Article

Cloud Point Methodology to Determination Pb^{+2} by 4-CMePADPI Reagent Coupled with Spectrophotometry

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Abstract.

A modern extraction method for separating, enriching and estimating Pb^{+2} by using the CPE extraction technique and coupled with the spectrophotometry. For the purpose of determination Pb^{+2}, it was prepared in the laboratory of 2-[4-carboxymethylphenylazo]-4,5-diphenyl imidazole 4-CMePADPI as an organic reagent to formation complex with lead, which is extracted to the non-ionic surface TX-100 by the volume of 0.8 mL at $80^{o}C$ degree of the critical temperature needed to form a cloud point. Where the rich phase by lead complex is separated and dissolved in ethanol and is determined by spectrophotometric method at λ_{max} = 437 nm. The optimum pH = 9 and 30 μg / 5 mL of Pb^{+2}. The values of the thermodynamic functions for extracting the ion association complex of Pb^{+2} ΔH_{ex} = − 0.005214 kJ, ΔS_{ex} = + 188.036 J, and ΔG_{ex} = − 66.382 kJ, as the study of the molar composition of the ion association complex obtained by following the slope analysis is (1:1). The method gave an enrichment factor 13.428 and a reconcentration's 6.25.

Keywords. Pb^{+2}, Azo compound, TX-100, Removal, Cloud point Extraction CPE, Spectrophotometry, Treatment

Introduction

The lead element or Pb is classified as a toxic metal that tend to be concentrated in humans and environmental systems. Lead has been demonstrated to be accumulated in bone and in some soft tissues, such as kidney, liver, and brain (1). The evaluation of heavy metal pollution in soil and plants is crucial and has garnered significant scientific interest in recent years. This is done to determine their specific effects, particularly on the ecology of arable soils.Many studies have examined the toxicity of Pb^{+2} among heavy metals (2). Its presence in biological fluids. These studies mostly look at the effects of overexposure (3-4). The safe concentration ranges for both elements (5-6). It is considered that acceptable concentrations of Pb^{+2} in human blood under 100 mg. However, individual susceptibility to biological effect can vary. Therefore, it is essential to closely observe the levels of lead in soils and plants during environmental research and to evaluate occupational and environmental exposure. To accurately detect lead ions at very low levels in environmental samples, it is important to separate and pre-concentrate them due to the intricate nature of soils and the relatively low concentration of this metal.

Lately, to find out how to study Pb^{+2} in different matrices, scientists have used spectrometric methods like ETAAS, FAAS, ICP-OES, and ICP-MS to separate and concentrate the particles (3). Another study investigation included deposition of electrochemical (4), precipitation and coprecipitation (5-6), liquid-liquid extraction LLE (7-8), SPE solid-phase extraction (9-11), and liquid-liquid microextraction LLµE (12). While many extraction methods have demonstrated satisfactory extraction efficiency and high preconcentration factors, they have also exhibited limitations related to sample contamination. The limitations encompass factors such as the consumption of significant time and resources, the inflexible regulation of conditions, the necessity for a substantial quantity of organic solvents, and the comparatively subpar level of precision. To separate and preconcentrate metal ions after they form chelates or ionassociation complexes, The CPE technology most environmentally friendly green chemistry techniques. It is also one of the important methods for separating, extracting, and enriching trace elements, which are present in very small quantities in different environmental and life models (13).

Analytical chemistry commonly employs the CPE method as a substitute preconcentration technique for classic extraction systems due to its effectiveness, easiness, affordability, commercially accessible surfactant, speed, and safety (14). The technique can analyze a diverse range of substances, including metal ions and organic species, whose characteristics can vary greatly. It is also applicable to a wide array of analyses (15). The researchers did another study using polyethylene glycol-mono-*p*-nonylphenylether PONPE 7.5 as a micelle-mediated extracting method (16) after mixing water samples with 1-(2-pyridylazo)-2-naphthol PAN. Researchers

