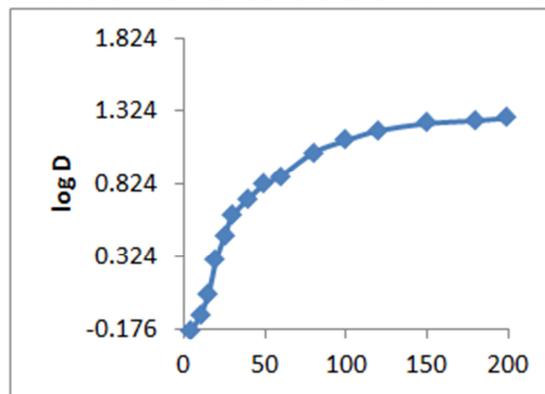
Any Concentration of HCl less than optimum value not allow to reach thermodynamic equilibrium for formation  $PtCl_4^-$  and partition into CPL that is mean giving decrease in absorbance and D-values . as well any concentration of HCl more than optimum value effect to decline efficiency of extraction and decrease absorbance and D-values . this high concentration effect to increase stability of ion association complex  $[JG^+ ; Cl^-]$  which is extracted to CPL . as well as high competition between high concentration  $Cl^-$  and low Concentration  $PtCl_4^-$  effect to increase rate of backward direction of equilibrium .

#### Effect of platinum concentration

10ml aqueous solution contain increasing quantity of platinum ion (2 – 200) $\mu g$  , 1MHCl ,  $1 \times 10^{-4} M$  JG and 0.5 ml of 1% Tritonx – 100 , heating these solutions in electrostatic water bath for suitable Temperature and time until form cloud point layer with smaller volume and higher density , at latter separate CPL from aqueous solution and dissolve in 5ml ethanol and measure it absorbance at  $\lambda_{max} = 690nm$  against blank prepared at the same manner without  $Pt^{2+}$  , and the aqueous solution treated according to  $SnCl_2$  spectrophotometric method and after return to calibration curve fig(2) to determine remainder quantity of  $Pt^{2+}$  in aqueous solution after extraction also determine transfer quantity to CPL and calculate D- value for each concentration the results was as in fig 5,6



**Figure5:** effect  $Pt^{2+}$  concentration on efficiency of extract

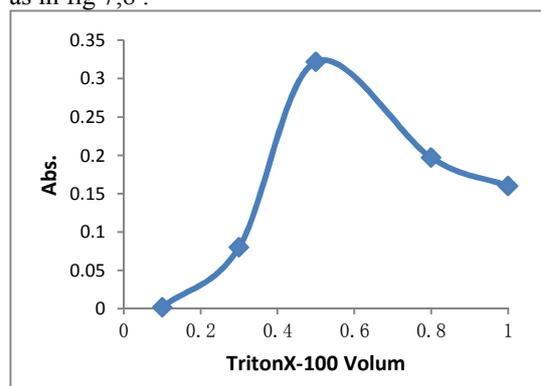


**Figure6:**  $\log D = f \mu g Pt^{2+}$

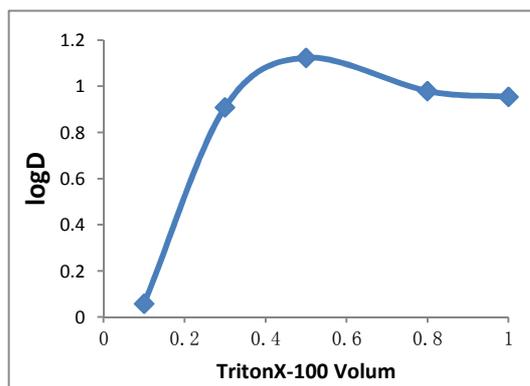
The results shows the concentration of platinum in aqueous solution behave as thermodynamic parameter effect on the activity of extraction by CPE method, and appear the efficiency of extraction increase with platinum concentration increasing, that is mean thermodynamic equilibria show increasing in the forward direction for extraction according to CPE method at constant of other parameter. Any Concentration less than optimum value not allow to reach thermodynamic equilibrium as well as Concentration more than optimum value effect to decrease extraction efficiency according to mass action law and le chatelier principle.

