

## Article

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## Cloud Point Extraction and Spectrophotometric Determination Zinc II Ion Complex in Real Samples Using BTAD Reagent

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### Abstract

New azo reagent 2-[Benz Thiazol azo]-1 -Dopamine , The reagent was Prepared through a coupled reaction and characterized using spectroscopic methods, including (FTIR) and (UV. -Vis.) is spectroscopy , as well as proton nuclear Magnetic resonance ( HNMR).to verify its chemical identity .This reagent was used to estimate Zinc( II ) ion through the formation of a doubly charged complex, Which was extracted and identified using cloud point extraction(CPE) technique , Optimization conditions and factors affecting is study that effected on extraction Efficiency E%. The measured of spectrophotometrically at a wavelength of at  $\lambda_{\max} = 515 \text{ nm}$  for  $\text{Zn}^{+2}$  complex . The conditions for complex formation and extraction Using (CPE)technique were studied and optimized , and the optimum pH is found =9 , critical volume the Triton X-100 concentration is at 0.5 mL, heating time is 85 C°. Thermodynamic study of parameters to CPE are also calculated ,and their values Were as follows  $\Delta H = 0.243874 \text{ KJ}$  ,  $\Delta G = -0.181914134 \text{ KJ}$  and  $\Delta S = 50.8821 \text{ J}$  Indicating that the reaction is endothermic (LOD= $6.4486 \times 10^{-6} \mu\text{g mL}^{-1}$ ) and LOQ= $6.4486 \times 10^{-5} \mu\text{g mL}^{-1}$  , with( Molar absorptivity  $\epsilon = 286.88 \text{ L.mol}^{-1}, \text{cm}^{-1}$ . The Stoichiometry of the  $[\text{Zn}^{+2}(\text{BTAD})]$  showed that the ratio of M:L obtained are (1:1). at optimum conditions , the analysis 10 mL of sample yielded pre concentration Factor and enrichment factor of (200 and 65.92366) respectively, while the Sandal's sensitivity( $4.1 \times 10^{-6} \mu\text{g cm}^{-2}$ ).Standard calibration curve was linearity at Range between 0.05-1ppm, with a correlation coefficient of 0.9933. The RSD% of Repeated measurements by a concentration of determinations at (90)  $\mu\text{g 10mL}^{-1}$  is 74.11%this developed method was applied to estimate Zinc concentration in Different samples and compered whit FAAS for samples and use t-test to compered

The results accept Nell hypothesis and this method can be depend at confidence Limit 95%.

**Key words:** Cloud point Extraction CPE , spectrophotometric Determination, Azo reagent Determination of  $Zn^{+2}$ , FAAS to calculate distribution ratio D.

## **1-Introduction**

"Green" chemistry encompasses all forms and facets of chemical processes to Reduce environmental risks and attempts to prevent pollution from the very Beginning of their development and execution. There are two primary categories into which the issues falling under the purview of "green" chemistry can be divided. The first concerns the use and handling of chemical industry byproducts and trash that poses a risk to the environment. The second, more hopeful, entails creating new industrial procedures to reduce or Completely eradicate the production and use of hazardous substances <sup>1</sup>. The use of Cloud point extraction (CPE) is thought to be a viable substitute for traditional Organic solvents. In the CPE, a surfactant (either ionic or non-ionic) is added to Separate the compounds from the main solution. Two phases—micellar and Aqueous—after heated to critical temperature known as the cloud point enrichment Phase <sup>2</sup>. The CPE is one of the most cutting-edge methods for antioxidant recovery Because of its minimal reagent requirements. Additionally, the CPE is often Conducted without the use of poisonous or dangerous chemicals and at moderate or Low temperatures. Numerous variables, including the kind and concentration to the Surfactants. pH to sample solution, the temperature ,time needed to establish Equilibrium, and the ionic strength, affect how well target compounds are extracted Using the CPE process<sup>3456</sup>. Malayappa and colleagues documented the preparation of four Benze thiazole-based disperse azo dyes, synthesized from 2-phenyl-2,4-Dihydro-3H-pyrazole-3-one through a diazo coupling reaction involving Electrophilic aromatic substitution conducted under controlled low-temperature Conditions (0–5 °C)<sup>7</sup>.

Such as the drug[3][4] to use it in green chemistry techniques<sup>81</sup>. thiazol liquid Crystals are a subclass of liquid crystalline substances that have thiazol rings as part of their molecular structure. The chemical formula for thiazol, a five-membered Heterocyclic molecule, is  $C_3H_3NS$ . Because of its unique electrical and structural Features, thiazol—which is known for its aromatic qualities—is frequently found in a wide range of natural and manufactured compounds, such as medications and Agrochemicals. A variety of techniques, such as the Vilsmeier-Haack reaction, Gewald reaction, or Hantzsch synthesis, are used to create thiazol-derived Molecules. For example,  $\alpha$ -halo ketones can be combined with thiourea or thi oamides in the presence of a base to create thiazol in the Hantzsch synthesis<sup>9</sup>.

Cloud Point Extraction CPE useful approach for routinely analyzing various Substances using surfactants instead of organic solvents.<sup>10 11</sup>.

to extracted  $Zn^{+2}$ <sup>12</sup> as a determined and treatment process, A very popular Technology used because it is easy, cheap and safe is the point cloud extraction Technique<sup>13</sup> used superficial material Triton X-100<sup>14</sup>. zinc extraction with the Thermodynamic behavior of chemical reactions<sup>15</sup>. In the coastal environment, Heavy metal contamination has been identified as a problem. Metal ions can enter Marine organisms through a variety of pathways, such as ingestion, absorption, and Respiration. Important biological functions depend on vital metals like copper, iron, Manganese, and zinc. When metal consumption is excessive, necessary metals may Have negative consequences. Given the significant amount of fish and mussels Consumed by humans, it is not surprising that numerous studies metal accumulation in the different fish species have been carried out. Since zinc is one of the most Important elements of enzyme cellular activity, a zinc deficit can result in illness. As a result, its application in food and water samples has been examined in a number of Studies<sup>16</sup>. Thiazole is a key heterocyclic ring incorporated in the structure of Numerous biologically active compounds due to its significant role in enhancing Pharmacological efficacy. Notable examples of thiazole-containing compounds Include sulfathiazole, which is used as an antimicrobial agent; ritonavir, classified as an antiretroviral drug; abafungin, employed as an antifungal agent; and bleomycin, Which is utilized as an antitumor agent. Thiazole derivatives exhibit a wide range of Medical applications, being involved in the treatment of various pathological Conditions such as hypertension, schizophrenia, bacterial infections, and infections Caused by the human immunodeficiency virus (HIV)<sup>17</sup>.