prepared a new azo substance, 2-(cefpodoximeazo)-4-nitro-2-phenol CefAN, using a united reaction for CPE for Ni^{+2} complex determine in real samples (17), as shown in FIGURE 1. In all of the above studies, lead has a high toxicity influence. So, in this study, we suggested the CPE method as a way to separate, enrich, and estimate Pb^{+2} by combining an organic reagent (18).
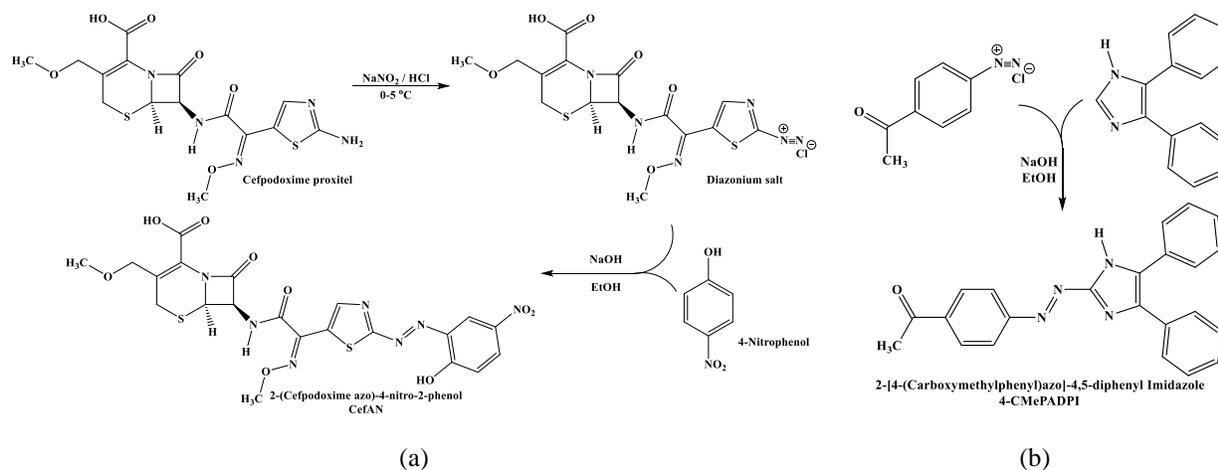

(a) (b)

FIGURE 1. The chemical structures of (a) CefAN (17) and (b) 4-CMePADPI (18)

Expermental Parts

Apparatus

The absorption spectra of the complex were scanned using the UV-Vis spectrophotometer model UV1700 from Japan. At the same time, absorbance measurements of all analytes were taken using the single-beam UV-Vis spectrophotometer TRIUP International CORP-TRUV 745 from Italy. The operating conditions adhered to the manufacturer's recommendations, unless otherwise indicated. A galvanothermy thermostatic bath from Gerhardt, Germany, was utilized to precisely regulate the appropriate temperature to induce phase separation.

Reagents and Solutions

Only high-quality analytical reagents have been used that did not require any further purification for our experiments. Purified water underwent two distillation processes to dilute the reagents and samples. The non-ionic surfactant Triton X-100, having a chemical structure of C8H17C6H4(OC2H4)n, where n is equal to 9-10, and an average molecular weight of 625 g/mol, was

obtained from Sigma (Sigma Ultra, > 99.6 %, UK) and utilized without any additional purification. A reagent called 4-CMePADPI was produced in the laboratory (18).

A 1% (w/v) solution of TX-100 is produced by dissolving 1.0 g in 100 mL of water. A solution with a concentration of 1.0×10^{-2} M of 4-CMePADPI is produced. A concentrated solution containing 1000 µg.mL-1 of lead ions is created by dissolving a suitable quantity from pure $Pb(NO_3)_2$ compound in water. The Pb^{+2} standard solutions use in the experiment is preparing by diluting the stock standard with water. The glassware was immersed in a solution of 4.0 M HNO_3 overnight and thereafter rinsed with double-distilled water prior to utilization.

