

## Liquid Ion Exchange Method for Extraction of Pb (II) as Anion by Using 15C5 Coupled with Spectrophotometric Determination in Different Samples

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### الخلاصة:

تم فصل وإستخلاص الرصاص (II) على هيئة معقد كلورو سالب وباستخدام الإيثر التاجي 15C5. تضمنت الدراسة تحديد الظروف المثلى مثل تركيز كل من حامض الهيدروكلوريك، كلوريد الصوديوم وأيون الرصاص (II)، تأثير زمن الرج، المذيب العضوي، المتداخلات، الاملاح الالكترووليتية وتأثير الميثانول. الدراسة الترموديناميكية أظهرت ان التفاعل هو ان التفاعل هو باعث للحرارة Exothermic. أما دراسة تركيب المعقد المستخلص فقد أوضحت ان المعقد كان بنسبة Cation: Ligand: Anion 1:1:1 وأظهر طيف الأشعة فوق البنفسجية للمعقد المستخلص اعلى قمة امتصاص عند  $\lambda_{max}=241nm$ . كما أستخدم الإيثر التاجي 15C5 لتقدير الرصاص في نماذج مختلفة.  $D.L=$  Sandell's Sensitivity=  $4.86 \times 10^{-7} \mu g/cm^2$ ,  $\epsilon= 2057.85 L.mol^{-1}.cm^{-1}$ ,  $D.L=5.04483 \times 10^{-5} ppm$ ,  $\%RSD=0.00672$

### Abstract

Separation and extraction of chloroanion complex of  $Pb^{2+}$  by using crown ether 15C5 had been investigated. This study includes determined hydrochloric acid and sodium chloride concentrations in aqueous phase and  $Pb^{2+}$  ions concentration as well as shaking time, organic solvent effect, interferences, electrolyte salts and methanol effect. Thermodynamic parameters shown the ion exchange reaction was exothermic. In addition stoichiometry study shown that the ion pair complex extracted was 1:1:1 Cation: Ligand: Anion. UV-spectrum of extracting complex show  $\lambda_{max}=241nm$ . 15C5 used as spectrophotometric reagent for the spectrophotometric determination of  $Pb^{2+}$  in different samples,  $\%RSD=0.00672$ ,  $D.L=5.04483 \times 10^{-5} ppm$ ,  $\epsilon= 2057.85 L.mol^{-1}.cm^{-1}$ , Sandell's Sensitivity=  $4.86 \times 10^{-7} \mu g/cm^2$ .

*Key Words: Liquid ion exchange, lead ion, Solvent extraction, crown ether, Spectrophotometric methods.*

### Introduction

Lead is one of the heavy metals which is considered as one of the dangerous environmental pollutants. It is emitted from many industries such as construction, electronics, motor vehicles, stationary fuel, road dust composition and traffic pattern. Lead is not only as a toxic element, but also can be accumulated in plant organs and agricultural products [1-2]. consequently enter the human food chain [3]. As a result of consumption of food, lead

accumulates in the human body <sup>[4]</sup>. Solvent extraction of gold (III) as  $\text{AuCl}_4^-$  with 18-crown-6 in 1,2-dichloro ethane, followed by FAAS<sup>[5]</sup>. Bismuth (III) was extracted quantitatively with n-octylaniline in chloroform from hydrochloric acid and hydrobromic acid medium the extracted species is  $(\text{RNH}_3^+)_2 \text{BiCl}_5^{2-}$ . This method applied to the separation of bismuth (III) from alloy samples <sup>[6]</sup>. Solvent extraction of lead (II) by 2-[Benzo thiazolylazo]-4-Benzylphenol in chloroform, as well used this organic reagent as spectrophotometric reagent for determination of lead (II) in different samples of plants, soils and water at different positions in Al-Najaf governorate <sup>[7]</sup>. Separation, preconcentration and determination of cadmium as  $\text{CdCl}_4^{2-}$  by crystal violet was extracted into nonionic surfactant Triton X-100 this method was applied for the determination of cadmium in soil, vegetables, plant leaves and water, followed by AAS<sup>[8]</sup>. Cloud point extraction for extraction of nickel (II) as  $\text{NiCl}_4^{2-}$  by use DB18C6 in the presence of 0.5 M hydrochloric acid, 0.25 M NaCl and 1% Triton X-100, absorbance spectrum for ion pair association complex extracted by CPE method  $\lambda_{\text{max}} = 295\text{nm}$ . And this study includes application about determination nickel (II) in different samples <sup>[9]</sup>. The spectrophotometric determination of manganese using micelle-mediated extraction. The method involved the formation of anion association complex between manganese oxyanion ( $\text{MnO}_4^-$ ) and brilliant green in acidic solution and the complex was extracted into the surfactant Triton X-100 <sup>[10]</sup>.

## **Experimental**

### **Apparatus:-**

The spectrophotometric measurements were carried out on double beam UV-Vis. spectrophotometer (Biochrom Libra S60) (UK) is used by 1cm quartz cells and pH was measured with pH-meter, WTW (Germany). For shaking used HY-4 vibrator with AD Just about speed multiple (Italy).

### **Reagents:-**

The solution of organic reagent crown ether 15C5 was prepared in chloroform by dissolving suitable quantity of 15C5 to obtain a solution at  $(1 \times 10^{-2}\text{M})$  in concentration and other working solutions prepared by dilution by chloroform. Lead (II) solution at a concentration of (1mg/mL Pb (II)) prepared by dissolving (0.1342gm) of  $\text{PbCl}_2$  [Fluka] in (100mL) distilled water, other working solutions prepared by appropriate dilution of the stock solution with distilled water by use volumetric flask. A stock solution of dithizone  $(1 \times 10^{-2}\text{M})$

was prepared by dissolving (0.0256gm) in (10mL) carbon tetrachloride in volumetric flask, working solution ( $1 \times 10^{-4}M$ ) was prepared instantaneously by diluting with  $CCl_4$ .