The two conventional way for prepared aromatic azo compounds are as follows: Diazo coupling reaction with electron-rich compound, which give a high yield, a Fast but its substrate scope is limited and its safety is low. Mills reaction, which Yields azo compounds have a larger  $\pi$  electron conjugation system in the aromatic Ring and  $-N=N-$  double bonds, giving them a plenty of applications in the Functional materials fields. The substituents on an aromatic rings of aromatic azo Compounds have a direct effect on their characteristics<sup>18 19 20 21</sup> aromatic azo Compounds from nitroso aromatic compounds and primary aromatic amines Catalyzed by acetic acid<sup>22</sup>. In recent years, spectrometric methods for determining Zn II in different matrices have involved separation and pre concentration processes.<sup>10</sup>, for example FFAAS<sup>23</sup>, ETFAAS<sup>24 25</sup>, ICP-OES<sup>26</sup> and ICP-MS<sup>27</sup>

## **2-Experimental**

**a.** Throughout this investigation, the absorption spectra of all reagents and Complexes were scanned using the Shimadzu Twin ray UV-Visible Spectrophotometer of UV-1700, Japan, with a length wave  $190-1100 \text{ nm} \pm 0.3 \text{ nm}$

Accuracy an D2 peak (656.1 nm). (486nm  $\pm$  0.1) replicability. Related to spectrum Width the 1 nm (190 toward 900 nm), and a 10-mm optical path the cell.

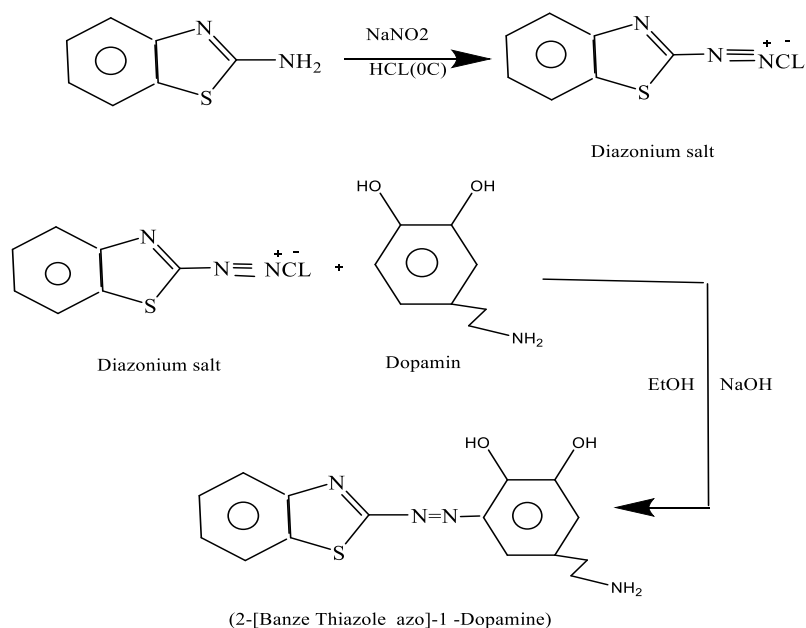
b. Single beam UV-Visible Spectrophotometer. TRIUP The worldwide Corp-TRUV. 74, S (Italy), was used to measure absorbance during the optimization study and metal identification The Spectrometer-HNMR Central Dastcami Laboratory for Nuclear Magnetic Resonance. Iran Shimadzu (Japan), FTIR8400S, and CHN/O Analyzer.

### **2-1:Reagent and Materials**

Since they came from a separate company, all analytical grade chemicals were Employed without additional cleansing. Samples, reagents, and the standard have all Been diluted. using doubled distilled water. The Sigma (Sigma Ultra, >99.6%) Supplied superficial material Triton X-100, which has the structure  $C_8H_{17}C_6H_4(OC_2H_4)_n$  (UK) and utilized without any additional purification. The Zn(II) stock solution (1 mg/mL) is prepared with dissolving (0.0439g)  $Zn\ So_4(7H_2O)$  (Merck, 99.97%) in 25 mL volumetric flask use distilled water. CDH (UK) supplied the NaOH (99%), HCl (37%), and  $NaNO_2$  (99%). Additionally, 0.606 g of 2-[Banze Thiazol azo]-1-Dopamin was dissolved in distilled Water after added 0.5 mL of Triton X-100 with a concentration  $1 \times 10^{-2}$  M.

### **2-2: Synthesis of ( 2-[Banze Thiazol azo]-1 -Dopamine) (B.T.A.D)as a Complexing Reagent**

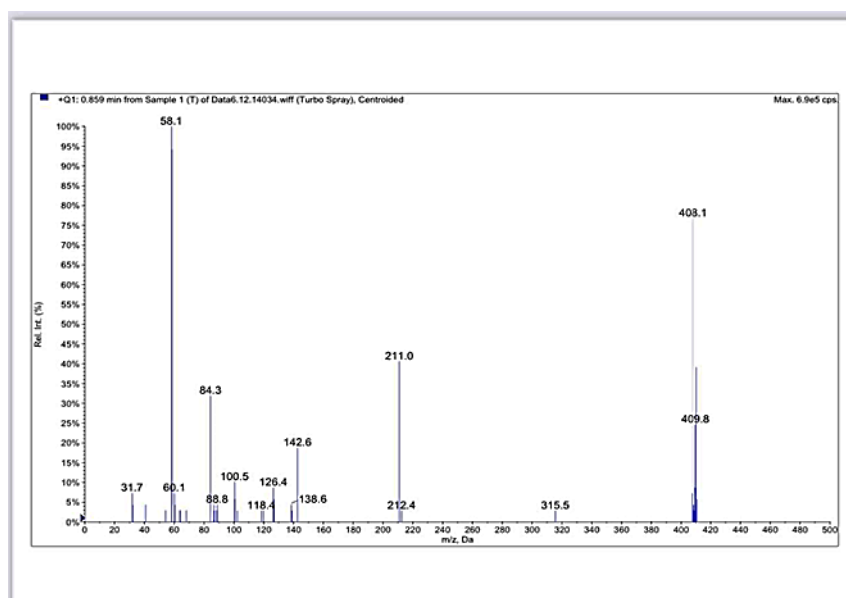
The reagents are prepared through solubilization 3.0244g (0.02 mole) for banze Thiazole with the mixture of 4mL hydrochloric acid concentration with 25 mL Deionized water , 10 mL with sodium nitrite containing 1.4 g of deionized water is Incorporated to this solution after cooled to 0 °C while keeping the temperature Constant. For the full diazotization process, the mixture was left aside for fifteen Minutes. The Diaz onium solution is then gradually added to a beaker that contains, to prepared Dopamine (3.0636, 0.02 mole solution dissolved in (150 milliliters of Ethyl alcohol containing 2g sodium hydroxide, maintained at 0 °C. In accordance With procedure outlined elsewhere [55], The yielded Mp (220-225 °C) and the Chemical formula  $C_{15}H_{15}N_4O_2$  with Mw (303g. mol<sup>-1</sup>). Figure 1 show chemical Pathway. azo reagents produced in this study were recognized via UV – Vis.H<sup>1</sup> NMR. FTIR the one that comes after , elemental analysis This reagent was prepared in 0.5% Triton X-100 to prevent dissolution in organic solvents. to application water Solution.



