Study of Liquid – Liquid Extraction of lanthanum(III)ion by derivative of amino acid N-Acetylcysteine .

دراسة في استخلاص سائل – سائل لأيون اللانثانوم الثلاثي بأستخدام مشتق الحامض الأميني N - اسيتايل- سستائين

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Abstract

The study of liquid - liquid extraction of lanthanum (III) with derivative of amino acid N-Acetyl-cysteine that refers by (NAC) had been made. The effect of different parameters on the percent of extraction and distribution ratio such as type of medium ; time of equilibration , type of solvent , effect of some cations and anions, effect of redox agents , enrichment extraction , concentration of metal ; reagent, effect of batch extraction, salting out , and effect of temperature . The function of thermodynamic parameter of (ΔH , ΔG , ΔS) were calculated .The stoichiometry of the extraction was determined using two methods Mole ratio and Job' s methods. It was found to be (M: L) (1:3). The stability constant of complex in mole ratio method was calculated. The study of UV-visible and FT-IR spectra were studied for both the reagent and complex in organic phase. Other physical constant namely such as temperture,melting point and specific conductivity..

الخلاصة:-

أجريت دراسة استخلاص سائل – سائل لأيون اللانثانوم الثلاثي بواسطة مشتق الحامض الأميني   N -اسيتايل- سستائين (NAC)   المذاب في الايثانول , حيث تم دراسة تأثير مجموعة من العوامل التي تؤثر على قيمة نسبة التوزيع والنسبة المئوية للاستخلاص متمثلة, بوسط الاستخلاص , زمن الاتزان , نوع المذيب العضوي , تأثير المتداخلات(ايونات موجبة – ايونات سالبه), تأثير عوامل الأكسدة والاختزال, طريقة الاغناء, تركيز العنصر والكاشف , عملية التمليح , تقنية الدفعات , درجة الحرارة. حساب الدوال الثرموديناميكية الخاصة بالنظام (ΔS , ΔG , ΔH)   كما تم دراسة تكافؤية المعقد المستخلص في الطور العضوي بطريقتين هما النسب الموليــة وطريقة جوب وقد أثبتت الطريقتين إن نسبــة الليكاند إلـى الفـــلز   (M: L)   هي نسبة (1:3) وبالاستعانة بطريقة النسب المولية تم حساب ثابت استقرارية المعقد المستخلص وتمت دراسة طيف الأشعة المرئية – فوق البنفسجية وطيف الأشعة تحت الحمراء لكل من الكاشف والمعقد المستخلص كما تم دراسة بعض الصفات الفيزيائية للمعقد مثل درجة الانصهار والتوصيلية النوعية للمعقد .

Introduction:-

Solvent extraction is a mature technique in that extensive experience has led to a good understanding of the fundamental chemical reactions. At the same time, compared to many other chemical separation processes like precipitation, distillation, or pyrometallurgical treatment, the large-scale application of solvent extraction. New reagents are continually being developed the efficiency and high selectivity of solvent extraction should make it an increasingly competitive separation process both in research and in industry[1].

N-Acetyl-Cysteine (NAC) (Acetylcysteinum) was a derivative of Cysteine , aceylated form of amino acid cysteine. It is one of the compound which on one side has a free Thiol group(SH), and on the other side its α -amino group is been protected with acetyl group. In fact acetyl group forms the simplest peptide bond in proteins. Many binary and ternary complexes of some metal ions with NAC and amino acid were prepared [2].
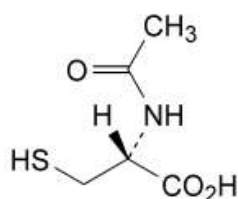
Mosander extracted lanthanum oxide as an impurity from cerium nitrate (hence the name from Greek), Lanthanum is the most strongly basic of all the trivalent lanthanides. It is found in some rare-earth minerals, usually in combination with cerium and other rare earth elements [3]. Lanthanum is a chemical element with the symbol La and atomic number 57. Lanthanum is a soft, malleable, ductile, silvery white metallic element It belongs to group 3 of the periodic table and is the first element of the lanthanide series. Lanthanum has hexagonal crystal structure at room temperature. At 310 °C, lanthanum changes to a face-centered cubic structure [4] .Slightly above room temperature the fcc structure becomes stable (Praseodymium and neodymium have the same structures, the main difference being that the temperature range in which the fcc structure is stable is smaller). mand at 865 °C into a body-centered cubic structure [5].

Many studies to extracted lanthanum were obtained. In , 2006 [6] reported equilibrium and kinetic studies on solvent extraction of single and binary La(III) and Nd(III) from nitrate solutions with (2- ethylhexylphosphonic acid mono-2-ethylhexyl ester) in kerosene at 298 K were studied. In [7], 2006 , investigated the synergistic solvent extraction of the lanthanoid(III) ions(La, Ce, Pr, Nd, Sm, Eu and Gd) with a ternary mixture of (4-benzoyl-3-mcthyl-lphenyl-2-pyrarolin-S-onc)and(2-thenoyltrifluoroacetone, Hexafluoroacetylacetone), and the quaternary ammonium salt Methyltrialkyl(C8,-C10) ammonium chloride (Aliquat 336,QCI) in C_6H_5 has bee investigated.In $2006^{[8]}$ studied the solvent extraction of trivalent lanthanoids (La, Nd, Eu, Ho, and Lu) with mixtures of the chelating extractant (2-thenoyltritluoro-acetone. HTTA) or (HP) and (4-(2-pyridylazo)-resorcin) in $CHCI_3$. In 2009, [9] reported the extraction of lanthanides(III)(La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y)from aqueous nitrate solutions with several phosphoryl-containing podands in 1,2-dichloroethane has been studied. In 2009 [10] study the extraction of rare earths(La^{+3}, Nd^{+3}) with mixtures of (HPMBP,HA) 1- phenyl-3-methyl-4-benzoyl pyrazalone-5 and $(CA12, H_2B_2)$ sec-octylphenoxyacetic acid in benzene from chloride medium. The synergistic enhancement coefficient decreases with increasing atomic numbers of rare earths . the synergistic extraction of La^{+3} is endothermically driven. The extracted complexes are determined as $LaH_2ClA_2B_2$ and $NdH_3ClA_3B_2$. In later studies, [11]showed that the extraction of rare earth metals(La, Nd, Sm Eu,Gd ,Dy,Ho, Er,Yb) from chloride and nitrate solutions by various binary extractants based on dialkylphosphinic, dialkylmonothiophosphinic and dialkyldithiosphinic acids has been examined under different conditions. In 2010 , [12] study the Extraction of mixture of heavy rare earths (Tb, Dy, Y, Ho, Er, Yb ,Lu) and mixture of (La , Ce, Pr and Nd) from phorphoric acid solutions(3-5)M extractant used are, Talcher organic phosphorus solvent(Di-2- ethylhexyl phosphoric acid), (2- ethylhexylphosphonic acid mono-2-ethylhexyl ester) and (Bis(2,4,4-trimethylpentyl)phosphinic acid) . In this study lanthanum (III) was extracted by using derivative of amino acid (NAC) and study the best conditions for this extraction to find fast and efficient method to extracted and determination of La(III) ion.