Recommended Procedure

The extraction experiments for Pb^{+2} was performed in the water solution under optimal conditions. A 5 mL water solution containing a specified amount of Pb^{+2} was obtained. The acidity of the solution is adjusted at the optimal acidic function and also contains 4-CMePADPI ion is under study with a specific amount of Triton X-100 and is put in a water bath at optimum thermal temperature and optimal heating time. The complex consists of metal ion with the organic reagent. The complex is assembled in the form of micelles on the surface and the surface is aggregated to be called the CPE point. For water solution and the residual is estimated from the ionized ion is obtained from water solution using the color method as diethiazone method (19), and by reference to the ion calibration curve we obtain the amount of residual metal ion in the water solution. By subtracting the amount of residual metal ion in the water phase from the total quantity already present in the solution, the metal ion distributed to the organic phase and the joint in the complex formation with the detector were estimated in the cloud point layer with the surface and Triton X-100. Then the calculate of the distribution ratio D for the metal ion under study according to the following relationship, Equation 1:

$$D = \frac{[M^{+2}]_{org.}}{[M^{+2}]_{aq.}}$$ (1)

Results and Discussion

Absorption Spectra

The UV-Vis spectra for 4-CMePADPI solution and its ion-association complex with Pb+2 were measured using a Shimadzu model UV1700 spectrophotometer. The measurements were taken after the addition of a surfactant, following the prescribed technique. The measurements were conducted using a quartz cell with a length of 1.0 cm. The concentration of Pb+2 in the 30 µg / 5 mL standard solution is selection to verify this product of the ion pair complex and determine the optimal wavelength. According to the CPE process, the absorption complex had a maximum wavelength of 437 nm, as shown in FIGURE 2.
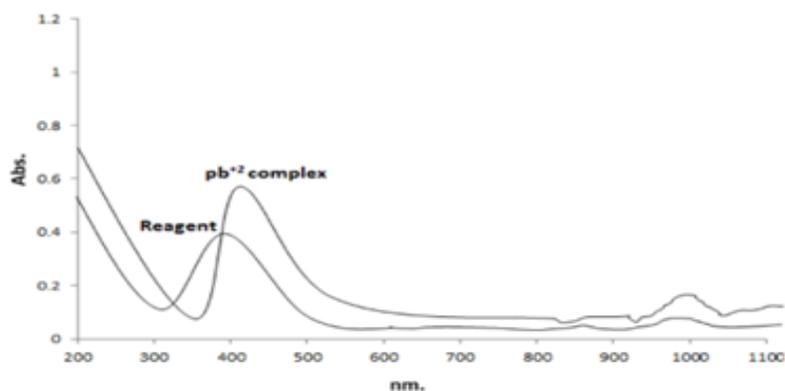

FIGURE 2. The molecular absorption spectra of 4-CMePADPI and Pb^{+2} complex in micelle dissolved in ethanol (Conditions: 0.8 mL 1% TX-100, 5 x 10^{-4} M of 4-CMePADPI and 30 µg / 5 mL Pb^{+2} mL^{-1}

Optimizing the variables of the CPE methodology

1) Impact of Changes in Triton X-100 Concentration

The CPE states that surface concentration is a key factor in defining extraction efficiency and the construction of the micelles. To illustrate this role, the extraction of Pb^{+2} as in recommended procedure in the presence at different concentrations of Triton X-100 within the range of volumes 0.1-0.9 mL. Then, the *D* distribution values were calculated. The results show as in FIGURE 3. Explain the optimum concentration of the Triton X-100 surface gave the highest absorption value of distribution ratios *D* and the percentage of extraction were 0.8 mL and when the detector was used, which is the optimum concentration in which we will reach the equilibrium state for extraction process to formation the smaller and denser cloud point layer. The lower concentration of the optimum concentration will not give us sufficient chance to form a point layer thus, the absorption value and the values of the distribution ratios *D* decrease due to the lack of access to the optimal equilibrium state as well as the distribution and spread of the micelle in the water layer. So, the larger sizes of the optimum size showed decreases in the absorption and distribution