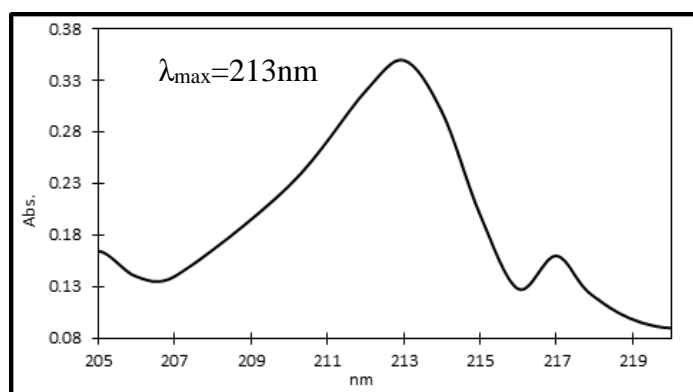
#### General extraction method:-

An aliquot of 5mL solutions containing a known quantity of  $Pb^{2+}$ , at optimum conditions such as concentration of HCl and NaCl shaken for 5 min. To form chloroanion complex  $PbCl_4^-$  or  $PbCl_3^-$  after that add 5mL of ( $1 \times 10^{-4}M$ ) organic reagent 15C5 the two layers shaking for optimum shaking time at  $25^\circ C$ , afterward anion exchange happen separate two layers, measure the absorbance of organic phase at a maximum wavelength against organic reagent as a blank. Remainder quantity of  $Pb^{2+}$  in aqueous phase was determined spectrophotometrically by dithizone method<sup>[11]</sup> and by return to calibration curve, at the last calculate distribution ratio (D) from metal ion quantity remain in aqueous phase and transferred quantity to organic phase.

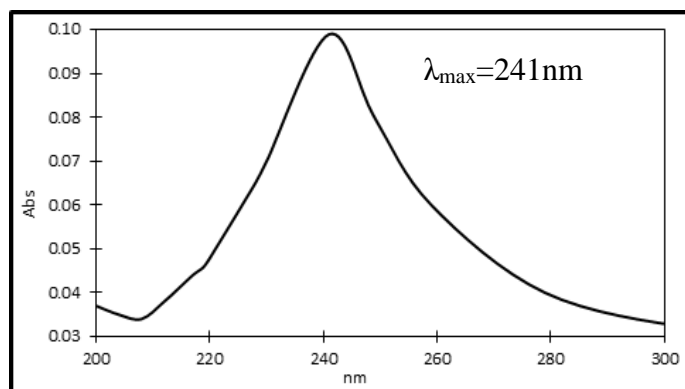
### Results and Discussion

#### Spectrophotometric studies:

Absorption spectra of crown ether 15C5 and its ion pair association complex with lead (II) as chloroanion complex  $PbCl_4^-$  or  $PbCl_3^-$  were recorded as in **Figures 1, 2**:



**Fig. 1:** Absorption Spectra of crown ether 15C5 in chloroform

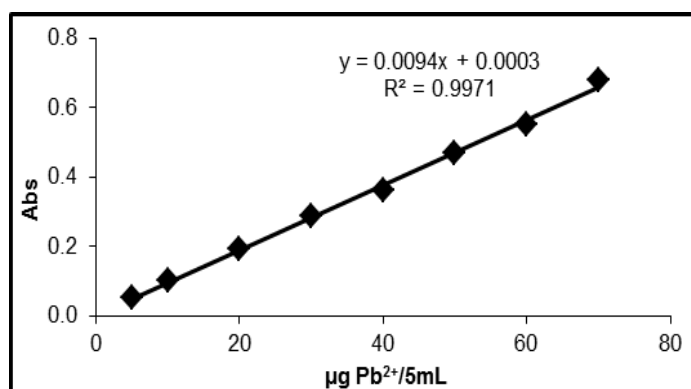


**Fig. (2):** Absorption Spectra of ion pair association complex

From the UV-Vis. Absorption spectrum in **Figures 1,2** show the wave length of maximum absorption for crown ether 15C5 was 213nm and for ion pair complex was 241nm with molar absorptivity  $\epsilon=2052.17\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ , these result appear deviation in the absorbance value in approximately 27nm which is giving attention about the ion pair complex formation.

### Effect of HCl Concentration

In the series of 5mL volumetric flasks, aliquots of aqueous solutions each one containing  $50\mu\text{g Pb}^{2+}$ , 0.4M of NaCl and different concentrations of HCl (0.1-2.5M) was mixed and dilute to the mark with distilled water this solutions shaking for 5min., after that transferred these solutions into 25mL volumetric flask then added 5mL of 15C5 solution at ( $1\times 10^{-4}\text{M}$ ) dissolved in chloroform to each solution and shaking the solutions to 10min. at  $25^{\circ}\text{C}$  in electrical shaker. Afterward separated aqueous phase from organic phase and determined absorbance of organic phase as well as D- values according to procedure detailed in general extraction method. The results were as in **Figures 4, 5**:



**Fig. 3:** Calibration curve of Lead (II) ion in aqueous solution by Dithizone method.

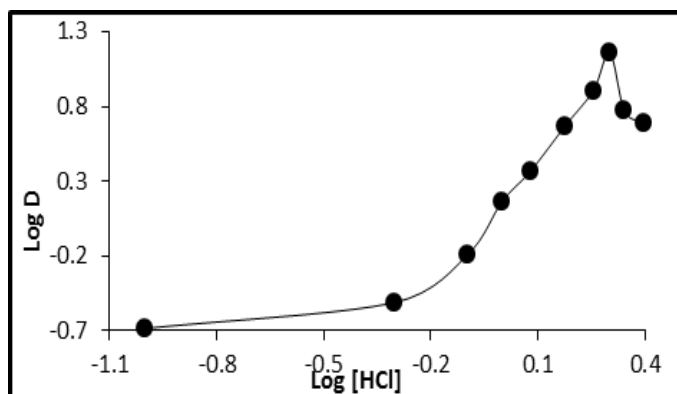


Fig. 4: D=F [HCl].