Experimental

Chemical
All chemicals and solvent were obtained from commercial and used as received

Preparation of standard solutions.

1- Standard solution of lanthanum (III)(1mg/mL)prepared by dissolving (0.2663 gm) of $LaCl_3.H_2O$ in double distilled water and the volume was completed to 100 mLwith double distilled water in a volumetric flask. Dilute Nd (III) solutions are prepared by diluting this standard solution with the necessary volume of water.

2- Reagent (NAC) solution (0.2% w/v) prepared by dissolving (0.2gm) of (NAC) in ethanol and the volume was completed to (100 mL) with ethanol in a volumetric flask.

3- Ascorbic acid solution (1% w/v) prepared by dissolving (1gm) of ($C_6H_8O_6$) in double distilled water and the volume was completed to (100 mL) with double distilled water in a volumetric flask..

4-Arsenazo (III) solution (0.05% w v) prepared by dissolving (0.05gm) of arsenazo (III)in double distilled water and the volume was completed to (100 ml) with double distilled water in a volumetric flask.

5- Format buffer solution (pH=3.5) prepared by Dissolving (28 gm) of NaOH and (60 mL) of formic acid in water, and dilute the solution with water to 1 liter.

6-Sodium hydroxide solution (1M) prepared series of NaOH solution from (0.1 to 0.8 M) by dissolving suitable weight of NaOH in doubled distilled water.

7- Cations solution of [Cd(II) , Hg(II) , Ni(II) , Mn(II) , Co(II) ,Fe(III) , Cr(III)] chloride salt prepared by dissolving salts of them depending on the molecular weight of salt used for these elements in (25mL) of distilled water.

8- Anions solution of ($Cr_2O_7^{=}$, Br^-, MnO_4^-, $SO_4^{=}$, PO_4^{-3}, $ClO_3^{=}$, NO_3^- $CO_3^{=}$) potassium salt prepared by dissolving salts of them depending on the molecular weight of salt used for these elements in (25mL) of distilled water.

9-Tin chloride solution (0.1M) prepared by dissolving (0.5640gm) of $SnCl_2.2H_2O$ in (1mL) of hydrochloric acid and the volume was completed to (25 mL) with double distilled water in a volumetric flask.

10-Ammonium chloride solution (1M) prepared by dissolving (1.3375 gm) of NH_4Cl in double distilled water and the volume was completed to (25 mL) with double distilled water in a volumetric flask.

Instruments

1- Single Beam UV-Visible Spectrophotometer Sp-300 (Japan).
2- pH-Meter-WTW-720-ionlab (Germany).
3- Electrical Shaker. (Scientific technical Supplies W-Germany) .
4- Melting point apparatus, England.
5- Digital conductivity meter-WT-270-ioolab (Germany).
6 - Temperature Control Circulator Laboratory Supply Company.
7- FT-IR 8400, Shamadzu, (Japan).
8- UV-visible Spectrophotometer -1800, Shamadzu, (Japan).
   Equipped with quartz cells (1cm).

Procedures

Calibration curve was prepared for La(III). depending on the color method for solution of arsenazo(III)[13]. To measure the absorption of the concentrations of standard solutions of La(III) as follows: -

1- Construction of calibration curve of La(III)

(5mL) of solutions containing different concentrations of La(III) ranged from (6.9328×10^{-6}M – 1.0399×10^{-4}M) equivalent to(5 μg- 75 μg.) Nd(III) were taken. To each solution (1mL) of (1%) ascorbic acid solution were added. After a few minutes (1mL) of the formate buffer (pH= 3.5) and (2mL) of arsenazo(III) solution (0.05%) were added. Diluted with double distilled water to (~ 20ml). The colored solution adjusted to pH (2-2.6) with (0.3 M) hydrochloric acid or sodium hydroxide. Transfer the solution to a volumetric flask (25mL), made up to the mark with double distilled water. The absorbance measured at (λ_{max} = 650nm) against a reagent blank solution using cell absorption radiance (1cm). The relationship between the absorption and concentration prepared for the calibration curve was drawn.

$$y = 0.0119x$$
$$R^2 = 0.9999$$
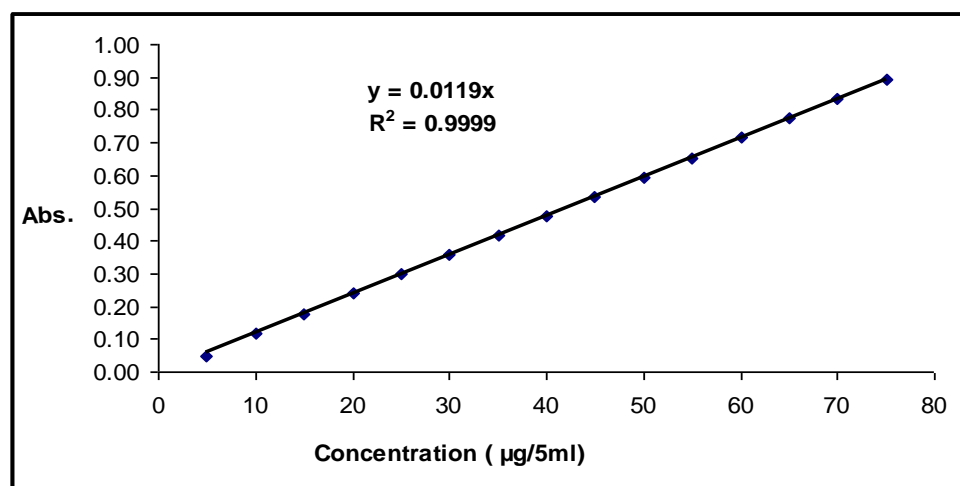
Fig. (1) Calibration curve for lanthanum (III).