**Figure1: Bath way to preparation ( 2- [(Banze Thiazole )azo]-1-Dopamine (BTAD) reagent.**

### 2-3 Mass

Mass spectrometry is one of the essential analytical<sup>28</sup> techniques used for the Identification of compounds, whether simple or complex, organic or inorganic .The Principle of this technique involves exposing the vapor of the analytic , under very Low pressure, to a beam of high –energy and ionization of the substance through the Loss of one or more electrons from its atomic components. The ionization process is Often accompanied by the fragmentation of weak bonds within the molecular, Leading to the formation of smaller ions known as fragments . These fragments are Separated based on their mass –to-charge ratio  $m/z$  using a magnetic fields. The Resulting data are displayed as a mass spectrum, which shows the ionized fragments Along with their relative retention times prior to complete breakdown. This Facilitates confirmation of the structural features of the compound under Investigation. In the present study, a novel thiazole-based reagent and its Corresponding azo dye were successfully synthesized. According to our knowledge, these compounds have not been previously reported. The mass spectrum of the Synthesized reagent BTAD as shown in revealed a known fragmentation pathway Commonly observed in azo compounds, characterized by the heterolysis cleavage of the azo group, with one end retaining both nitrogen atoms. This behavior was Clearly demonstrated in the obtained mass spectrum<sup>2930</sup>

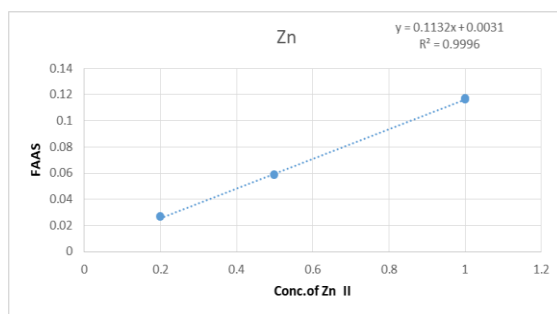


**Figure :2 Mass Spectral Analysis (MS) for the synthesized reagent BTAD**

The mass spectrum of the compound shows a prominent molecular ion peak at  $m/z = 315$ , which corresponds to the molecular weight of the thiazole ligand. This peak Undergoes fragmentation due to bond cleavage, leading to the formation of Characteristic fragment ions. The first major fragmentation gives a peak at  $m/z = 158$ , Followed by another significant fragment around  $m/z = 135$ , indicating a sequential Breakdown of the molecular structure. These fragment ions confirm the presence and Integrity of the thiazole-based ligand and provide insight into its structural features.

#### **2.4- Suggested Method**

The sample solution containing the analytic ( $90\mu\text{g}$ ) $\text{ZnSO}_4 \cdot (7\text{H}_2\text{O})$  during  $\text{pH} = 9$  and  $0.5\text{ mL}$  from Triton X-100 ( of  $0.1\%$  w/v) were heated for 10 minutes in a Thermostat bath during  $80\text{C}^\circ$  in order to separate the cloud point. The two layers Immediately separated from one another (without need of centrifugation and Cooling) the aqueous ] separation by decantation . then, the organic was dissolved CPE in  $5\text{ mL}$  of ethanol, and the absorbance at  $\lambda_{\text{max}} = 515\text{ nm}$  in a  $1\text{ cm}$  cell was Measured in opposite to a reagent blank prepare in same manner. The remaining Zn II in the aqueous solution was determined using the spectrophotometric method FAAS to compute the D value distribution ratio. and, as seen in Figure 3, a Calibration curve is produced by charting the FAAS against  $\text{Zn}^{+2}$  concentration.



**Figure 3 : Calibration curve To the spectrophotometric FAAS quantification of Zn II**

### 2.5-Making of the Sample.

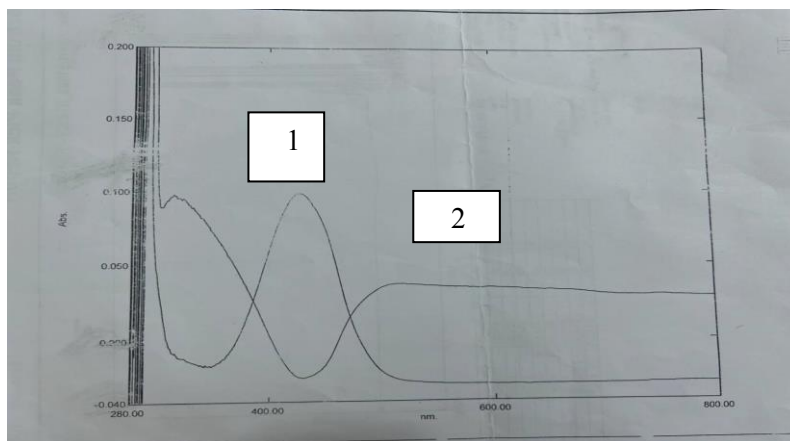
Samples of (plant and fish) solution is arranged using Wight 5 gram of dry Samples put in 250 mL laboratory flask and inserting 10 mL from concentrated  $\text{HNO}_3$ . heat on hotplate until two to three milliliters of liquid were left. Once cooled, then 10 mL from concentrated solution  $\text{HNO}_3$ , 4mL of  $\text{H}_2\text{O}_2$  and a 5ml Concentration of  $\text{H}_2\text{SO}_4$  were added. re heat ten milliliters in water were then added Until a colorless solution is achieved. After cooling, the contentener was transferred in to 100 mL laboratory flask, and filled to the brim with distilled water, following Filtration. <sup>31</sup> . 5 mL of the sample solution is taken is put within a 25 milliliter Conical a flask shaken with 1 milliliter from a 5% potassium cyanide solution, and Filtered. After filtering, the filtrate is put into a 10-milliliter volumetric flask and Dilute with water to the appropriate level. The suggested method was followed in Determining the zinc II, Without the analytic, the blank solution is made in the Same way.