**Effect of surfactant volume**

Extracted platinum (11) as anion  $PtCl_4^-$  in CPE method from 10ml aqueous solution contain  $100\mu g Pt^{2+}$ , 1M HCl and  $1 \times 10^{-4} M JG$  and different volume of 1% Tritonx – 100 in the range 0.1 – 1 ml, afterward heating these solution to suitable temperature and time until cloud point layer formation then separate this layer from aqueous solution and dissolved in 5ml ethanol and measure its absorbance at 690 nm against blank prepared at the same manner without presence  $pt^{2+}$ , as well as treated aqueous solution according to  $SnCl_2$  spectrophotometric method [15] and calculate D- values after return to calibration curve fig(2), the results was as in fig 7,8.



Figure(7): ion pair complex extracted = f(TritonX-100) volume



Figure(8): D = f(TritonX-100) volume

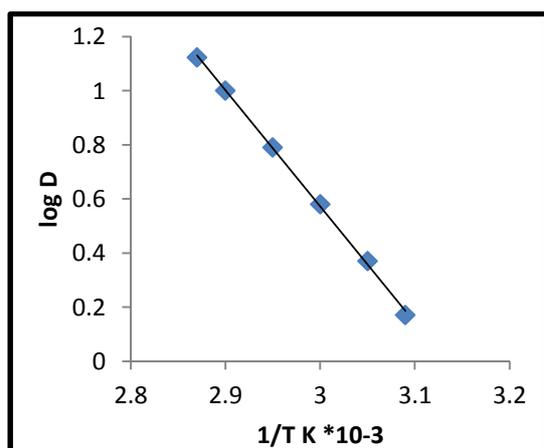
The results show 0.5 ml of 1% Tritonx – 100 was favorite volume giving higher value of absorbance for ethanolic micelles rich phase and D- value, whereas any volume less than 0.5 ml not enough to giving full extraction of ion pair complex for platinum (11) effect to show decrease in absorbance and D- value – as well as surfactant volume more Than 0.5 ml effect to decline extraction efficiency by effect of increase diffusion of micelles rich phase.

**Temperature effect**

10 ml aqueous solutions contain  $100\mu g Pt^{2+}$ , 1M HCl,  $1 \times 10^{-4} M JG$ , 0.5ml of 1% Tritonx – 100 heating in electrostatic waterbath for different temperature at the rang of  $(50 - 75)^{\circ}C$  at fixed time, and at latter separate CPL from aqueous solution and measure absorbance and determine D- value as detailed in fundamental procedure, the results was as in fig 9, afterward calculate extraction constant  $k_{ex}$  by application relation below

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

Plot  $\log k_{ex}$  against  $1/TK$  as in fig 10 as well as from the slope of this straight line and relations below calculate thermodynamic data of extraction



Figure(9):  $D=f(T^{\circ} K)$

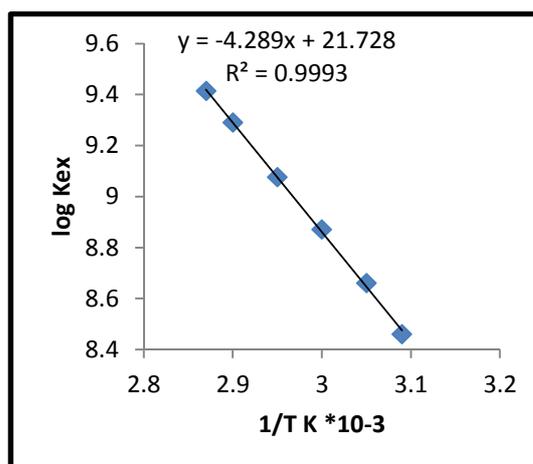


Figure10:  $K_{ex}=f(T^{\circ} K)$

The results show the extraction behavior in CPE method is endothermic and the maximum temperature of heating giving higher absorbance and D- value was 75°C any temperature less than 75°C not enough to complete formation of micelle – rich phase layer that is mean increase diffusion of micelle with decrease heating temperature , as well as any temperature more than 75°C effect to increase diffusion of micelle and decline extraction efficiency and from the slope value of the straight line in fig (10) which is equal to (- 4.34) calculate

$\Delta H_{ex}$

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

$$\Delta H_{ex} = 0.0814 \text{ KJ mol}^{-1} \quad \Delta G_{ex} = RT \ln k_{ex} \quad \Delta G_{ex} = - 61.42 \text{ KJmol}^{-1}$$

$$\Delta G_{ex} = \Delta H_{ex} - T \Delta S_{ex} \quad \Delta S_{ex} = 176.7 \text{ J Mol}^{-1} \text{ k}^{-1}$$