ratios D values. This confirms the main fact that the technique drawspoints a cloud requires the smallest size of the surface, which is the critical size that will lead to optimal clustering under the conditions of the thermodynamic equilibrium.
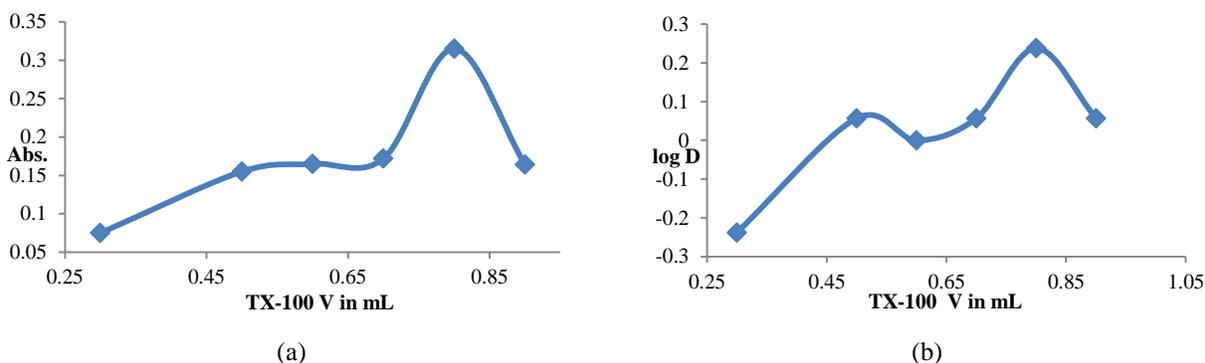

(a)   (b)

FIGURE 3.(a) The influence of Triton X-100 on the absorbance of Pb+2 complex formed by CPE with reagent at 30 μg /5 mL Pb^{+2}, pH = 9 and 5 x 10^{-4} M of 4-CMePADPI, and (b) Effect of Triton X-100 of Pb^{+2} complex formation with reagent by CPE on D distribution values at 30 μg / 5 mL Pb^{+2}, pH = 9 and 5 x 10^{-4} M of 4-CMePADPI

2) Effect of pH on CPE

The pH which contributes in ion bonding between organic reagent and Pb^{+2}. In order to demonstrate this effect, the extraction processes of lead acid ions have very important role and effect to formation the active aggregates in the organic reagent molecule as in recommended procedure in the presence of pH = 7-10. Then, the calculation of the values for the distribution ratios D and the results shown in FIGURE 4. That optimal acid function value to extraction process is optimum pH = 9 of Pb^{+2} with 4-CMePADPI. The absorption values and distribution ratio D at acid pH are low, due to the acid medium is an unsuitable medium for extraction that caused lone ion pair protonation in low pH as well as in high pH Pb^{+2} give OH complex compete the ion pair association complex this procedure sensitive Pb^{+2} in pH 9.

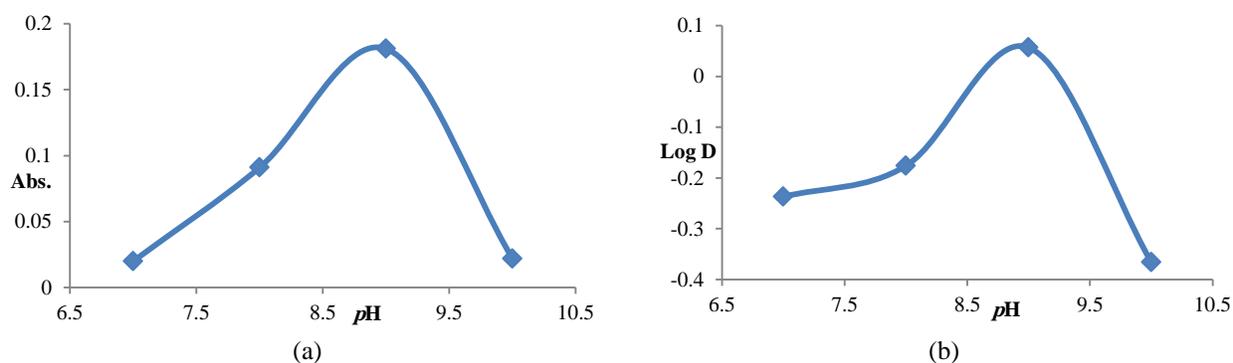(a)   (b)