2-Extraction of La (III) ion by using reagent (NAC)

A solution containing (2.5ml) (1.4398×10^{-3}M) (500 μg)of La(III) and (2.5ml) (0.2%) of ligand (NAC) in ethanol is poured into a separatory funnel as aqueous phase. The PH of the solution is adjusted with diluted HC1 and NaOH solutions. The aqueous phase is equilibrated with (5mL) of chloroform for (60) minutes. The aqueous and the organic phase were allowed to separate. La(III) ion determined spectrophotometrically after extraction in aqueous phase with arsenazo (III)[13] .An aliquot of the aqueous phase in the cells for absorbance measurements at (λ_{max} = 650 nm) .

Results and discussion

To reach to the best conditions of extraction, the effects of the following factors in the value of distribution ratio (D) were studied, represented by : -

1-Effect of pH

In order to settle the solvent extraction system for the extraction of La(III) the effect of pH on the extraction was studied for the pH range from (1-10)with (NAC) solution dissolved in ethanol with chloroform as organic phase .The result in table (1).

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Table: (1) The influence of pH in the extraction of La(III)
by using(NAC).

pH	D	E%
1.08	11.768	92.168
2.03	12.311	92.487
3.08	12.934	92.824
4.34	13.521	93.114
5.29	15.437	93.916
6.02	10.226	91.092
7.41	10.081	90.976
8.41	10.080	90.975
9.27	9.897	90.823
10.35	9.625	90.588

Aqueous phase: - (2.5 mL) solution of La (III) ion concentration (500µg),
$(1.439 \times 10^{-3}$ M) with (2.5 mL) (0.2% NAC) solution dissolved in ethanol
in different pH.Organic phase: - (5mL) Chloroform. Equilibrium time: - Sixty minutes.
Temperature: - (25 ± 2) C°.

From the results in the table (1) the distribution ratios and (E%) increases with increasing pH up
to 5 and than decreases .Thus could be due to the nature of the properties of organic reagents used
in solvent extraction process and its impact on pH . Derivatives of amino acids behaves as di
dentate ligand in acidic and basic media , therefore La(III) had high (E%) in acid media. This
results are in agreement with the previously studies [14] .

2-Effect of shaking time

For the kinetic side of extraction method studied effect of shaking time on the extraction activity
and distribution ratios values, the results of this study in table (2) demonstrate the optimum shaking
time of two layers was (60 min) to reach the equilibria of extraction and at this time obtain the
maximum distribution ratio value, down optimum shaking don't reached the equilibria of extraction,
and over optimum shaking time favorite the dissociation equilibria and minimize the distribution
ratio. This results in agreement with the previously studied [15][16].

Table (2): The effect of time of equilibrium in the extraction of
La(III) by using (NAC) .

Time	D	E%
5	5.474	84.555
10	5.531	84.689
15	7.008	87.512
20	7.041	87.563
30	7.095	87.647
40	12.193	92.421
50	12.554	92.622
60	15.437	93.916
70	14.025	93.345
80	12.678	92.688

Aqueous phase: - (2.5 mL) solution of La (III) ion concentration (500μg) (1.4398x10^{-3} M)
with (2.5 mL) of (0.2% NAC) solution dissolved in ethanol
at (pH=5).Organic phase: - (5mL) Chloroform. Equilibrium time: - (X) minutes.
Temperature: - (25 ± 2) C^o.

5-Effect of organic solvents:

According to solvent extraction method which was depend on the organic solvent used in extraction method the results in table (3) demonstrate there is no any linear relation between distribution ratio and dielectric constant of the organic solvent .This is in contrast with born relationship of the following equation [17]: -

$$\Delta Gt = \frac{Z^2}{Zr}\left(\frac{1}{\varepsilon_w} - \frac{1}{\varepsilon_o}\right)\dots\dots \quad (1)$$

Where Z is the ion charge, r the radius of the ion, εw, εo dielectric constant of water and organic solvent, respectively, ΔGt free energy to move the ion. figure(2) appear chloroform was the best solvent for extraction La(III) ion .

Table (3): The effect of polar organic solvent to extract La(III) by using(NAC)

Organic Solvent	ε	1/ε	D	E%
Nitrobenzene	35.600	0.028	9.171	81.981
Benzaldehyde	17.800	0.056	5.959	77.695
1,2-dichloroethan	10.420	0.095	5.230	74.209
chloroform	4.810	0.207	15.437	93.916
Toluene	2.380	0.420	6.580	84.484
Benzene	2.280	0.438	7.586	82.652
Carbon tetra chloride	2.240	0.446	8.154	82.218

Aqueous phase: (2.5 mL) from La (III) ion with (2.5 mL) (0.2% NAC) at (pH = 5) .
Organic phase: (5mL) different solvents.Contact time: Sixty min. Temperature: (25 ± 3) C^{o}
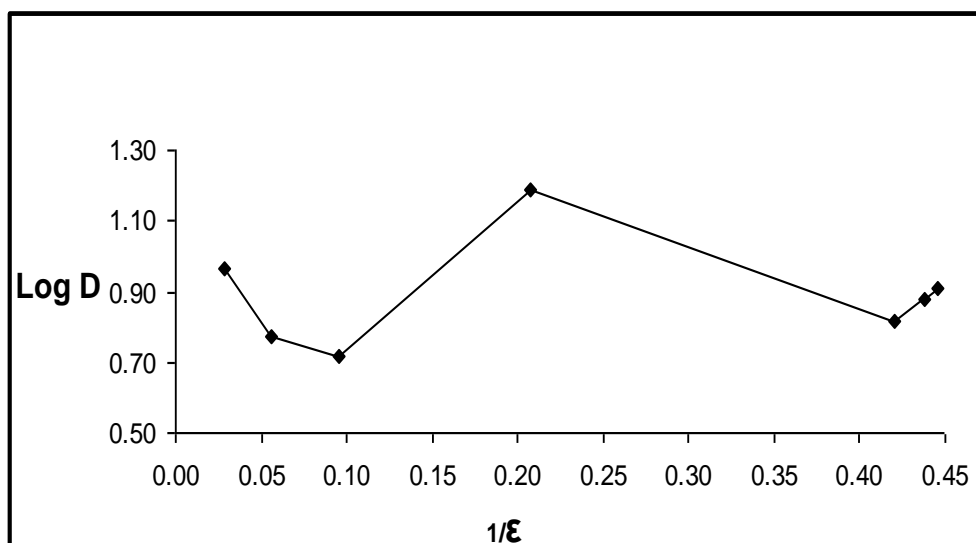
Fig. (2) The effect of polar organic solvent to extract La(III) using (NAC).