#### Effect of heating time

Extracted platinum (II) as chloroanion  $ptcl_4^-$  from 10ml aqueous solution contain 100  $\mu\text{g}$  , 1M HCl ,  $1 \times 10^{-4}$  M JG and 0.5ml of 1% Tritonx – 100 , and heating these solutions to 75°C for different time (2-30) min . at latter separate cloud point layer from aqueous solution and measure the absorbance of ethanolic solution of CPL and calculate distribution ratio (D) of each time of heating , the results was as in fig 11,12

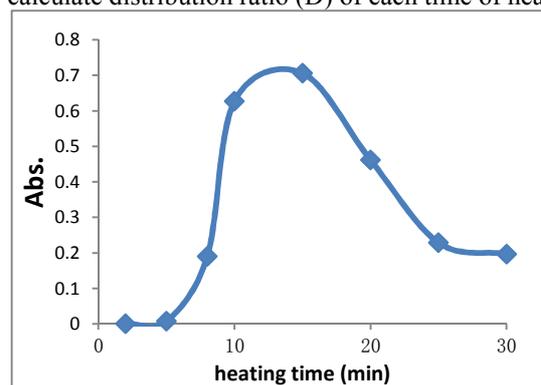


Figure11: heating time effect on complex Formoe and extraction efficiency

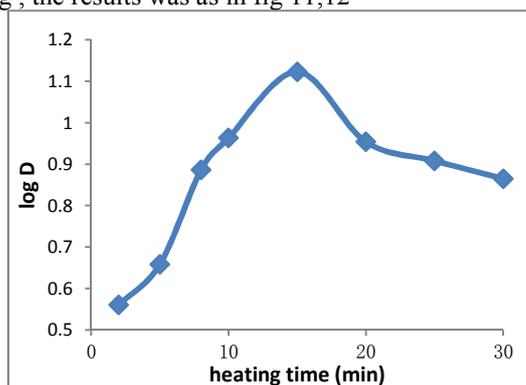


Figure12: heating time = f(D value)

The Results show 15 min . was the optimum time of heating to reach favorite thermodynamic equilibrium and giving higher Absorbance and D- value , any time of heating less than optimum value not allow to reach equilibrium and effect to decrease extraction efficiency , also any time of heating more than optimum effect to decrease extraction activity and absorbance by reason of increase diffusion of micelles rich phase layer .

#### Stoichiometry

To know and limitation the structure of ion pair association complex Extracted to cloud point layer applicated two spectrophotometric method which is slope analysis method and slope ratio method , the results of these

method appeared in figure 13 so figure 14 a and b.

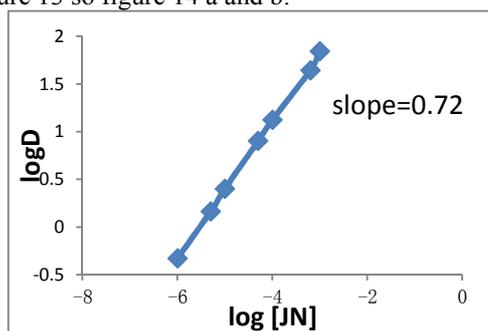


Figure13:slope analysis method

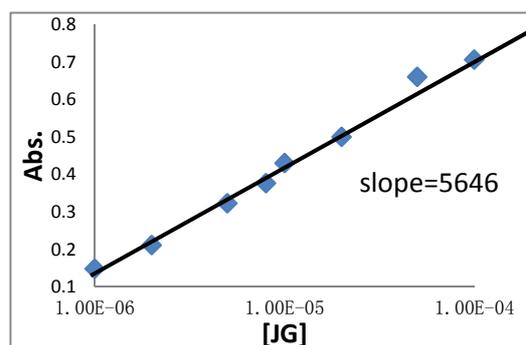


Figure14b: Abs. = f[JG]