FIGURE 4. (a) Effect of pH on the complex formation by CPE at 30 μg / 5 mL Pb^{+2}, 5 x 10^{-4} M of 4-CMePADPI and 0.8 mL of 1% (W/V) Triton X-100, and (b) Effect of pH on distribution ratio D

3) Kinetic study and Effect of Heating Time in the Extraction Process and CPE

To explain a role heating time effective on extraction process, the formation, stability complexes, formation CPL, effect on the absorption values of the extracted complex to the cloud point layer and the values D ratios. Therefore, extraction of Pb^{+2} ion as in recommended procedure. The results are shown in the FIGURE 5. The results and graphs showed that the optimum heating time values in the extraction process were 10 min. to reach the equilibrium state as the kinetic process, which allows the formation of the cloud point layer in the smallest size, highest density and high stability and access. At this time and at optimum temperature, the solution will be separated into two distinct layers of high density layer formed from the conglomerate and the mass of the micelle and the water solution layer. The process of heating below optimum time will not provide sufficient opportunity to form the cloud layer containing the lead complex with the organic reagent, which is mainly related to the complexity and stability of the complex and this will cause a decrease in absorption values and distribution ratios.
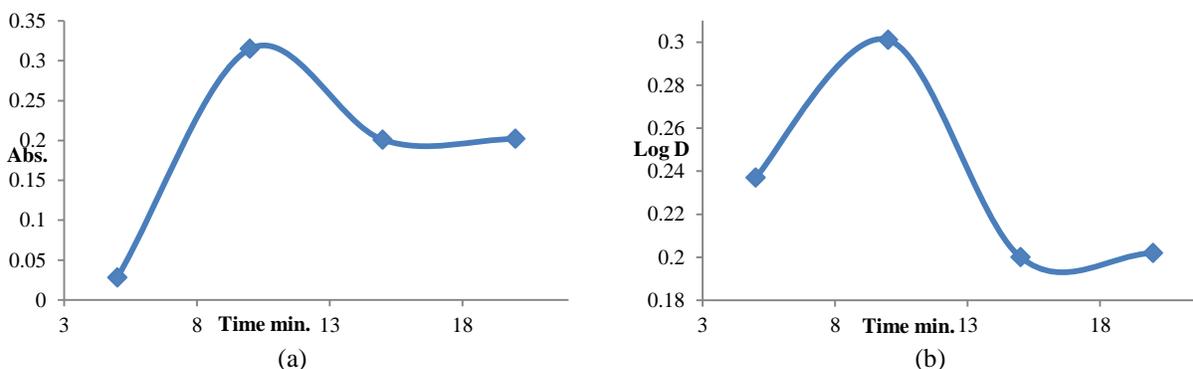

FIGURE 5. (a) Effect of time on the complex formation by CPE at 30 μg / 5 mL Pb^{+2}, 5 x 10^{-4} M of 4-CMePADPI and 0.8 mL of 1% (W/V) Triton X-100, and (b) Effect of heating time on the values of the distribution ratios of the Pb^{+2} with the organic reagent 4-CMePADPI

4) Complex Structure and Effect of Reagent Concentration: The Extraction Process and CPE

To illustrate the role of the organic reagent on the extraction process, the formation, stability complex, the formation cloud point layer COL and its effect on the absorption values of the extracted complex to the cloud point layer and the values of the D distribution ratios, as in recommended procedure. The following results are explained in FIGURE 6a. When plotting the Log D vs Log 4-CMePADPI give a linear line of slope calculation. FIGURE 6b shows that the complex structure is 1:1.