This demonstrated that the system of extraction in this study can not be controlled by the dielectric constant of the solvent and the reason was attributed to the extracted complexes were no charge chelate. These types of complexes were affected by many factors including the solubility of the extracted complex or geometry of organic solvent. This is supported the role of organic solvent composition to achieve the best extraction away from the polar organic solvent that used as to have a role in creating the best extraction, but its role was not a major, it's not exclude the possibility of participation of organic solvent in the process of extraction, the results of these study are in agreement with the previously studies [14].

8- Effect of anions on the extraction

The results in the table (4) shows that the presence of anions disparate influence in the process of extracting of La(III) ion depending on the nature of the anions added .Some anions had a great effect on decreasing the values of distribution ratio and therefore on the (% E) to extract La(III) by using (NAC), this ion was ($Cr_2O_7^{=}$) Where these ions added to the aqueous phase which contains the elements of lanthanides formed compounds do not dissolved in aqueous solution[18] and therefore they behave as masking agent working to reduce the combination of cations with reagents[19]. Anions had a great effect on increase the values of distribution ratio and therefore on the (% E) to extract La(III) ,this ion was (MnO_4^{-}), These ions decrease hydration energy for ions and then facilitate formation of complex in organic phase . this result are in agreement with the previously studies [20] .

Table (4): The effect of adding negative ions to extract La(III) by using (NAC)

Anions	0.2% (gm/mL)		0.4% (gm/mL)	
	D	**E%**	**D**	**E%**
---------	13.523	93.114	13.523	93.114
$Cr_2O_7^=$	3.460	77.579	2.431	70.857
PO_4^{-3}	7.934	88.807	7.162	87.748
$SO_4^=$	7.598	88.370	10.080	90.975
ClO_3^-	5.283	84.084	7.416	88.118
NO_3^-	5.670	85.008	7.275	87.916
$CO_3^=$	12.902	92.807	9.663	90.622
Br^-	10.829	91.546	8.326	89.277
MnO_4^-	10.996	91.664	134.230	99.261

Aqueous phase: - (2.5 mL) solution of La(III) ion concentration of(500 M) ,
 $(1.4398x10^{-3}$ μg)+(2.5 mL) ,(0.2% NAC) dissolve in ethanol +(1 mL) (0.2% and
 0.4%) , from some of the negative ions at (pH = 5). Organic phase: - (5 mL) Chloroform.
Equilibrium time: - Sixty minutes. Temperature: - $(20± 3)$ C^o.

7- Effect of cations on the extraction
   A number of cations surrounding Nd(III) ion in periodic table was selected to study the influence of the extraction of Nd(III) ion using (NAC). Table   (5) shows the data of this study

Table(5): The effect of some cations in the extraction of La (III) with(NAC)

Cations	500 μgm/2.5mL		1000 μgm/2.5mL	
	D	E%	D	E%
----------	13.523	93.114	13.523	93.114
Cd^{+2}	8.675	89.664	13.442	93.076
Hg^{+2}	8.444	89.412	7.241	87.866
Ni^{+2}	5.078	83.546	6.881	87.311
Mn^{+2}	9.587	90.555	8.430	89.395
Co^{+2}	12.252	92.454	11.553	92.034
Fe^{+3}	17.829	94.689	12.252	92.454
Cr^{+3}	3.514	77.849	3.889	79.546

 Aqueous phase: - (2.5mL) solution of La(III) ion concentration of(500 μg),
 $(1.4398x10^{-3}M)$+(2.5 mL)(0.2%NAC) dissolve in ethanol +(0.5 mL)of some
 cations (500 μg) and (1000μg) at (pH = 5). Organic phase: - (5mL) Chloroform.
 Equilibrium time: - Sixty   minutes. Temperature: - (20± 2) Co.

From Table (5) the results shows that the extraction of La(III) ions in presence of a number of cations leads to disparate results, since the presence of some cations such as (Ni^{+2} and Cr^{+3}) were working to reduce the value of distribution ratio (D) When .The reason was attributed to competition cations with La(III) ion to coordinate with (NAC) to form complexes[14] .

11- Effect of oxidation & reduction on the extraction .

The effects of oxidation was studied by adding (1mL) solution of hydrogen peroxide with concentration (35%) as an oxidant agent in extraction of La(III) ion with (NAC) under the experimental conditions   . Distribution values of La(III) ion with (NAC) was calculated after separating aqueous phase from organic phase . The amount of remained ion was calculated in aqueous phase by using colorimetric method [13] . To study the influence of reducing agent on (D) value to extract La(III) ion with (NAC) , (1mL) of $SnCL_2.2H_2O$ solution (1M) had been added to the aqueous phase and by following the same method used with the studying the influence of oxidizing agent . Results had been obtained in the table (6).

Table (6): The effect of oxidation - reduction factors in the extraction
of La(III) with (NAC)

Extraction	D	E%
La(III) with (NAC) In absence of oxidation- reduction factors	13.523	93.114
La(III) with (NAC) In presence of oxidation factors	9.512	90.487
La(III) with (NAC) In presence reduction factors	184.943	99.462

Temperature:-$(20\pm3)C^o$.

The results of this study show that the extraction processes is inefficient in presence of oxidizing agents because of its effect on the reagent. It probably works on the oxidation and changing nature of chelating reagent. As well as the oxidation of La(III) ion is also expected . This oxidation distorts the system of complex formation extracted. The results of reducing agent show that distribution ratio was increased because of increasing in stability of trivalent oxidation state La(III) , So La(III) ion do not reduced by using $SnCl_2 .2H_2O$.

12 –Effect of enrichment extraction on the extraction
   (Volume concentration technique)

The values of distribution ratios for extraction of La(III) ion was calculated from volumes ranged from (7.5- 52.5) of aqueous phase by using (5 mL) of organic phase . Table (7) shows the results.

Table (7): The effect of enrichment method to extract La (III) using (NAC).