## 3- Desiccation and Results

### 3.1- Spectrum Absorption of Prepared (B.T.A.D) Reagent and Ion Pair

#### Association Complex[Zn ; (B.T.A.D)] Extracted Through CPE Technique

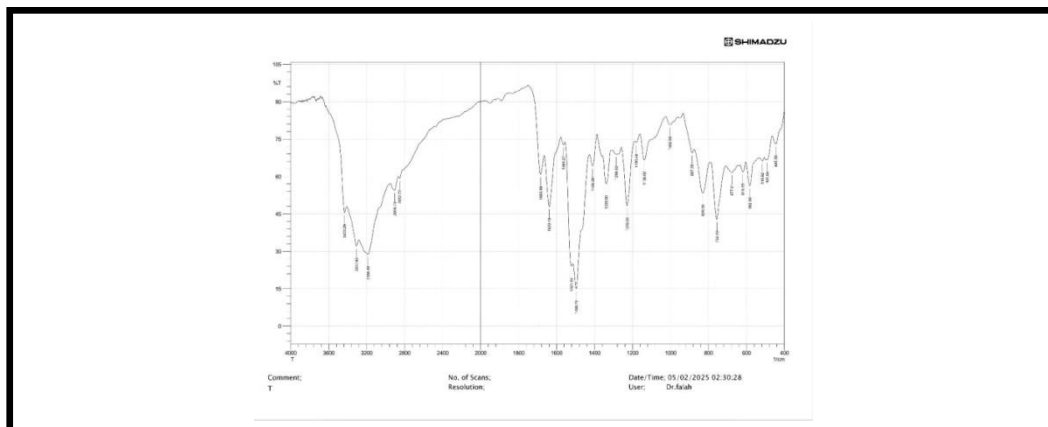
The visible spectrum of the ultraviolet new B.T.A.D syntheses substance that was Dissolved in water contain 0.5 mL from Triton X-100 (0.1% w/v) and  $\text{Zn}^{+2}$  Complex were measured Show in Figure 4, one of the two primary absorbent Maximum peaks. The complex and reagent formation between Zn II and B.T.A.D Within pH=9 critical concentration the TX-100 is 0.5 mL, heat temperature =85C°, Heat time =15 min. and [B.T.A.D] is ( $2 \times 10^{-4}\text{M}$ ), give absorption maxima at  $\lambda_{\text{max}} = 401$  for reagent B.T.A.D alone and  $\lambda_{\text{max}} = 515 \text{ nm}$   $\text{Zn}^{+2}$  complex as illustration in the spectra (1) and (2) of (Figure 5).



**Figure :4 Spectra in ultraviolet-visible of  $1 \times 10^{-4}$  M B.T.A.D in dilute TX-100 was 0.5mL.and  $(1.3752 \times 10^{-4}$  M of  $Zn^{+2}$ ) Absorption spectra of (1)  $Zn^{+2}$  complex (2) BTAD reagent**

**3.2: FT-IR Spectrum of the Reagent BTAD**

Spectrum FTIR the [B.T.A.D] is measured by utilizing a Shimadzu FT-IR Spectrophotometer series 8400S to prepare the sample in KBr disk b, Figure 5 ,FT-IR the Table-1 ft-IR data summary, the reagent B.T.A.D. The occurrence of the azo Bands at  $(1409.96 \text{ cm}^{-1})$  .

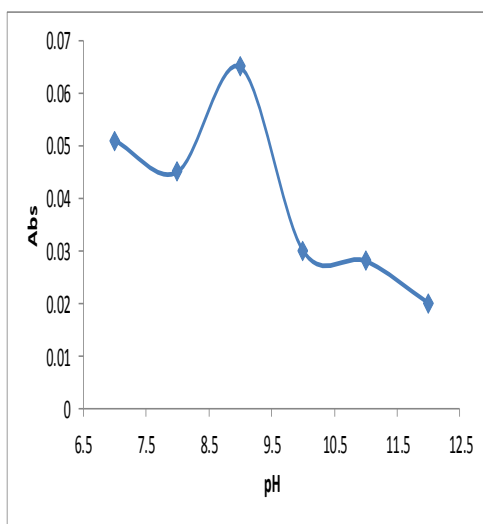


**Figure 5: IR Spectrum (KBr) of BTAD**

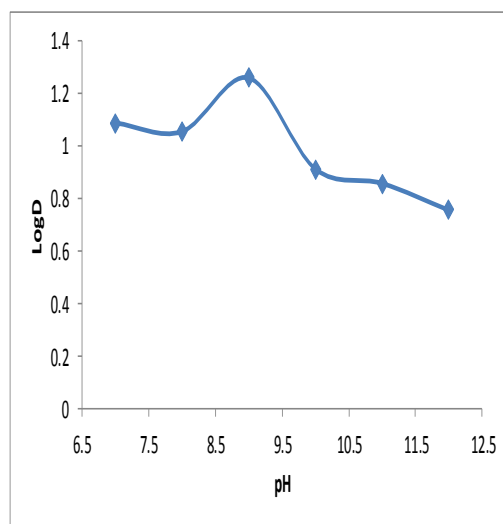
**Table 1 IR data (400-4000cm-1) of BTAD**

IR bands	The Wave number $\text{cm}^{-1}$
O-H stretching (m, v)	3433.29
C=N (s, v)	1604
N=N(m, v)	1409.96
C=C(m, v)	1639.49
C-O(m, v)	1002.98
C-N(m, v)	1228.66
C-H (s, $\delta$ , bend aromatic)	2906.73
C=O	1521.84





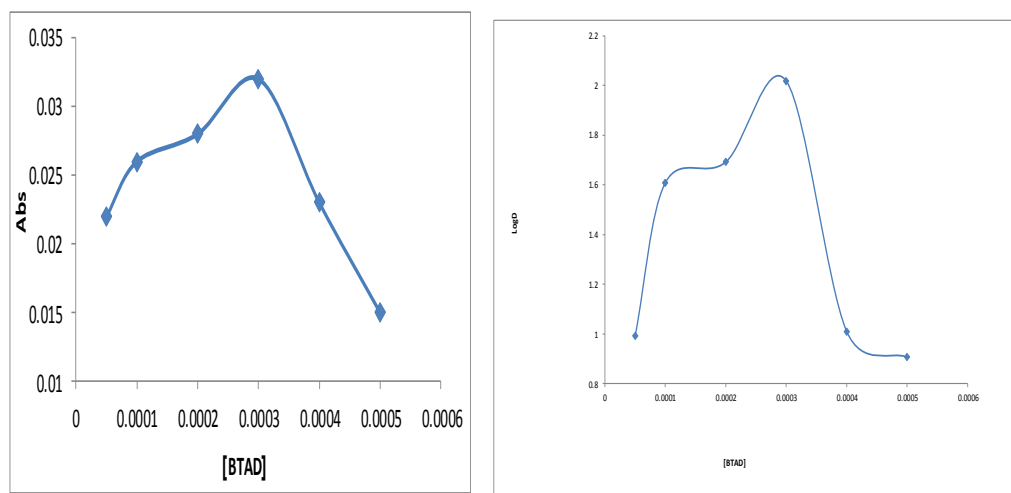
**Figure 7.1 : Effect  $pH_{ex}$  concentration on formation stability the species extracted .**