(a)

$y = 0.5759x + 2.4967$
$R^2 = 0.9012$

(b)

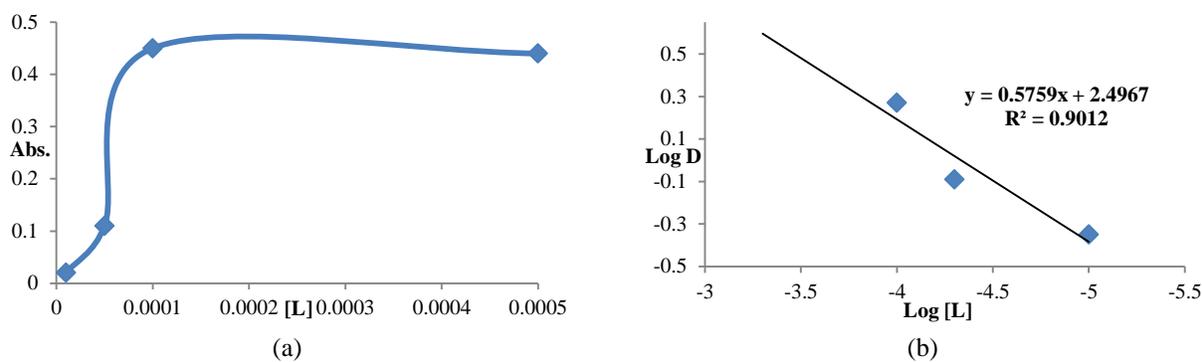**FIGURE 6.** (a) Effect of reagent concentration on extracted Pb^{+2} complex by CPE at 30 μg / 5 mL Pb^{+2}, and 0.8 mL of 1% (W/V) Triton X-100, and (b) Effect of 4-CMePADPI concentration on D values at 5 mL of aqueous soln. have the residual of Pb^{+2} ion at pH = 9 and 1 x 10^{-4} M D_zH Reagent in CCl_4

5) Thermodynamic Study and Effect of the Equilibration Temperature on the Extraction Process and CPE

Extraction process according to CPE have isotherm of the separation and extraction processes requires heating the water solution to a certain temperature to form the small and high-density cloud point layer resulting from the micelle to determine the optimum thermal degree as in recommended procedure. The values of K_{ex} extraction constant were calculated at each temperature by applying the following relationship, Equation 2:

$$K_{ex} = \frac{D}{[M^{+2}]_{aq.} * [L]_{org.}} \qquad (2)$$

Due to the large number of micelles that formed at CPE, there was great phase separation at 80^oC. This allowed big hydrophobic complexes to move into an organic-rich phase which made it more sensitive. Thermal decompose for ion-pair association complexes may occur over 80^oC, resulting in decreased separate of efficiency, as shown in FIGURE 7. The equilibrium temperature is 80^oC use in all experiments.
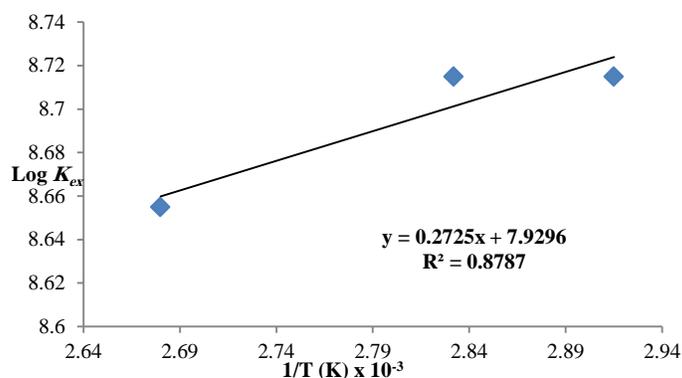
FIGURE 7. Illustrates the impact of temperature on the production of ion pair complexes by CPE at 30 µg / 5 mL Pb^{+2}, 1×10^{-3} M CV and 0.8 mL of 1% (W/V) Triton X-100 with heating time 10 min. at 80°C and $pH = 9$

6) Thermodynamic Study

The parameters for equilibrium extraction are found out what K_{ex} and the thermodynamic factors are for getting the association complex out during the cloud point. The equilibrium constants K_{ex} at the specified temperature were computed using Equations 3, 4, 5, and 6. TABLE 1 and FIGURE 7 present the findings. Thermodynamic parameters were computed using the aforementioned relationships (20). The results are summarized in TABLE 2.