Volume of Aqueous phase (mL)	Volume of Organic phase (mL)	D	E%
5	5	13.523	93.114
7.5	5	10.892	87.834
12.5	5	3.362	57.353
17.5	5	2.881	45.151
22.2	5	1.619	26.456
27.5	5	1.917	25.842
52.5	5	No Extraction	

Aqueous phase: - (XmL) of a solution of La(III) ion concentration of (500 μg), (1.4398×10^{-3} M) with (2.5 mL) of (0.2 % NAC) at (pH=9). Organic phase: - (5 mL) Chloroform. Equilibrium time: - Sixty minutes. Temperature:- $(20\pm2)C^o$.
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The results of table (7) show the possibility to extract La(III) ion by the reagent (NAC) under study from large volumes of aqueous phase , but in low distribution ratio and (% E) was an efficient . The results of this study approved with other recent studies [21] .

3-Effect of metal ion concentration

La(III) ion was extracted from aqueous solution which containing increasing concentrations of the ion ranged from (250 μg/2.5mL to 1250μg / 2.5mL), (7.1991×10^{-4} M to 3.5995×10^{-3} M) for La(III) with the reagent(2.5ml),(0.2% NAC) and within the best conditions reached from the previous experiences of this study. Results of this study were described in figures (3).
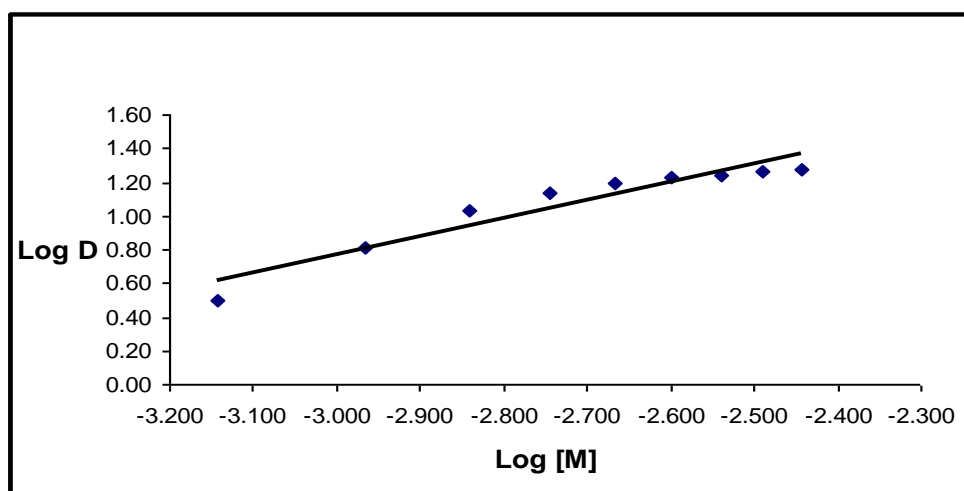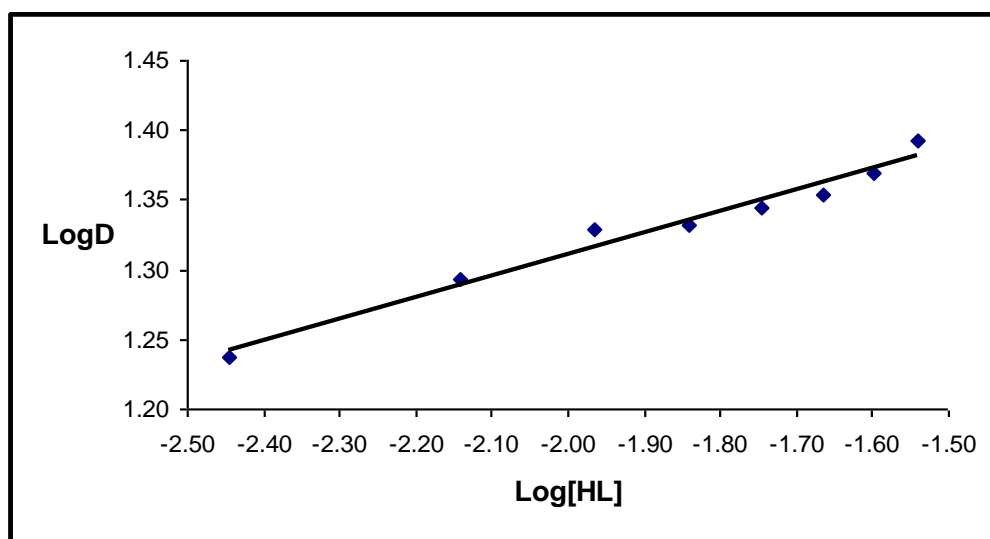

Figure (3) The effect of different concentration of La(III) using (NAC) in the extraction.

Figure(3) show that the value of (D) increased with increasing concentration of La(III) in aqueous phase when extracted by (NAC) , It should be noted that this expected behavior due to continued interaction between the ion and NAC .Thus enhancing fully interaction in constant mole ratio without any adduct that leads to deviation from the linearity. This results   are in agreement with the previously studied [22].

4-Effect of reagent (NAC) concentration on the extraction.

Values of distribution ratios was calculated to extract a fixed amount of La(III) (1250 μg/2.5 ml), (3.5995×10^{-3} M) ion by different concentrations of reagent (NAC) under the experimental conditions. The results of this study illustrated in figure (4).

Fig.(4) The effect of different concentration of reagent (NAC) to extract La(III) ion.

Plots of Log D vs. Log NAC gave straight line . An expected result to increase the extraction of La(III) ion with (NAC) according to the following equation: -

$$\text{Log } D = \text{Log } K_{ex} + n\text{Log } [HL] \text{ org} + n \text{ pH} \quad ......(2)$$

The results of this study approval with the results of a recent study [23].

10-Effect of salting out on the extraction

Table (8) shows that the value of distribution ratio (D) to extract La(III) ion with (NAC) decreased in the presence of salting factor. The reason for this could be attributed to the behavior of chloride ion as masking agent which decrease the coordinate linkage of (NAC) with ions .

Table (8): The effect of salting to extract La (III) with (NAC).

Extraction conditions	D	E%
La(III) with (NAC) In absence of salting factor	21.564	95.564
La(III) with (NAC) In presence of salting factor	12.377	92.524

Aqueous phase: - (2.5mL) of a solution of La(III) ion concentration of (1250 μg), $(3.5995 \times 10^{-3}$ M) with (2.5 mL) of (0.2 % NAC) at (pH=9).Organic phase:- (5 mL) Chloroform. Equilibrium time: - Sixty minutes. Temperature:- $(20 \pm 2)C^{o}$

9- Effect of batch method on the extraction

The effect of using batch extraction to extract La(III) ion with (NAC) was studied. Extraction held in three stages after partition of organic phase into three volumes. Equal volume for each extraction stage has been part of this phase . Values of distribution ratio had been calculated after the end of part three of extraction process , table (9) show the results of this study.