**Figure7.2 : Effect  $pH_{ex}$  on D value distribution ratio**

### 3.6.2 Stoichiometry and Effect of B.T.A.D Concentration on Extraction Efficiency by CPE

By using the CPE technique was the  $pH = 9$  and adjusting with dribbles of Ammonium dilution solvent mixture and 0.5 milliliter (0.1% w/v) from the Triton X-100 an surface-active agent ,  $100\mu g \setminus 10ml$   $Zn^{+2}$  of (B.T.A.D) extracted from 10 mL of aqueous solution by varying concentrations. ( $1 \times 10^{-5} M \setminus 10ml$ . and  $5 \times 10^{-4} M \setminus 10ml$ ) after being dissolved in water with 0.5 mL Triton X-100 of (B.T.A.D.) After 15 minutes of heating in a thermostat set to 85 C, the cloud point Phase(Concentrated -phase) was separated by decantation Thereafter diluted with Ethanol solvent in a 5 mL measuring flask. The absorbed was determined at  $\lambda_{max} = 515$  nm compared to the blank that was formulated in the same as manner. The Remaining  $Zn^{+2}$  in the solution in water was determined using the Spectrophotometric FAAS method in order to compute the distribution ratio D. As Shown in Figures 8: 1. and 8:2., the results



**Figure 8. 1 : Effect of reagent concentration on CPE . Figure 8.2 : Effect of reagent concentration on D Distribution ratio**

The findings demonstrated that. At lower than  $4 \times 10^{-4}$  M B.T.A.D, The formation of an unstable ion-pair complex suppressed the extraction of surfactant. However, More complex dissociation may take place at concentrations greater than  $3 \times 10^{-4}$  M, Which could cause a negative deviation in the absorbance values due to mass action. Another hand prepared it and reported the analysis of the dependence  $\log D$  vs ( $\log$  CBTAD).  $90 \mu\text{g}$  \ 10ml of  $\text{Zn}^{+2}$  and  $2 \times 10^{-4}$  M B.T.A.D. are present in 10 mL of Aqueous solution as a compound that forms complex of ion pairs  $[\text{Zn}^{+2};\text{B.T. A.D}]$  that extracted within CPE technique within  $\text{pH} = 9$  and 0.5 Milliliters of 0.1% w/v Triton X-100 used as a surface-active agent and drops of Diluted ammonium solution were added after 10 minutes to create the enrichment Layer. After a heating period at 80 C, the "CP" (rich-layer) was separated with Decantation, the concentration was decreased use the ethanol solvent at a 5 milliliter Measuring flask, the absorption was measured  $\lambda_{\text{max}} = 515 \text{ nm}$  against a blank Prepared in the same manner, and the remaining  $\text{Zn}^{+2}$  in the aqueous solution was Determined using the spectrophotometric FAAS technique to calculate the D values of distribution. enables the extracted complex's stoichiometry to be determined. Complex formed with ion pairs "Zn II" is indicated by the slope analysis method in Figure 9  $\log D$  vs. ( $\log$  [B.T.A.D]) coordinates, which is almost equal to one: A 1:1 B.T.A.D ratio is introduced into the layer rich in surfactants.

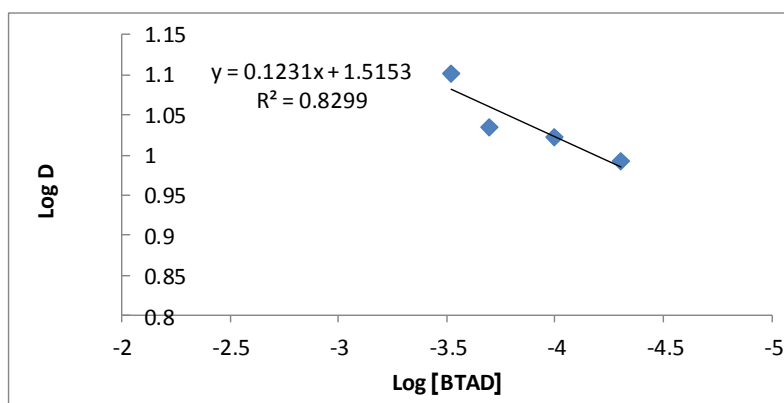


Figure9: Slope analysis method log D vs (log [BTAD])

### 3.6.3 Kinatic Study and Effect of Heating Time on CPE' Technique Extraction Efficiency

Process of import layer isolation and initial concentration from an effective Analysis.. the best time are extremely important factors to entire reaction with Duration incubation were investigated. resulting from completion of the reaction and efficient separation of the phases,  $90\mu\text{g}\backslash 10\text{ml}$   $\text{Zn}^{+2}$  ion in 10mL aqueous Solution was extracted at varied and different incubi time ( $70\text{ }^{\circ}\text{C}$ ,  $75\text{ }^{\circ}\text{C}$ ,  $80\text{ }^{\circ}\text{C}$ ,  $85\text{ }^{\circ}\text{C}$ ,  $90\text{ }^{\circ}\text{C}$ ,  $95\text{ }^{\circ}\text{C}$ ,  $100\text{ }^{\circ}\text{C}$ ) in thermostat and  $[\text{B.T.A.D}] = 2 \times 10^{-4}$  by CPE method at  $\text{pH} = 9$  after adjusted by drops of dilution ammonium solution and (0.2 mL of 0.1% w/v) of Triton X-100 as a surfactant that formation rich- phase at temperature  $80\text{ }^{\circ}\text{C}$  after that separation cloud point layer ( rich- phase ) determination of the residual  $\text{Zn}^{+2}$  in Aqueous solution by spectrophotometric FAAS technique. decantation and dilution with ethanol solvent at 5 mL solution preparation flask, along with absorption Measured at  $\lambda_{\text{max}} = 515\text{ nm}$  against blank prepared in the same manner. to Calculate d value distribution ratio . the results were showed in Figures 10:1,10:2

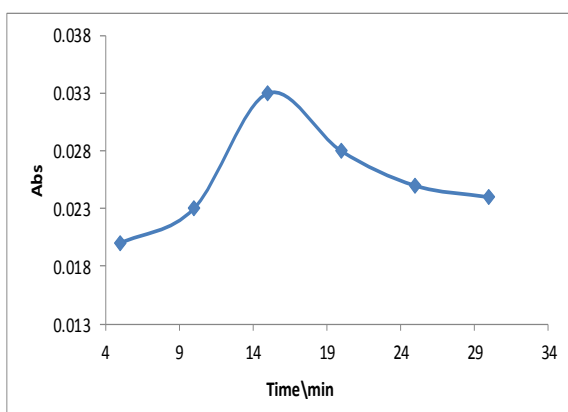


Figure 10. 1: Effect of incubi time on formation of ion pair complexation on extraction efficiency association and D value.