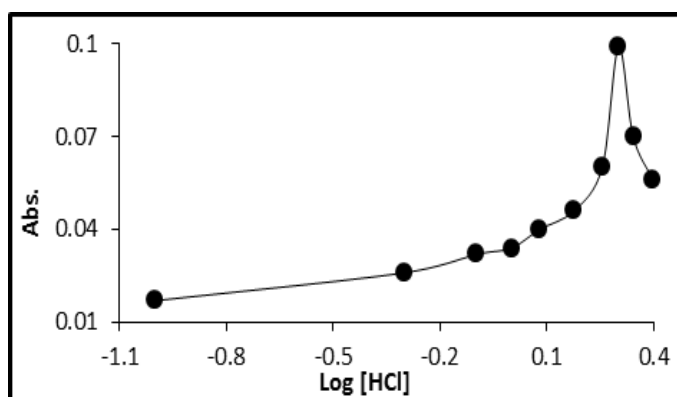
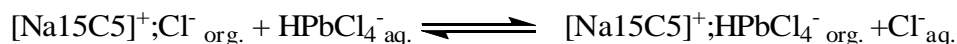
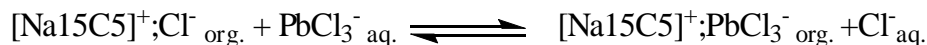
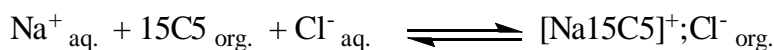
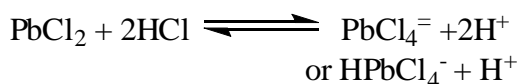


Fig. 5: Effect of HCl concentration on ion pair complex formation and extraction.

The results shows optimum concentration of HCl was 2M, this concentration is necessary for formation of stable chloroanion complexes  $PbCl_4^-$  or  $PbCl_3^-$  which is exchange with  $Cl^-$  ion in liquid anion exchanger  $[Na15C5]^+;Cl^-$  to produce ion pair association complex according to thermodynamic equilibrium below:

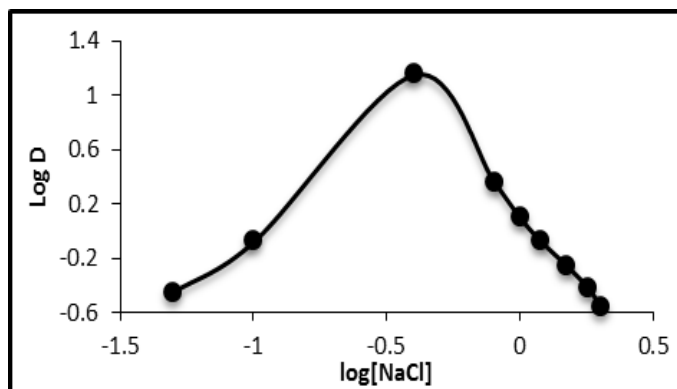


Any concentration of HCl less than optimum value not enough to reach thermodynamic equilibrium to produce anion complex  $PbCl_4^-$  or  $PbCl_3^-$  that is mean not enough to reach thermodynamic equilibrium of extraction then giving decline in absorbance of organic phase and distribution ratio (D) value. As well as any concentration of HCl more than optimum concentration effect to decrease extraction efficiency and decline absorbance and distribution

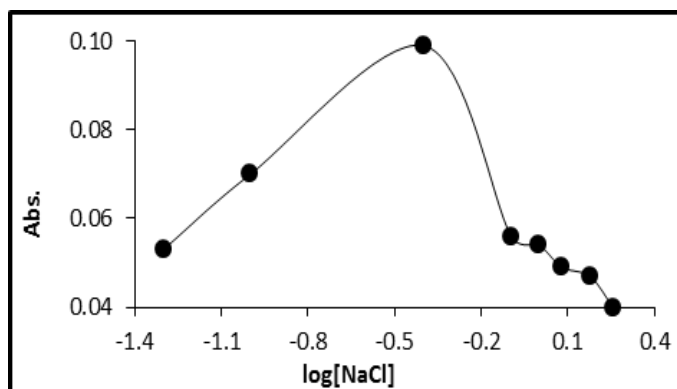
ratio (D) value by the reason of high concentration of  $\text{Cl}^-$  effect to increase stability to ion exchanger  $[\text{Na15C5}]^+$ ;  $\text{Cl}^-$  and decrease of liquid ion exchange between  $\text{Cl}^-$  and  $\text{PbCl}_4^-$  or  $\text{PbCl}_3^-$ , in addition to increase partition  $[\text{Na15C5}]^+$ ;  $\text{Cl}^-$  into aqueous phase and dissociated.

**Effect of NaCl Concentration**

5mL aqueous solutions containing  $50\mu\text{g Pb}^{2+}$ , 2M HCl and varying concentration of NaCl ranging from (0.05-2.00M), and shaking for 5min. after that 5mL of 15C5 solution dissolved in chloroform at ( $1 \times 10^{-4}\text{M}$ ) were added to each solution and shaking the two layer to 10min. at  $25^\circ\text{C}$  in electrical shaker. Afterward separated aqueous phase from organic phase and determined absorbance of organic phase as well as D-values according to procedure detailed in general extraction method. The results obtained were as in **Figures 6, 7**:



**Fig. 6:** D=F [NaCl].



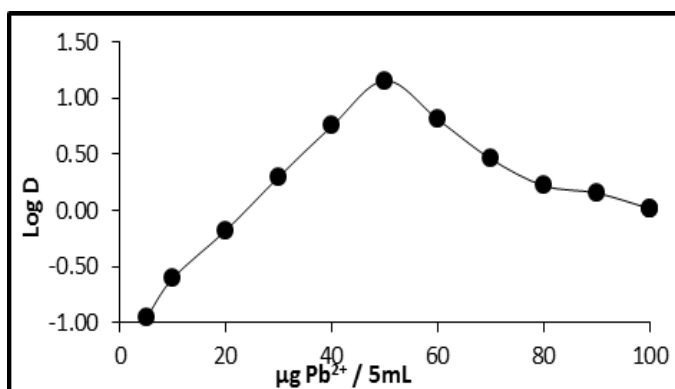
**Fig. 7:** Effect of NaCl concentration on ion pair complex formation and extraction.