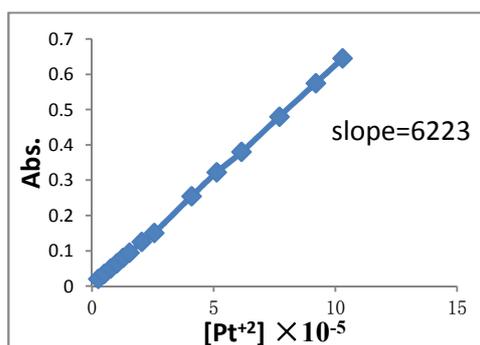


Figure14 a: Abs. = f[Pt<sup>2+</sup>]

$$\text{Slope} = \frac{5646}{6223} = 0.902$$

The results show the more probable structure of ion association complex extracted into CPL wa 1:1 [JG<sup>+</sup> ; Hptcl<sub>4</sub><sup>-</sup>]

### Interferences

Extracted platinum (11) as chloroanion PtCl<sub>4</sub><sup>-</sup> according to CPE method from 10ml aqueous solution contain 100µg pt<sup>2+</sup> 1M HCl, 1x10<sup>-4</sup>M JG, 0.5 ml of 1% TritonX-100, and 0.1M from different anions, after heating to optimum Temperature and time separate CPL from aqueous solution and determine the absorbance of ethanolic solution of CPL and D- values as in fundamental method detailed the results appear as in Table (1).

Table(1): Effect of interference on extraction efficiency

Interferences	Abs. = 640	D
CH <sub>3</sub> COONa	0.329	7.33
K Mn O <sub>4</sub>	0.153	3.15
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	0.113	1.1
KNO <sub>3</sub>	0.565	11.25
Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	0.434	8.524
K I	0.533	10.41

The results show all anions interfere in the formation of ion association complex and extraction into CPL. but in different activity, whereas dichromate anion giving the major interference as well the less interference with nitrate anion

### Effect of Electrolyte

Extracted platinum (11) as chloroanion ptcl<sub>4</sub><sup>-</sup> from 10ml aqueous solution contain 100µg pt<sup>2+</sup>, 1M HCl, 1x10<sup>-4</sup>M JG, 0.1M from different electrolyte salts and 0.5 ml of 1% Tritonx - 100 after heating to optimum temperature and time separate cloud point layer from aqueous solution and dissolved in 5ml ethanol and measure Absorbance at 690 nm against blank prepared at the same manner without platinum ion and aqueous solutions treated according to SnCl<sub>2</sub> spectrophotometric method and return to calibration curve fig (2) to calculate D-values as in fundamental method detailed, the results was as in Table (2):

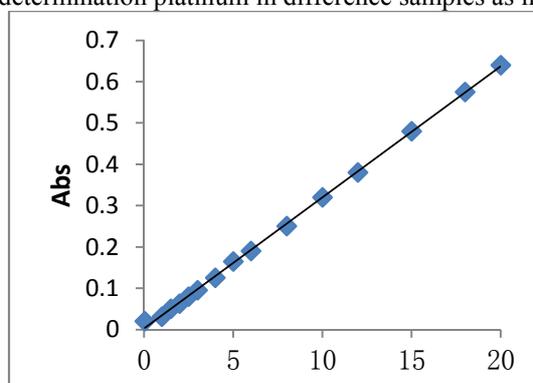
**Table (2) : Electrolyte Effect on extraction efficiency of platinum (11)**

Electrolyte	Abs. at 69	D
LiCl	11.076	99
NaCl	10.982	49
KCl	0.809	24
NH <sub>4</sub> Cl	0.789	21.22
Mg Cl <sub>2</sub>	0.895	24
CaCl <sub>2</sub>	0.863	19
SrCl <sub>2</sub>	0.788	18
AlCl <sub>3</sub>	0.803	21.2

The results show presence of Electrolyte salts effect to increase efficiency of extraction by CPE method because the cation of these electrolyte salts effect to increase dehydration of micelle – rich phase layer as well LiCl giving higher Absorbance and D- value because Li<sup>+</sup> have smallest ionic Diameter and larger hydration shell then this ion can withdrawing larger quantity of water molecule from micelle – rich phase further to more destroy hydration shell of platinum ion that is mean increase the chance of complex formation and extraction , so as for other ions of Electrolyte .

### Spectrophotometric determination

Prepared calibration curve for determination platinum in difference samples as in fig (15)



**Fig (15):** Calibration Curve for spectrophotometric determination of Pt<sup>2+</sup>

After perform Calibration curve for spectrophotometric determination of platinum (II), determined platinum(II) in different samples after treated the sample according to the fundamental method detailed and measure the absorbance of ethanolic solution of CPL according blank prepared at the same manner with out platinum(II) and from the absorbance value and return to Calibration curve and determined quantity of platinum in the sample.

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