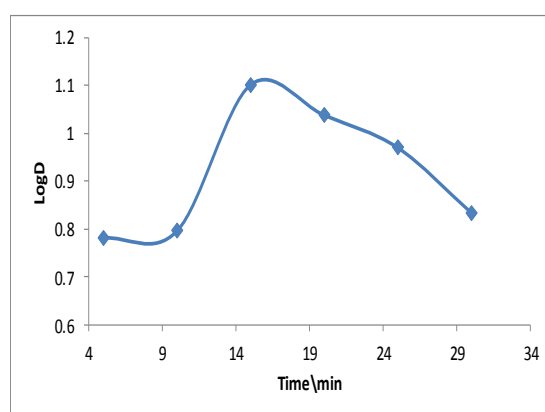


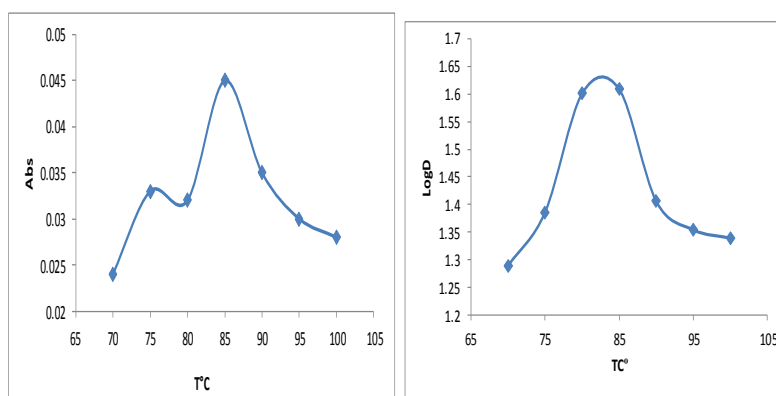
Figure10.2 : Effect the time on ion pair association and D value.

According to the conclusive results. 15 minutes was the ideal total heating time ,to Achieve the process ability to extract substances more effectively compared to

Standard methods, total Heating time also represents the aspect of a reaction that Involves its rate and the factors affecting it .the separate a substance at this point, Achieving maximum extraction and formation of ion pair association complexes; at any time below optimal does not permitted for achievement of a favorable quality of being steady and unchanging .. for that any excess total heating time has the Effect of decreasing extraction efficiency because it increases the equilibrium's Backward direction, which means that the the speed at which a molecule or complex Breaks apart into its components increases also the amount of association extraction Decreases. Additionally, it is noted this a 15-minute incubation period is adequate to Achieve the highest absorbance of the zinc ion complex,,

### 3.6.4 Thermodynamic Study and the Effect of Temperatures on the Extraction Efficiency of the CPE Technique

At varying temperatures, 90  $\mu\text{g}$  \10ml  $\text{Zn}^{+2}$  and  $2 \times 10^{-4}$  M of B.T.A.D. are present in 10 mL of aqueous solution. The ideal temperature was sought by varying it between 70 and 100  $^{\circ}\text{C}$ . Figure 11-1 and 11-2 demonstrate that the temperature of 85  $^{\circ}\text{C}$  yielded the maximum absorbance signals, enabling quantitative extraction. The CPE cannot be performed at high temperatures because the thermal breakdown the ion-pair Complex held results in complex in stability. ideal temperature for the experiments that follow in this study is 85  $^{\circ}\text{C}$ .



**Figure. 11.1 : Effect the temperature on Figure. 11.2 : Effect the temperature into ion pair formation and stability . extraction efficiency After calculated.**

#### Thermodynamic study

Through the use of Triton X-100 as an substance for extraction at different Temperatures, thermodynamic parameters and The constants of equilibrium to the Distribution reaction ( $K_{ex}$ ) for extraction of the  $[\text{Zn}^{+2}:\text{B.T.A.D}]$  ion pair complex During the CPE were established. The following formula was applied to ascertain the Equilibrium constants ( $K_{ex}$ ) at the chosen temperature. The complex thermal Transport constant that comes from complex transportation constant from the Aqueous layer to the surfactant layer , the clustering micelle steady as the

Temperature rises, the association does not change for the complex, the surface Distribution does not change between the aqueous layer ,the surface active agents Micelles layer are all examples of equilibrium constants that are actually represented by these thermodynamic equilibrium constants ( $K_{ex}$ ). and Table 2 and Figure 12 Display the outcomes.  $[Zn^{+2}] [BTAD]$

$$K_{ex} = \frac{D}{[Zn+2][BTAD]}$$

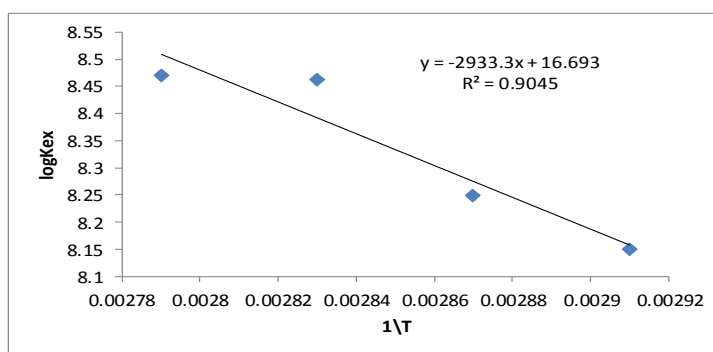


Figure12 : Effect of temperature in to equilibrium constant

Based on non-curved line slope from  $\log K_{ex}$  against  $1/T$  plot (Figure :12) ,the Relationships at a lower level the computed thermodynamic properties shown in the Table 2:

$$\text{Slope} = \frac{-\Delta H_{ex}}{2.303 R} \quad \Delta G_{ex} = - R T \ln K_{ex} \quad \Delta G_{ex} = \Delta H_{ex} - T\Delta S_{ex}$$