The results show 0.4M NaCl giving higher extraction efficiency with higher absorbance and D-values that is mean 0.4M of NaCl help to reach best thermodynamic equilibrium for extraction by formation of high concentration ion exchanger and stability of high extraction of  $\text{Pb}^{2+}$  by ion exchange of  $\text{PbCl}_3^-$  or  $\text{PbCl}_4^-$  instead of  $\text{Cl}^-$ , any concentration of  $\text{Na}^+$  less than 0.4M not allow to reach thermodynamic equilibrium and giving low concentration of ion exchanger which is decrease extraction efficiency of lead. As well as any concentration more

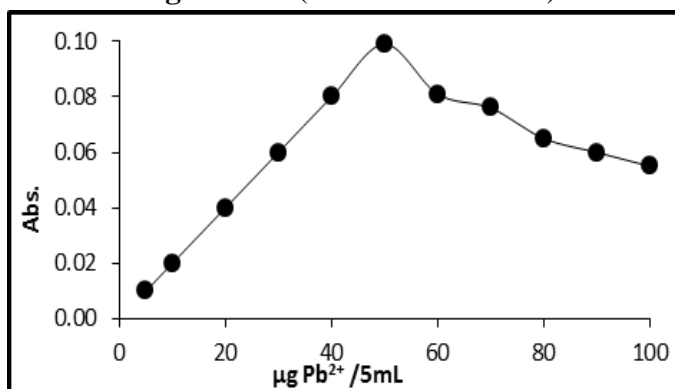
than 0.4M NaCl also effect to decline extraction efficiency, by electrophoretic effect in aqueous solution and restriction  $\text{PbCl}_3^-$  or  $\text{PbCl}_4^-$  in aqueous solution and prevent  $\text{PbCl}_3^-$  or  $\text{PbCl}_4^-$  to participate in liquid ion exchange to produce ion pair complex for lead (II).

### Effect of $\text{Pb}^{2+}$ Concentration

Different concentrations of lead (II) ranging from (5-100 $\mu\text{g}$  of  $\text{Pb}^{2+}$ ) extracted from 5mL aqueous solutions in presence 2M HCl, 0.4M NaCl. This solutions shaken for 5min., then added 5mL of ( $1 \times 10^{-4}$  M) 15C5 dissolved in chloroform and shaking it for 10min. at 25°C in electrical shaker. Afterward separated aqueous phase from organic phase and determined absorbance of organic phase as well as D-values according to procedure detailed in general extraction method. The results were as in **Figures 8, 9**:



**Fig. 8:**  $D = f(\text{Pb}^{2+}$  concentration)



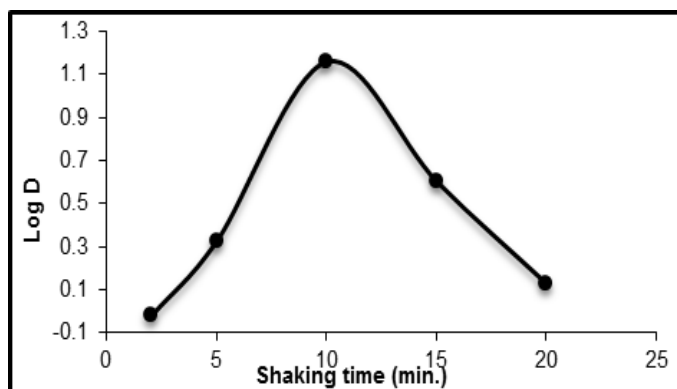
**Fig. 9:** Effect of  $\text{Pb}^{2+}$  concentration on ion pair complex formation and extraction.

The results clarify 50 $\mu\text{g Pb}^{2+}$  giving the best equilibrium relation to formation more stable chloroanion complex of lead  $\text{PbCl}_3^-$  or  $\text{PbCl}_4^-$  which share to produce more stable ion pair association complex and giving higher absorbance and D-values. Concentrations less than 50 $\mu\text{g}$  not enough to produce chloroanion complex of lead, then the concentration of  $\text{PbCl}_3^-$  or  $\text{PbCl}_4^-$  produce not allow to reached favorable thermodynamic equilibrium to formation ion pair complex then giving low absorbance and D-values. While  $\text{Pb}^{2+}$  concentration more than

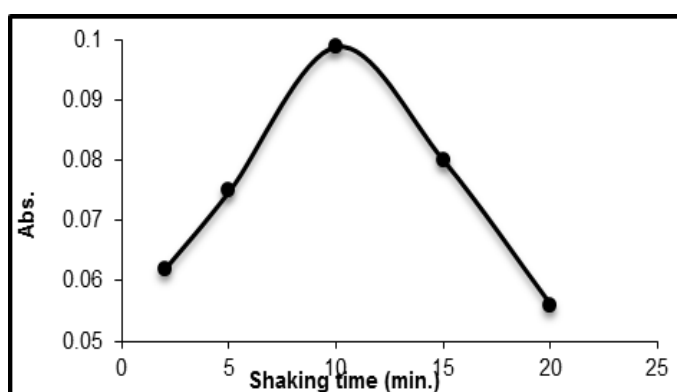
50 $\mu$ g effect to decrease absorbance and the D-values, because the high concentration of Pb<sup>2+</sup> at constant other parameters effect to increase the rate of backward direction of thermodynamic equilibrium for formation PbCl<sub>3</sub><sup>-</sup> or PbCl<sub>4</sub><sup>=</sup> whereas this behavior effect to decline extraction efficiency, according to mass action law and Le chatelier principle.