Table (9): The influence of batch method in the extraction of La (III) with (NAC).

Extraction Technique	D	E%
La(III) with (NAC) Continuous extraction	21.543	95.564
La(III) with (NAC) Batch extraction	21.368	95.529

Temperature:-$(20 \pm 3)C^{o}$**.**
The results of table (9) show increasing in the values of distribution ratio (D) and (% E) for La(III) ion extraction with (NAC), so using a single batch extraction save effort and time.

6-Effect of temperature

Extraction of La(III) ion from aqueous solution at optimum by temperature from (15-35 C°) as illustrated in table (10) .

Table: (10) The values of distribution ratios for the extraction of La(II) ion   by using the reagent (NAC) at different temperatures**.**

T(K)	$1/T*10^{-3}$	D
288	3.472	18.807
293	3.412	21.543
298	3.355	22.346
303	3.300	23.036
308	3.246	23.895
318	3.144	24.915

Aqueous phase : - (2.5mL) solution of La(III) ion concentration (1250 μg) (3.5995×10^{-3}) , with (2.5 mL) of (0.2%NAC) dissolve in ethanol at (pH = 5).
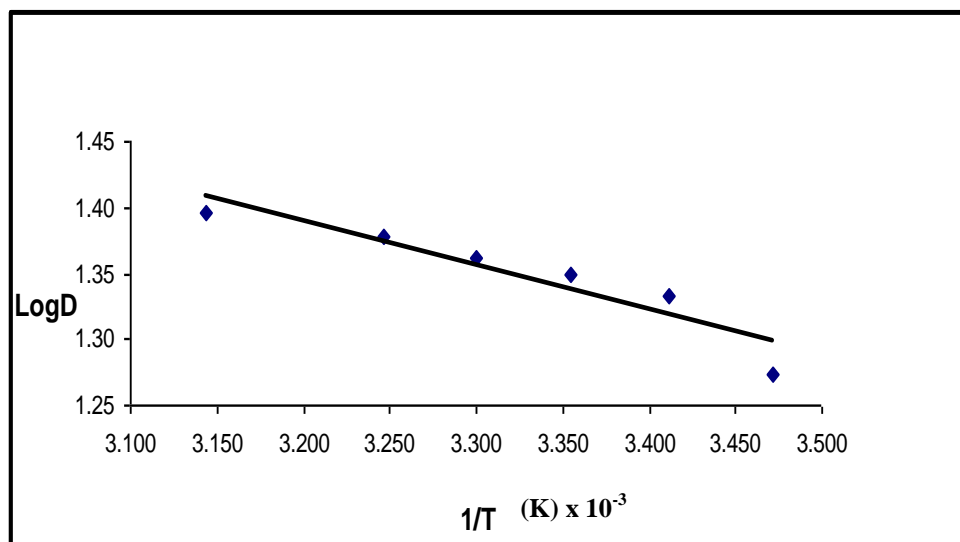Organic phase: - (5mL) Chloroform. Equilibrium time: - Sixty minutes.
Temperature: - (x) C ^{o}.

By using Vant-Hoff Equation: [24]

$$2.303 \, Log \, K_{ex} = \frac{-\Delta H}{RT} + C \quad \ldots \ldots (3)$$

By drawing the relationship between Log D versus 1 / T the figures (5) had been obtained and the value of enthalpy (ΔH_{ex}) had been calculated.

The results in figure (5) demonstrate that the reaction between La(III) and ligand(NAC) was endothermic .

Values of (ΔG_{ex}), (ΔS_{ex}) were calculated by using Gibbs equations described below [24]: -
$\Delta G_{ex} = \Delta H - T\Delta S \ldots \ldots (4)$
$\Delta G_{ex} = -RT \ln K_{ex} \ldots \ldots (5)$, where $Log \, D = Log \, K_{ex}$

Table (11) The values of thermodynamic functions to extract La(III)
By using (NAC).

T (K)	$\Delta H(Kj.Mol^{-1})$	$\Delta G(Kj.Mol^{-1})$	$\Delta S(Kj.Mol^{-1}K^{-1})$
288	6.423	-7.014	0.0466
293	6.423	-7.466	0.0474
298	6.423	-7.684	0.0473
303	6.423	-7.889	0.0472
308	6.423	-8.113	0.0471
318	6.423	-8.487	0.0468

From the results in table (11) the positive sign of the values of enthalpy show that the reaction between La(III) ion with (NAC) was Endothermic and thus means increase in the possibility of formation extract complex with increasing temperature ,while the negative sign of free energy for extraction demonstrate that reaction is and this is favorite thermodynamically in high temperature this study agree with a lot of studies [25] .

13-Stoichiometry determination

The stoichiometry of the extraction species (M:L) is determined by different methods.

a.   Job's method :