Table2: Thermodynamic parameters for  $Zn^{+2}$  ion extraction

T°C	TK	$\Delta H_{ex}$ KJ	$\Delta G_{ex}$ K J	$\Delta S_{ex}$ J
70	343	2.4384962	- 53.51945753	163.1427
75	348		-54.94934141	164.9075
80	353		-57.1879579	168.9134
85	358		-58.05019045	169
90	363		-57.45059005	164.9837
95	368		-50.84624588	144.7954
100	373		-58.55951381	163.5335

Enthalpy value ( $\Delta H_{ex}$ ) found to be  $2.43874 \text{ kJ mol}^{-1}$  At varying temperatures, However, the values of Gibbs free energy ( $\Delta G_{ex}$ ) were measured. Following the Acquisition of these two parameters, entropy ( $\Delta S_{ex}$ ) values were also computed. The Findings showed that the small value of  $\Delta H_{ex}$ , leading to micelle dehydration (i.e., a

Decrease in value of  $\Delta H_{\text{solv}}$  and an increase in  $\Delta H_{\text{hyd}}$ , prepared it easy and using Thermodynamics favorable to extract the ion-pair complex. This increases the Phase-volume ratio, which in turn improves extraction efficiency.

$$\Delta G_{\text{ex}} = \Delta H_{\text{ex}} - T\Delta S_{\text{ex}}$$

is as pointed out from **-Table: 2-** that worth of  $\Delta G_{\text{ex}}$  decreased roughly as the Temperature rose. The negative numbers of  $\Delta G_{\text{ex}}$  show that the process of double Ion-pair compound solubilization is likewise spontaneous. and thermodynamically Favorable[64]. The CPE technique extraction reaction is endothermic, and an Entropic, entropic in region is indicated by a positive value of the  $\Delta S_{\text{ex}}$

### 3-6-5: Effect the Salts of Electrolytes During Extraction Performance with Cloud Point Extraction Technique

Because they increase the dehydration of the surfactant-rich phase, certain electrolyte Salt solutions are known to behave in a way that increases the extraction percentage During the CPE process. Some ionic salts such as metallic in groups I and II, like Nitrates and chlorides. was chosen because he complex's anionic is not in competition With them, and exhibit variable behavior into raising the D value distribution ratio the ion molecular complex that CPE technique is extracting. as shown in Table 4. In the presence of 0.01M of certain electrolytes in aqueous solutions, 90 $\mu\text{g}$  of  $\text{Zn}^{+2}$  ions into 10mL of Water solution were isolated using the CP approach, following steps Outlined in the standard procedure. The findings were displayed in Table3:

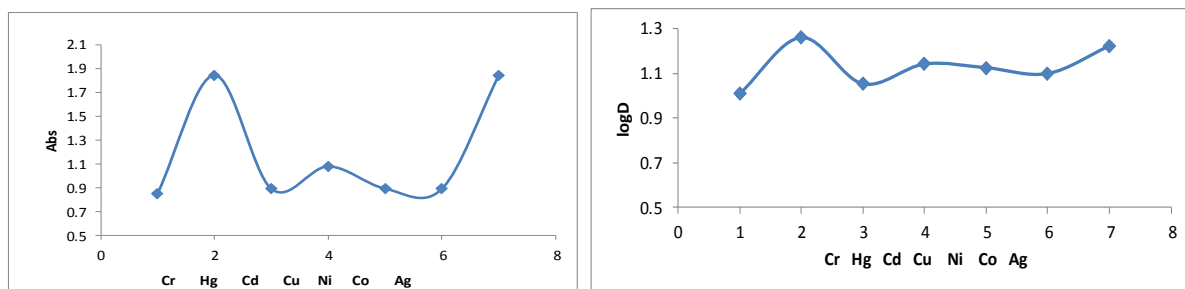
**Table- 3 : Effect the electrolytes into Recovery efficiency of  $\text{Zn}^{+2}$  ion**

Electrolyte	Abs- $\lambda_{\text{max}}=515\text{nm}$	E%
$\text{CaNO}_3$	0.049	88.15%
$\text{NaNO}_3$	0.035	86.14%
$\text{KNO}_3$	0.032	85.11%
$\text{NH}_4\text{NO}_3$	0.042	87.13%

According to the findings, the aqueous layers electrolyte salt content has the effect of Increasing recovery efficiency because electrolyte causes the ionic activity in the Aqueous phase solution to increase and destroys the hydration shell of the metal ion  $\text{Zn}^{+2}$ , which changes the ionic radius with a higher charge density and has a greater Effect..

### 3-6-6: Effect the Interference into Effectiveness of Extraction Using CP Extraction Technique

Following general the procedure, 90 $\mu\text{g}$ \10ml  $\text{Zn}^{+2}$  is extracted from 10mL aqueous Solutions using the cloud point method, with 0.01M of some contaminating metal Cations present. results are shown in Figure 13.

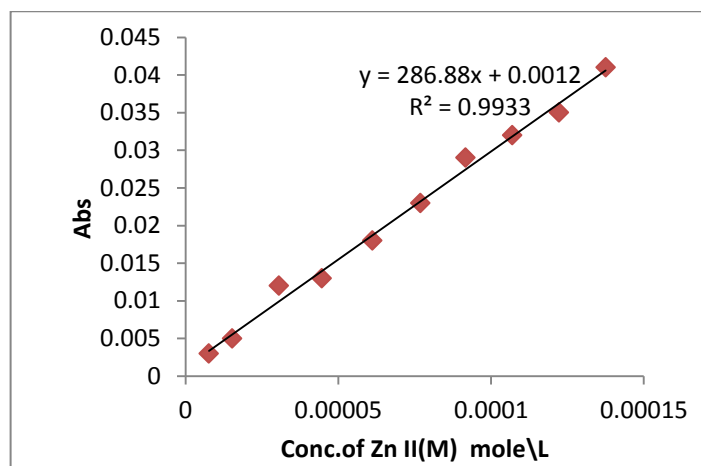


**Figure :13. 1: Effect the interferences on extraction and D value**      **Figure:13. 2 : Effect the interferences on effectiveness of extraction and D value**

Certain salts that contain both cations and anions when  $Zn^{+2}$  is extracted through CPE technique . Since they operate in the ideal conditions for  $Zn^{+2}$ , cations like  $Cd^{+2}$ ,  $Hg^{+}$ ,  $Ag$ , and  $Cr^{+2}$ ,  $Cu$ ,  $Ni$ , and  $Co$ , typically cannot provide evidence that they interfere with  $Zn^{+2}$  because they are unable to form cation complexes that can compete with analytic cations of metal complexes. Ion-pair complexes are formed Under of requirements the CPE technique that resulting in a significant decrease in the interference a cation extraction distribution ratio.