**Effect of Shaking Time**

5mL aqueous solutions and keeping optimum conditions constant (concentrations of Pb<sup>2+</sup>, HCl and NaCl) shaking for 5min. then added 5mL of (1 $\times$ 10<sup>-4</sup> M) 15C5 dissolved in chloroform and shaking the two layers at different shaking time ranging from (2-20min.) at 25 $^{\circ}$ C in electrical shaker. Afterward separated aqueous phase from organic phase and determined absorbance of organic phase as well as D-values according to procedure detailed in general extraction method. The results demonstrate as in **Figures 10, 11**:



**Fig. 10:** D=F (Shaking time).

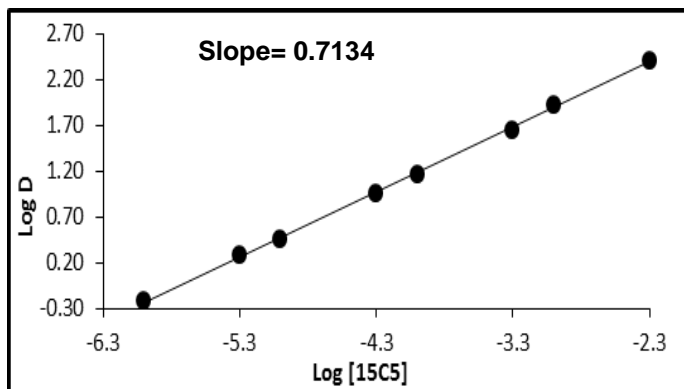


**Fig. 11:** Effect of shaking time on complex formation and absorbance value.

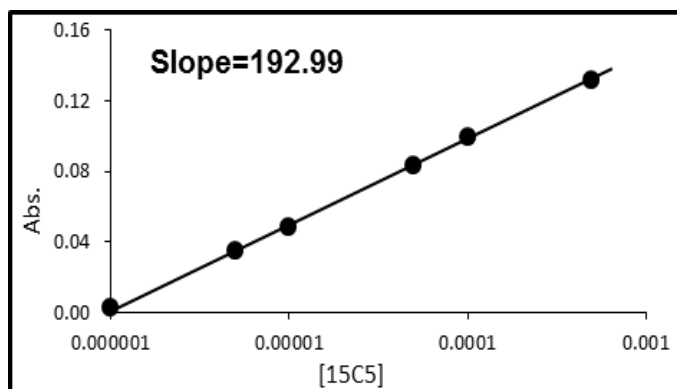
The results show optimum shaking time which allows reaching the equilibrium of higher extraction efficiency was 10min., shaking time less than 10min. not allow reaching equilibrium and decrease absorbance and D-values, but shaking for time longer than 10min. effect to dominate the dissociation equilibria and also decrease absorbance and D-values.

**Stoichiometry:**

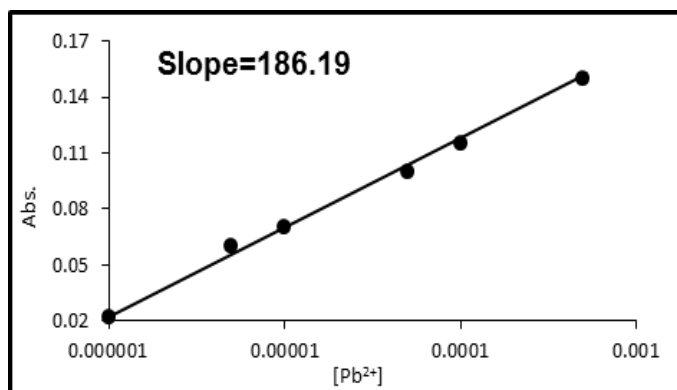
To know probable structure of extracted complex used two method: Slope analysis and slope ratio. The results as in **Figures 12-14**



**Fig. 12:** Slope analysis method



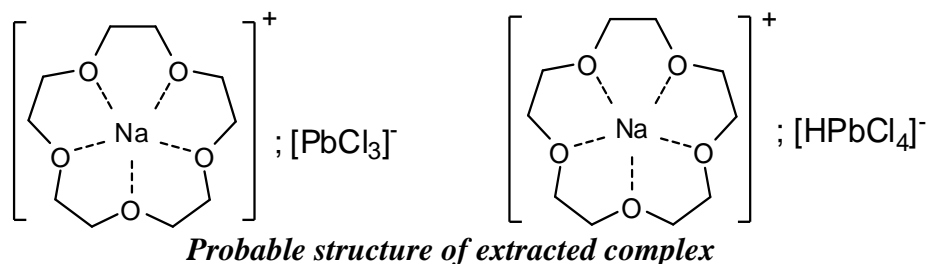
**Fig. 13:** Slope ratio method Change 15C5 concentration



**Fig. 14:** Slope ratio method Change lead (II) concentration

$$\text{Slope ratio} = \frac{\text{Slope}_{15C5}}{\text{Slope}_{Pb(II)}} = \frac{192.99}{186.19} = 1.03$$

The two methods show the more probable structure of extracted complex was 1:1:1 [Na15C5]<sup>+</sup>, PbCl<sub>3</sub><sup>-</sup>, [Na15C5]<sup>+</sup>, HPbCl<sub>4</sub><sup>-</sup>.



### Effect of Organic Solvent:

5mL aqueous solutions at optimum conditions (concentrations of  $Pb^{2+}$ , HCl and NaCl) shaking for 5min. then added 5mL of ( $1 \times 10^{-4}$  M) 15C5 dissolved in different organic solvents differ in dielectric constant and shaking the solutions for 10min. at  $25^\circ C$  in electrical shaker. Afterward separated aqueous phase from organic phase and determined D-values according to procedure detailed in general extraction method. Afterward all the factors reflect the effect of organic solvents on extraction efficiency, were calculated as:

$$\Delta G_t = \frac{Z^2}{2r} \left( \frac{1}{\epsilon_w} - \frac{1}{\epsilon_o} \right) \quad \dots \dots \dots (1)$$

$$K_A = \frac{[Na15C5]^+; PbCl_3^-]_{org.}}{[PbCl_3^-]_{org.} [15C5]_{org.}} \quad \dots \dots \dots (2)$$

$$K_{ex} = \frac{K_A \cdot D \cdot [Na15C5]^+; PbCl_3^-]_{org.}}{[PbCl_3^-]_{aq.} [15C5]_{org.}} \quad \dots \dots \dots (3)$$

$$\Delta G_{ex} = -RT \ln K_{ex} \quad \dots \dots \dots (4)$$

The results were as in **Table 1**.