The results in figure (6) demonstrate that the more probable structure of Chelate complex extraction was (1:3)(M: L) identify with the results of mole ratio for structure which is [La (NAC)$_3$].
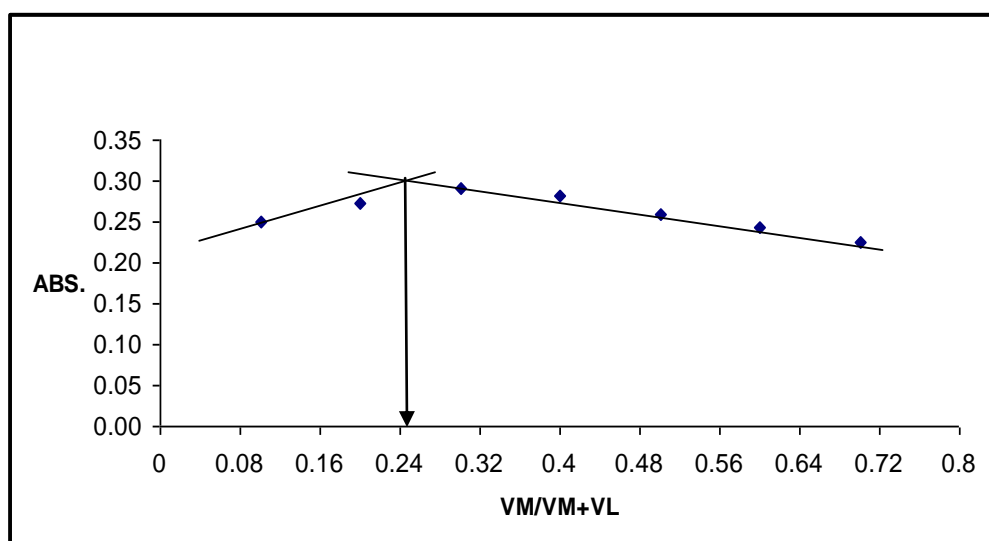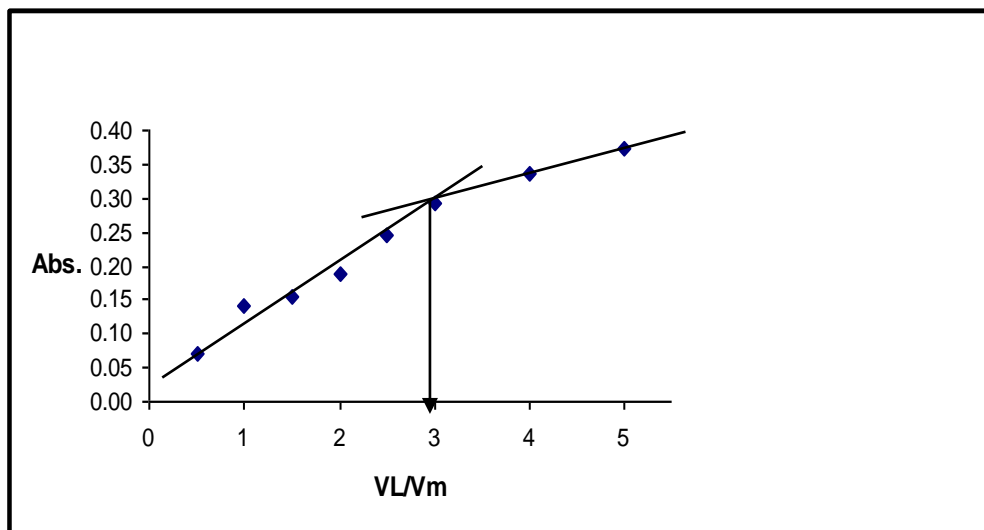

Fig.(6) Job's method (continuous variables) for the La(III) ion with (NAC) dissolved in ethanol .

b. Mole ration method

The results in figure (7) for mole ratio method study demonstrate that the more probable structure of chelate complex extraction was (1:3) (M: L) [La(NAC)$_3$] which is identify with the results in Job's analysis.

Fig.(7) The molar ratios method to extract La(III) by (NAC)

Study the stability for the extracted complex in organic Phase.

Stability constant of the extracted complex in the organic phase was calculated (ML$_3$) by drawing the equilibrium reaction for extracted complex

$$M^{+3} + 3L \longleftrightarrow ML_3$$

$$\alpha C \quad 3\,\alpha C \quad (1-\alpha)\,C$$

$$K = (1-\alpha)\,C \,/\, \alpha C\,(3\alpha C)^{\,3}$$

$$\alpha = \frac{A_m - A_s}{A_m} \quad \ldots\ldots\ldots(6)^{\ (26)}$$

where α : the degree of dissociation.

       C : Concentration of metal.

       K : Stability constant.

       A$_m$: The greatest absorption.

       A$_s$: Absorption at the end point.

Table (12) Data of dissociation constant and stability constant for
extracted complex.

| Complex	A_m	A_s	α	$K_{sta.}$
La(NAC)$_3$	0.374	0.294	0.2139	2.1673×10^{17}

(UV –Vis.) spectrum

1- The (UV –vis.) spectrum for the ligand (NAC) (at pH=5) dissolve in ethanol, figure (8) exhibits a high intense absorption peak at (241nm).
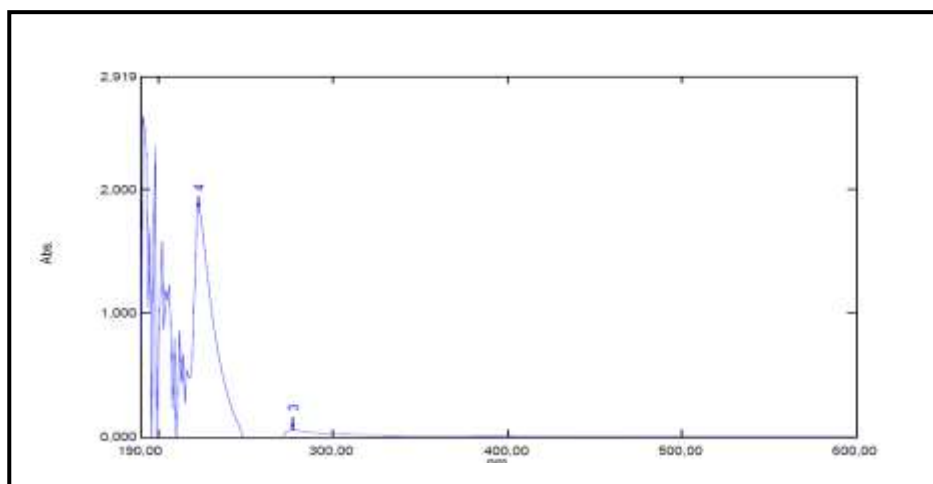
Figure (8) Electronic spectral data of the ligand (NAC)