### 3.6.7 Calibration Curve the of Zinc ion Concentration in the Extraction Through CPE Technique

Obtained the charged metal ion  $Zn^{+2}$  at varying concentrations from (10  $\mu g/10ml$ , -90  $\mu g/10ml$ ), with 10mL water contain in solutions  $2 \times 10^{-4} M$  BTAD as a Complexing agents ionic association formation ion par molecular linkage [Zn II-B.T.A.D] that extracted with CPE technique at pH =9 following modified through a Drop of dilution ammonia solution along with 0.5 milliliter (0.1% w/v) for Triton X-100 as the surfactant forms abundant -layer by 15 minutes. Then, the cloud point Technique layer (rich-layer ) is separated by decanting and diluted using ethanol Alcohol within 5 mL into a measuring flask. The absorbed is determined at  $\lambda_{max} = 515 \text{ nm}$  toward a blank that was made in similar manner. The residual  $Zn^{+2}$  in the Fluid solution is determined using the spectrophotometric FAAS technique to Compute D value distribution ratio . The findings are displayed in Figure 14, and Evaluation criteria that were based on statistical data calculated using this curve for Calibration are displayed in the Table 4.



**Figure14: Calibration Curve for spectrophotometric determination of Zn<sup>+2</sup>**

According to the results, The metal's concentration ions was one the in effect Heat dynamic variables, raising concentration the metals ions Zn<sup>+2</sup> in the water Solution helps to increase the flow in the forward motion. The highest effect appears at 90 $\mu$ g\10ml, which is the highest concentration. However, any concentration above this point will decrease the yield of extraction through accelerating the process or Rate reverse path heat balance, that was much more dissociative , reduces the Concentration to kinds formation in compliance with the law of mass action.

**Table4: Figure of merit for determination to Zn<sup>+2</sup> with the suggested procedures**

variables	Value
$\lambda_{\max}$ nm	515nm
Equation of regression using CPE technique	$y = 286.88x + 0.0012$
Coefficient of correlation: r	0.9933
Determination coefficient -R <sup>2</sup>	100%
Range of concentration- ppm	(0.05-9)\10ml,
Detection Limit $\mu$ g mL <sup>-1</sup>	$6.4486 \times 10^{-6}$
Quantitation Limit ( $\mu$ g mL <sup>-1</sup> ),	$6.4486 \times 10^{-5}$
Sensitivity of sandal's - $\mu$ g cm <sup>-2</sup> /0.001A.U	$4.1 \times 10^{-6}$
absorptivity of Molar -L.mol <sup>-1</sup> .cm <sup>-1</sup> -	286.88
Complex composition: -M: L	1:1
RSD% n=10 at 90 $\mu$ g- mL <sup>-1</sup>	105.4079
Pre concentration ratio	200
Factor of enrichment	65.9236

### 3.6.9: Application.

The analytic concentration in the sample was estimated using regression line., which seems to be supported by statistical evidence. To test the applicability and Reliability of the suggested method .it was used to determine the amount of Zn II in a Variety of samples, including water, fish, and vegetable plants that were randomly Selected from various parts of Hila City which is in the middle of Iraq . This was

Accomplished by pre-concentrating an aliquot of each sample Prepared in accordance with the suggested protocol after CPE for Zinc determined spectrophotometry. Flame Atomic absorption spectrometry FAAS in our lab was used to . The results are Summarized from **Table5**.

name of The Sample	Proposed method for $\mu\text{g}/10\text{ml}$	FAAS technique ppm	Paired t –test		
			$S_d$	Tcal (n=5)	$t_{\text{crit.}}$ 95% DF=5
Local fish from the Euphrates River	$6.4549 \times 10^{-3}$	1.708	$1.5485 \times 10^{-3}$	-1.999	2.571
Sunflower Seeds	$2.9168 \times 10^{-3}$	1.112			
Apricot	$3.1051 \times 10^{-3}$	1.563			
Banana	$3.0633 \times 10^{-3}$	1.545			
Almonds	$2.9064 \times 10^{-3}$	1.116			

**Table5: Concentrations  $\text{Zn}^{+2}$   $\mu\text{g G-1}$  various the samples Hilla City central region of Iraq .**

Each statistical findings were obtained using a paired t-test to compare their means of All samples using the suggested and FAAS techniques (Table 6). have shown that all [P(tcal.<tcrct.) two-tailed according to the 5% threshold values to 2.571 ((t critical Two tailed))were greater the computed the values .. shows that the hypothesis Without value  $H_0$  was accepted. Consequently, suggested approach under Investigation is superior to the FAAS technique. Note: FAAS measurements were Only prepared for watery solutions with noCP. the water here alone did not produce an FAAS result.

#### 4-Conclusions

The first time. an essay for extraction and detection of  $\text{Zn}^{+2}$  is examined using a Newly formation organic reagent. from drugs to minimizing pollution through Organic reagent. in an attempt to extend the analytical capacity of the CPE method in Conjugation using spectrophotometry. To best about our knowledge, this separation and the pre-concentration of  $\text{Zn}^{+2}$  as an ion-association complicated into a surfactant Rich layer in a single-step extracting is in comparison with to the use of metal Complexes.. We are confident the results we have obtained will be sufficient to move Forward with additional work pertaining to the development of more sensitive Techniques in this field. To completely comprehend the workings of solubilization for sort of molecules within molecular aggregates . thermodynamic study still Requires a lot more engage in examin6e the impact of additional parameters, like

Change in a surface-active agents the quantity added as well as the level to Concentration of Reacting species at the same time in temperature to development of An association complex of ions, even though most analytical information has Significantly improved and there was good extraction efficacy with a good Biological and environmental application. Nevertheless, It ought to be kept keeping in mind that use from metal cations to be joint ones, such as zinc analysis by CPE Technique , is not as simple as it may seem due to limitations like interfering species, Because the preparation of an additional metal cation with that prepared reagent in Optimum condition to Zinc, the surfactant type, and electrolyte salts can be resolved when it works. Through careful optimization for the chemical elements in this study. these limitations may have been somewhat mitigated. The suggested method, However, enables the UV-visible spectrophotometric technique gain more traction Following CPE technique in addition to free of solvents extraction to metal cations to complex media, which has proven to be reasonably easy, sensitive, accurate, and Precise as a result, it may be taken into consideration as a substitute to atomic Spectrometric methods.

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