**Table 1: Organic solvent effect on Liquid ion exchange of Pb (II)**

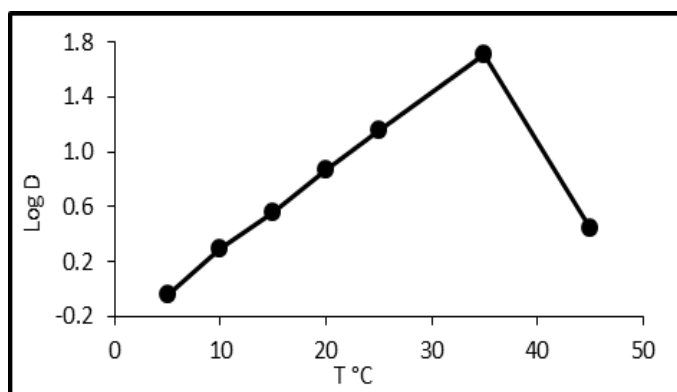
| <i>Organic Solvents</i>               | $\epsilon$ | <i>D</i> | <i>%E</i> | $-\Delta G_t$ | $K_A^* 10^4$ | $K_{ex}^* 10^8$ | $-\Delta G_{ex}$ |
|---------------------------------------|------------|----------|-----------|---------------|--------------|-----------------|------------------|
| <i>Nitro benzene</i>                  | 35.74      | 1.67     | 62.58     | 0.026         | 5.54         | 5.80            | 45.61            |
| <i>Amyl alcohol</i>                   | 15.80      | 1.48     | 59.64     | 0.084         | 5.14         | 4.53            | 45.05            |
| <i>50% Nitrobenzene +50% Toluene</i>  | 15.6       | 0.14     | 12.00     | 0.0853        | 2.36         | 0.0386          | 34.28            |
| <i>1,2-Dichloro ethane</i>            | 10.65      | 0.98     | 49.60     | 0.1345        | 4.11         | 2.01            | 43.21            |
| <i>30% Nitrobenzene + 70% Toluene</i> | 10.65      | 0.11     | 10        | 0.1345        | 2.03         | 0.0256          | 33.35            |
| <i>Dichloro methane</i>               | 9.08       | 4.34     | 81.28     | 0.1614        | 11.08        | 39.15           | 49.92            |
| <i>Chlorobenzene</i>                  | 5.708      | 1.52     | 60.28     | 0.2689        | 5.22         | 4.78            | 45.17            |
| <i>Bromo benzene</i>                  | 5.40       | 3.55     | 78.00     | 0.2854        | 9.42         | 26.08           | 49.00            |
| <i>Chloroform</i>                     | 4.806      | 14.45    | 93.52     | 0.3233        | 32.02        | 432.98          | 55.35            |
| <i>5% Nitrobenzene +95% Toluene</i>   | 3.40       | 1.60     | 61.6      | 0.4655        | 5.40         | 5.34            | 45.42            |
| <i>Benzene</i>                        | 2.804      | 0.90     | 47.40     | 0.5689        | 3.94         | 1.68            | 42.81            |

|                              |       |      |       |        |      |       |       |
|------------------------------|-------|------|-------|--------|------|-------|-------|
| <i>Toluene</i>               | 2.438 | 1.65 | 62.20 | 0.6574 | 5.48 | 5.62  | 45.53 |
| <i>Carbone tetrachloride</i> | 2.38  | 0.15 | 13.32 | 0.6739 | 2.39 | 0.049 | 34.82 |

The results indicate there is not any linear relation between D-values and dielectric constant values of organic solvents used, but there is an effect of organic solvents structure on extraction efficiency. The values of free energy for ionic transfer ( $-\Delta G_t$ ) from aqueous phase to organic phase increase with dielectric constant decrease for organic solvent used. As well as extraction constant  $K_{ex}$  and free energy for extraction  $\Delta G_{ex}$  values don't show any linear relation with increasing or decreasing dielectric constant values of organic solvents. So these results clear the role of these organic solvents is effect on extraction efficiency by participation of organic solvents in the formation and stability of ion pair association complex extracted to organic phase.

**Effect of Temperature**

Aqueous solutions at 5mL in volume at optimum conditions (concentrations of  $Pb^{2+}$ , HCl and NaCl) shaking for 5min. then added 5mL of ( $1 \times 10^{-4}$  M) 15C5 dissolved in chloroform and shaking for 10min. At varying temperature (5-45°C) in electrostatic water bath shaker. Afterward separated aqueous phase from organic phase and determined absorbance of organic phase as well as D-values according to procedure detailed in general extraction method. The results demonstrate as in **Figures 15, 16**:



**Fig. 15:** D=F (Temperature °C)

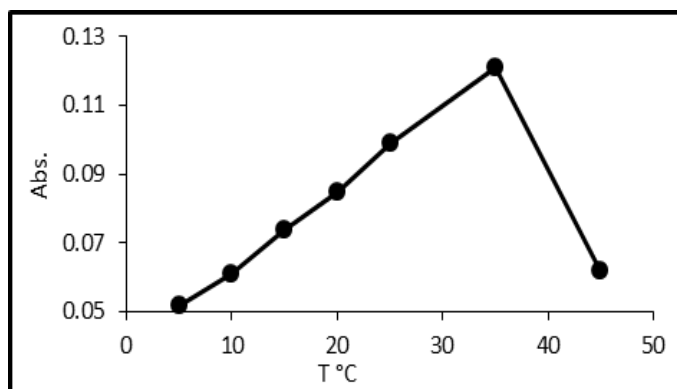


Fig. 16: Effect of Temperature on absorbance value.

The results in **Figures 15, 16** show the optimum temperature for extraction was 35°C, this energy absorbed from the Pb(II) ions and another species in extraction method help to destroy hydration shell of metal ion and increase binding to formation ion association complex until reach optimum 35°C then reach to the maximum energy for binding and extraction ion pair complexes, any temperature more than optimum value effect to giving higher energy for needing which is effect to dissociation of ion pair complex and partitioning into aqueous phase. From D-values calculated extraction constant by relation below:

$$K_{ex} = \frac{D}{[PbCl_3^-]_{aq.} [15C5]_{org.}} \dots \dots \dots (5)$$

The results show anion exchange reaction was exothermic. The graph of log K<sub>ex</sub> versus 1/T in Kelvin was shown in **Figure 17**.