$$K_{ex} = \frac{D}{[Pb^{+2}]_{aq.}*[4-CMePADPI]} \qquad (3)$$

$$Slope = \frac{-\Delta H_{ex}}{2.303\,R} \qquad (4)$$

$$\Delta G_{ex} = -R\,T\,\ln K_{ex} \qquad (5)$$

$$\Delta G_{ex} = \Delta H_{ex} - T\,\Delta S_{ex} \qquad (6)$$

TABLE 1. Illustrates the relationship between the equilibrium constant and the temperature during CPE

$T^{o}C$	$T^{o}K$	$1/T\ ^{o}Kx10^{-3}$	$K_{ex}x10^{8}$
70	343	2.915	5.19
80	353	2.832	6.92
90	363	2.754	3.02
100	373	2.680	4.52

The plot of log K_{ex} vs 1/T in FIGURE 7 yielded the value of enthalpy ΔH_{ex}, which was $- 0.005214$ kJ.mol^{-1}, value Gibb's free energy ΔG_{ex} is $- 66.382$ kJ. The values of entropy ΔS_{ex} are calculated, all data in TABLE 2. Due to ΔH_{ex} is negative, the results showed that getting an ion-pair complex out of a solution is simple and thermodynamically good. This makes micelles less watery (*i.e.*, $\Delta H_{solv.}$ goes down

and $\Delta H_{hyd.}$ goes up), which raises the phase-volume ratio and improves the efficiency of the extraction, Equation 7.

$$\Delta H_{ex} = \Delta H_{solv.} - \Delta H_{hyd.} \qquad (7)$$

TABLE 2. Thermodynamic Parameters for the Extraction of Ion-Pair Complex by CPE

$T°$K	ΔH_{ex} kJ	ΔG_{ex} kJ	ΔS_{ex} J
353	− 0.005214	− 66.382	+ 188.036

7) Application on Real Samples

To apply this method on real samples, the calibration curve was studied, and it was giving following figures of merit y = 0.0078x − 0.0014, r = 0.9983, r2 =99%, rang ppm 1-9, LOD 0.6215 and LOQ 6.215. The applied of [Pb] in TABLE 3 in real samples use *t*-test was Xd = 69.9925, Sd =13.0121, t_{cal} at (n5) = − 9.9998, t_{crit} at 95% 2.571, and *p*-value = 10.5693.

TABLE 3. Some Applications of the Method on Real Samples the samples prepared by wet digestion(16)

Samples	[pb] ppm	FAAS ppm
Fish from River	1.4875	0.18008
Water River	0.4052	0.15312
Eggplant	0.4976	0.39012
Cucumber	0.4991	1.9584
Pumpkin	0.51251	0.0421

Conclusion

The essay discusses the process of separating, removing, and concentrating lead as an ion-association complex into a phase rich in surfactants. This is achieved through a one-factor extraction method using chelate reagents. The essay also explores the use of organic reagents and the CPE technique in conjunction with spectrophotometry for the extraction and determination of Pb^{+2}. The findings we have achieved are sufficient to proceed and do additional work. 1. Our primary objective is to enhance the sensitivity of approaches used in this particular field. Despite the overall improvement in analytical data, we have successfully achieved high extraction efficiency with positive applications in biological and environmental fields. 2. The thermodynamic study still requires significant work, to understand solubilization mechanism of molecular structure in CPL. To do this, they need to

look into how other factors, like changing the amount surfactant, reacting species at room temperature in $^{\circ}$C, affected in creation of an ion-pair association complex. However, remember that implementing a metal cation, such as the Pb analysis by CPE. 3. It can be challenging. Optimization chemical variables is study has partially alleviated these limitations. 4. The proposed procedure has the popularity of the UV-Vis spectrophotometric by CPE, solvent-free cations extraction from matrices. This method has proven relatively simple, sensitive, precise, and accurate, making this method a viable alternative to atomic spectrometric techniques. 5. Water can be removed and purified from heavy metal ions and organic compounds using inexpensive assay methods.

Conflicts Of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

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