2- The (UV –vis.) spectrum for the complex [La(NAC)$_3$] , figure (9) exhibits a high intense absorption peak at (252 nm) which used to measured absorption of the complex .By comparing absorption spectrum of ligand there was red shift for complex.
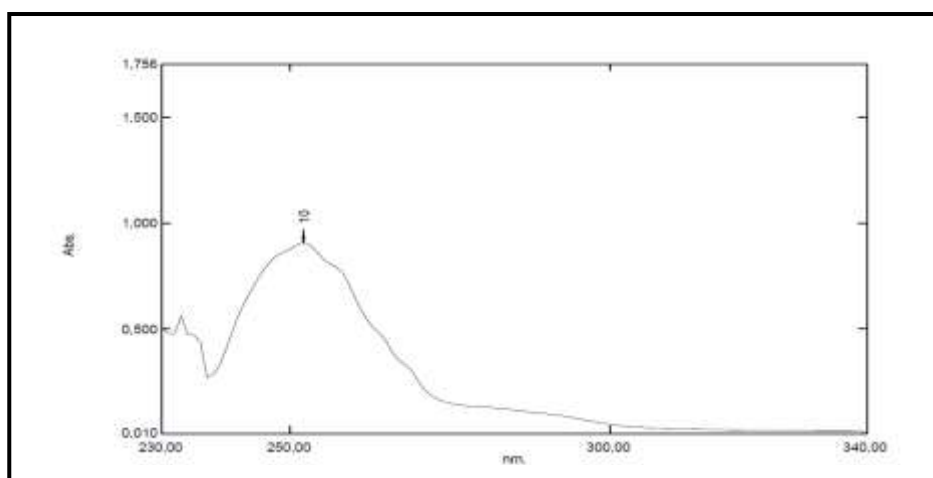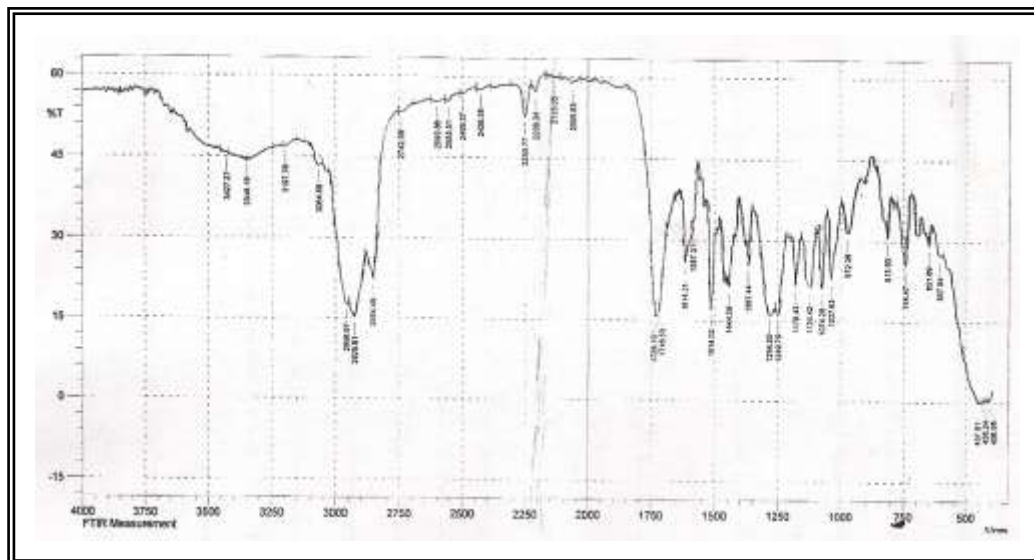

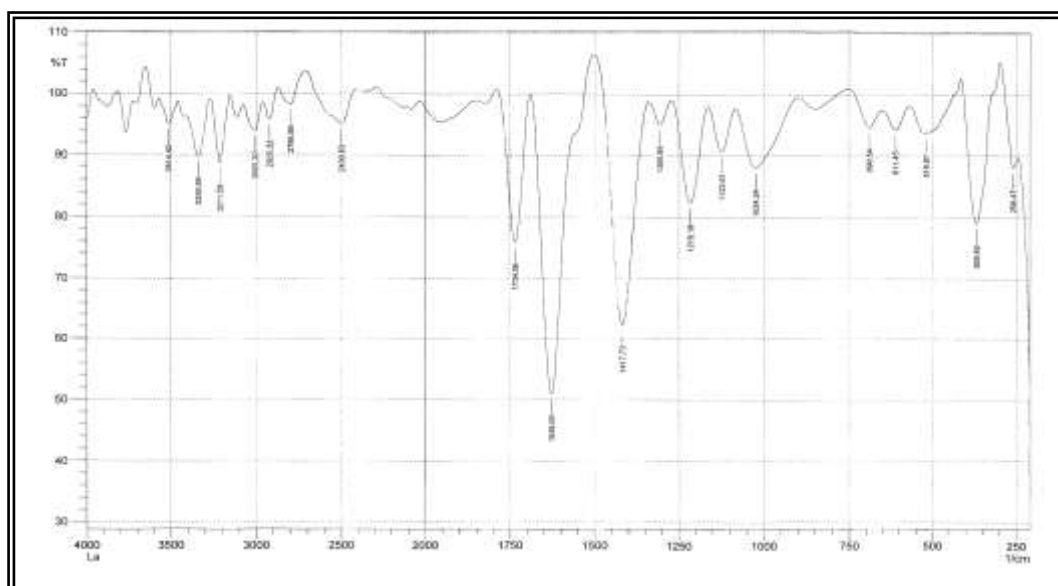**Figure (9) Electronic spectral data of the complex[La(NAC)$_3$]**

I.R spectrum

Figures (10) and (11) display the I.R spectrum for(NAC) and the complex which exhibit bands in table (13).(NAC) coordinate link to metal through the oxygen of O-H group and electron pairs in N-H group .

Figure (10) Infrared spectrum of ligand

Figure (11) Infrared spectrum of complex

Table (13) Result of I.R spectrum for ligand and complex

Compound	Stretching vibration ν N-H	Amide group ν C=O	Acidity ν C=O	Bending Vibration ν O-H	δN-H	δO-H	νS-H	νM-O	νM-N
Ligand	3380-3275	1632-1610	1743	3093-2891	1569-1521	1348-1272	2563-2522	---------	---------
complex	3211.89	1626.05	1734.06	---------	1610	---------	2499.83	518.87	368.42

Some physical properties of the extracted complex :-

1- Melting point

Melting point of extracted complex was measured. It was found (95-97 C^o) while melting point for Ligand (NAC) was (160-163C^o).

2- Electrical conductivity

Table (14) show that the value of electrical conductivity of extracted complex at room temperature approaches to the conductivity of solvent so the conductivity for complex can be neglected

Table (14) Electrical conductivity

Material	Electrical conductivity µS.cm-1
Chloroform	**0**
Complex	**0.2**

Statistical treatment of data

Relative standard deviation dependent as a measure for precision of data in all experiments . For this purpose extraction done in $(1.440 \times 10^{-3}M)$ and $(1.800 \times 10^{-3}M)$ for La(III) by using (2.5 mL) of reagent (NAC) dissolved in ethanol with (5mL)chloroform .The results obtained in table(15) shows that (RSD)in permitted rang in the experimental .

Table (15) Statistical treatment of data

Exp. NO.	Abs. $1.440 \times 10^{-3}M$	Abs. $1.800 \times 10^{-3}M$
1	0.439	0.512
2	0.432	0. 495
3	0.450	0.502
4	0.444	0.515
RSD%	**1.7299**	**1.8148**

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