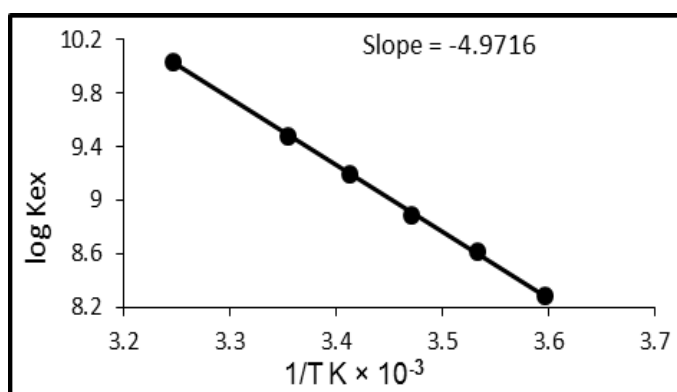


Fig. 17: Extraction constant K<sub>ex</sub> as a function of temperature.

From the slope value of **Figure 17** calculate enthalpy of extraction ΔH<sub>ex</sub> according to **Van't Hoff equation** <sup>[12]</sup>:-

$$Slope = \frac{-\Delta H_{ex}}{2.303R} \dots \dots \dots (6)$$

From optimum value of extraction constant K<sub>ex</sub> ΔG<sub>ex</sub> was calculated from the relation:-

$$\Delta G_{ex} = -RT \ln K_{ex} \quad \dots \dots \dots (7)$$

And the entropy of extraction  $\Delta S_{ex}$  was calculated from *Gibbs equation*:-

$$\Delta G_{ex} = \Delta H_{ex} - T \Delta S_{ex} \quad \dots \dots \dots (8)$$

The results obtained are shown in **Table 2**:-

**Table 2:** Thermodynamic data.

| $\Delta H_{ex}$            | $\Delta G_{ex}$            | $\Delta S_{ex}$                          |
|----------------------------|----------------------------|--|
| <i>KJ.mol<sup>-1</sup></i> | <i>KJ.mol<sup>-1</sup></i> | <i>J.mol<sup>-1</sup>.K<sup>-1</sup></i> |
| 0.095                      | -59.126                    | 192.270                                  |

It can be seen from **Table 2** the change in enthalpy  $\Delta H_{ex}$  was positive which indicating that reaction was exothermic. While  $\Delta G_{ex}$  value was found to be negative indicating the direct reaction (complex formation) was favorable and the extraction process is a spontaneous reaction. Whilst the high positive value of  $\Delta S_{ex}$  prove the high stability of ion pair association complex, as well as the extraction method was entropic in region.

### Effect of Interferences:

5mL aqueous solutions at optimum conditions (concentrations of  $Pb^{2+}$ , HCl and NaCl, at presence 0.1M of different anions, shaking for 5min. then added 5mL of ( $1 \times 10^{-4}$  M) 15C5 dissolved in chloroform and shaking for 10min. at 25°C in electrostatic shaker. Afterward separated aqueous phase from organic phase and determined D-values according to procedure detailed in general extraction method. The results obtained were as in **Table 3**.

**Table 3:** Interferences effect of some anions on extractability of Pb (II)

| <i>Anions</i>                                 | <i>Abs. at <math>\lambda_{max}=241nm</math></i> | <i>D</i> | <i>%E</i> |
|---|---|----------|-----------|
| NaI   | 0.067   | 0.559    | 35.840    |
| K <sub>2</sub> HPO <sub>4</sub>               | 0.063   | 0.511    | 33.840    |
| KSCN  | 0.059   | 0.467    | 31.840    |
| KClO <sub>3</sub>                             | 0.055   | 0.425    | 29.840    |
| KHPO <sub>4</sub>                             | 0.026   | 0.386    | 27.840    |
| K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> | 0.093   | 2.081    | 67.540    |
| NaNO <sub>3</sub>                             | 0.018   | 0.011    | 1.1000    |
| Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub> | 0.039   | 0.393    | 28.220    |
| NaCN  | 0.060   | 0.423    | 29.740    |
| NH <sub>4</sub> Cl                            | 0.095   | 2.333    | 70.000    |

The results demonstrate all anions giving interferences in extraction but it's having different ability due to structure and nature of anion in addition to its behavior in aqueous solution depending on its charge density and hydration shell, for all that differences appear different interference and this results demonstrate there is no selectivity for  $Pb^{2+}$  as anion  $PbCl_3^-$  or  $PbCl_4^-$  but all these anions able to formation of ion pair complex with  $[Na15C5]^+$  as  $[Na15C5]^+$ ; anion. This led to decreasing the absorbance and D-values and the efficiency of extraction of  $Pb^{2+}$ .

### Effect of Electrolyte salts:

5mL volumetric flask, aliquots of solutions at optimum conditions constant (concentrations of  $Pb^{2+}$ , HCl and NaCl in presence of 0.1M of different electrolyte salts, shaking for 5min. then added 5mL of ( $1 \times 10^{-4}$  M) 15C5 dissolved in chloroform and shaking for 10min. at  $25^\circ C$  in electrostatic shaker. Afterward separated aqueous phase from organic phase and determined D-values according to procedure detailed in general extraction method. The results obtained were as in **Table 4**.

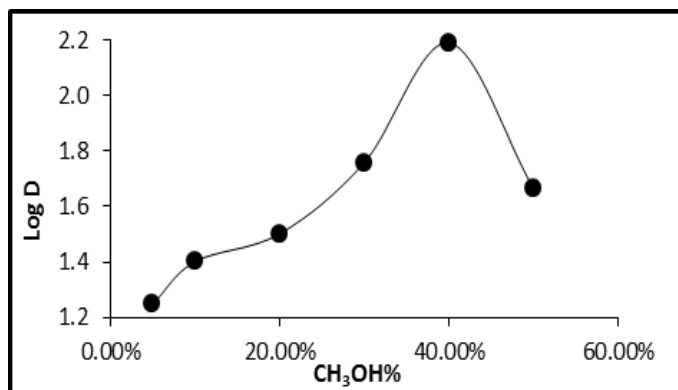
**Table 4:** Effect of some electrolyte salts on extractability of Pb(II)

| <i>Electrolyte salt</i> | <i>Abs. at <math>\lambda_{max}=241nm</math></i> | <i>D</i> | <i>%E</i> |
|-------------------------|---|----------|-----------|
| $Cu(NO_3)_2$            | 0.165   | 55.00    | 98.217    |
| $Cr(NO_3)_3$            | 0.186   | 82.00    | 98.804    |
| $Co(NO_3)_2$            | 0.170   | 66.00    | 98.377    |
| $Cd(NO_3)_2$            | 0.144   | 42.00    | 97.690    |
| $Ni(NO_3)_2$            | 0.178   | 65.00    | 98.489    |

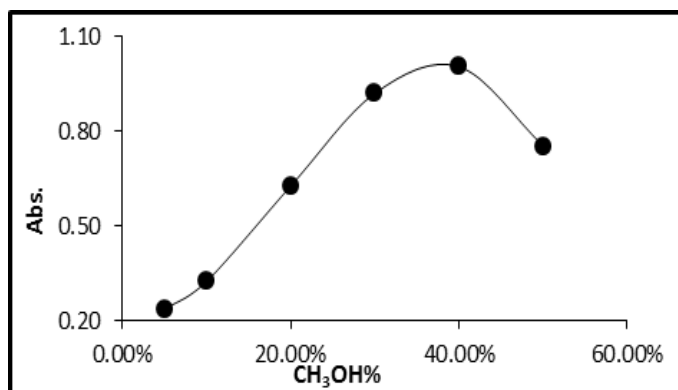
The results demonstrate absorbance values were higher than the values obtained in the absence of electrolyte salts that is mean these salts play important and efficient role in enhancing the extraction and separation. By reason of presence the electrolyte salt effect to destroy the hydration shell of metal ion  $Pb^{2+}$  by withdrawing the water molecules and increase concentration of sex ion and increase chances of binding to increase formation  $PbCl_3^-$  or  $PbCl_4^-$  as well as increase ion exchange to form ion association complex in addition to increase partitioning to organic phase but this effect different with differ in nature of metal cation in aqueous solution as well as behavior in aqueous phase by different formation of hydration shell in aqueous solution with different in thickness and stability.

## Effect of Methanol

Aqueous solution 5mL in volume contain optimum values of (concentrations  $Pb^{2+}$ , HCl and NaCl, different percentages of methanol, shaking for 5min. then added 5mL of 15C5 and shaking for 10min. at 25°C in electrostatic shaker. Afterward separated aqueous phase from organic phase and determined D-values according to procedure detailed in general extraction method. The results demonstrate as in **Figures 18, 19**:



**Fig. 18:** Effect of methanol percentage on extraction efficiency.

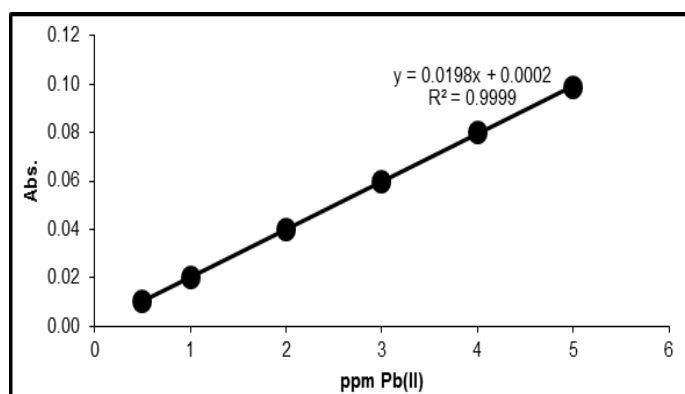


**Fig. 19:** Effect of Methanol% on absorbance value.

The result shows absorbance and D-values increasing with methanol percentage increase in aqueous solution to optimum percentage value was 40%. Where the presence of methanol effect to decline polarity of aqueous solution and increase destroy hydration shell of  $Pb^{2+}$  that is mean increase produced of chloroanion complex  $PbCl_3^-$  or  $PbCl_4^{2-}$  as well as increase partitioning to organic phase as ion pair complex, as well as maximum effect at 40% of methanol, but percentage more than optimum effect to decrease extraction efficiency of  $Pb^{2+}$  by effect of more decline polarity of aqueous phase and partitioning part of 15C5 to the aqueous phase and minimize the concentration of ion pair complex extracted to organic phase.

### Spectrophotometric determination of Pb<sup>2+</sup>

Liquid ion exchange as sensitive and selective method used for spectrophotometric determination of Pb<sup>2+</sup> in different samples such as soil, water, vegetable, fruit etc. The samples digestion it has been using wet digestion method [13]. Prepared calibration curve at  $\lambda_{\max}=240\text{nm}$  to the determination lead (II) in different samples as in **Figure 20**. Afterward prepared sample solution according to liquid ion exchange method and after separation the two layers measured the absorbance of organic phase at  $\lambda_{\max}=240\text{nm}$  against 15C5 solution as blank. %RSD=0.00672, D.L=  $5.04483 \times 10^{-5}$  ppm,  $\epsilon = 2057.85 \text{ L.mol}^{-1}.\text{cm}^{-1}$ , Sandell's sensitivity=  $4.86 \times 10^{-7} \mu\text{g}/\text{cm}^2$ .



**Fig. 20:** Calibration curve for spectrophotometric determination of Pb<sup>2+</sup> in different samples.

**Table 5:** Accumulated quantity of lead (II) in different samples.

| Samples                               | ppm Pb <sup>2+</sup> |
|---------------------------------------|----------------------|
| <i>Strawberry(imported)</i>           | 0.0620               |
| <i>Pomegranate (imported)</i>         | 0.0419               |
| <i>Orang (imported)</i>               | 0.0734               |
| <i>Banana (imported)</i>              | 0.0818               |
| <i>Garden cress</i>                   | 0.105                |
| <i>Spinach</i>                        | 0.243                |
| <i>Radish</i>                         | 0.317                |
| <i>Leek</i>                           | 0.200                |
| <i>Dates</i>                          | 0.723                |
| <i>Onion</i>                          | 0.245                |
| <i>Fish farms</i>                     | 0.0740               |
| <i>White meat of chicken (breast)</i> | 0.156                |
| <i>Cow meat (Beef)</i>                | 0.178                |
| <i>Water of Euphrates river</i>       | 0.032                |
| <i>Tap water</i>                      | 0.007                |

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