

Cloud Point Extraction and Micro Amount Determination of Cadmium as Chloro Anion Complex in Real Samples by using Molecular Spectrophotometry

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الخلاصة

طريقة جديدة لفصل واغناء وتقدير الكاديوم على هيئة ايونات سالبة بتقنية الاستخلاص بنقطة الغيمة بالازدواج مع تقنية التقدير الطيفي . تتضمن طريقة الاستخلاص بتحويل الكاديوم الموجب الثنائي بواسطة محلول حامض هيدروكلوريك الى معقد ايوني سالب واستخلاصه على هيئة معقد ترابط ايوني كاره للماء مع صبغة البلورات البنفسجية ككاشف عضوي والذي يستخلص بدوره الى السطح غير الايوني عند درجة الحرارة الحرجة لنقطة الغيمة . بعد فصل الطور الغني بالمعقد يذاب في الايثانول وقد قدر ايون الكاديوم بالطريقة الطيفية عند الطول الموجي 449 nm وكانت الظروف المثلى للتعقيد والاستخلاص والاغناء باخذ نموذج 10 مل اعطى معامل اغناء 125 واستعدادية 150 واعطى منحني المعايرة خطية ضمن مدى من التراكيز 0.25-5 مايكروغرام وبمعامل تصحيح 0.9995 وحدود كشف 0.042 مايكروغرام و كان الانحراف القياسي للتقدير عند الاستعدادية ل 3 مايكروغرام بحدود 2.68% كما طبقت الطريقة لتقدير الكاديوم في التربة والخضروات و الاوراق و النباتات وعينات الماء والذي تمت مقارنتها مع نتائج قياس الامتصاص الذري اللهب.

Abstract

A new procedure for the separation, preconcentration and determination of cadmium as a chloro anion was presented by using the combined cloud point extraction (CPE) methodology and molecular spectrophotometry. The extraction process involved the conversion of cadmium (II) ion in acidic aqueous solution into chloro anion $[CdCl_4]^{2-}$ complex and subsequently the hydrophobic ion-pair complex formed with crystal violet (CV) cation was extracted into the nonionic surfactant (Triton X-100) rich phase at a temperature above its cloud point (CPT). After phase separation, the surfactant-rich phase was diluted with ethanol and cadmium (II) ion determined by UV-Vis spectromphotometric technique at λ_{max} of 449 nm. The optimization of complexation and extraction conditions was investigated. Thermodynamic parameters of CPE for solubilization process of the ion-pair complex in Triton X-100 were also considered. Under the optimized conditions, the preconcentration of a 10 mL sample gave preconcentration and enrichment factors were of 125 and 150 respectively. The calibration graph was linear in the range of $0.25-5 \mu\text{g mL}^{-1}$ with a correlation coefficient of 0.9995 and limit of detection of $0.042 \mu\text{g mL}^{-1}$. The relative standard deviation for replicate determinations at $(3) \mu\text{g mL}^{-1}$ level was of 2.68%. The proposed method was applied for the determination of cadmium in soil, vegetables, plant leaves and water which gave satisfactory results relative to results obtain by AAS method

Keywords: Cadmium chloro anion, Crystal violet cation, Triton X-100, Cloud point extraction, Spectrophotometry.

Introduction

The verification of the heavy metals contamination in soil and plants is of vital importance which has occupied much attention by researchers in the last years, in order to pinpoint their impact, especially on the arable soils ecology. Among heavy metals, cadmium is one of the most toxic metals that enter the soil environment via countless routes including industrial and

human activities. Anyhow, anthropogenic influence on cadmium levels in soils depends on the intensity of human activity, distance from pollution sources, and pollutant dispersion pattern [1].

Cadmium accumulates in soil where it can be transferred to plant nutrition, followed by a transfer to humans through the food chain, and causing a potential risk to human health [2]. The long-term exposures to cadmium by humans result in kidney damage, bone deformities, and cardiovascular problems. However, FAO/WHO recommends that a tolerable intake for cadmium of 7 $\mu\text{g}/\text{kg}$ body weight/week [3]. Thus monitoring of cadmium in soils along with plants becomes necessarily of a high primacy and significance in environmental researches and humans health in order to evaluate occupational and environmental exposure. Due to the low concentration for this metal and the complexity of soil matrices, separation, preconcentration, and accurate determination of cadmium ion at trace and sub-trace levels in environmental samples are a must.

Recently, procedures involving separation and preconcentration for the determination of cadmium in various matrices using spectrometric techniques, such as FAAS, ETAAS, ICP-OES and ICP-MS, are well reviewed [4]. These include electrochemical deposition [5], precipitation and coprecipitation [6, 7], liquid-liquid extraction (LLE) [8, 9] solid phase extraction [10-12] and liquid-liquid microextraction [13]. Although, some of these protocols of extraction have offered appropriate extraction efficiency and high preconcentration factor, but they have presented some drawbacks associated with sample contamination, relatively time consuming or high cost, rigid control of the conditions, require a large volume of organic solvents and relatively poor accuracy.

In the last decade, the separations and preconcentrations of metal ions, after the formation of chelates or ion-association complexes, based on cloud point extraction (CPE) has been extensively used in analytical chemistry as an alternative preconcentration method to traditional extraction systems due to its efficiency, simplicity, low cost, commercially available surfactant, rapidity and safety [14] compared with majority of the above-mentioned procedures. Numerous reports have been published in the chemical literatures on the preconcentration of cadmium, alone or with other elements, by CPE methodology prior to its determination using different instrumental techniques including flame atomic absorption spectrometry [15-19] electrothermal atomic absorption spectrometry [20-22] and inductively-coupled plasma atomic emission spectrometry [23, 24].

UV-Vis. spectrophotometry is still the most attractive and popular method and employs in different fields of chemical analysis, especially in quality control due to availability of the instrument in many laboratories, the simplicity of analytical procedure, and satisfactory precision and accuracy. The combination of spectrophotometric detection with cloud-point extraction was first proposed by Watanabe and co-workers [25, 26] who studied the extraction for the preconcentration of Mn and Zn in water samples after complexation with 1-(2-

Pyridylazo)-2-naphthol (PAN) using polyethylenglycol-mono-p-nonylphenyl ether (PONPE 7.5) as a micelle-mediated extracting. To the best of our knowledge, there is no application of the combined CPE-spectrophotometric determination of cadmium in soil and plant matrices.

In this work was describes a developed method for the determination of cadmium in soil, plant and water samples by using the combined CPE UV-spectrophotometry. The method involved the conversion of cadmium (II) ion in acidic aqueous solution into chloro anion $[\text{CdCl}]^{2-}$ complex and subsequently formation of hydrophobic ion-pair complex with crystal violet (CV) cation in the presence of Triton X-100 as a nonionic surfactant for the first time. The separated surfactant-rich phase was diluted with ethanol and cadmium (II) ion determined by UV-Vis spectromphotometry in soils plant matrices and water. The possibility of thermodynamic behavior of the extraction of cadmium as ion-pair by CPE was also considered.

Experimental

Apparatus

A Shimadzu double beam UV-Vis spectrophotometer model UV1700 (Japan) and single beam (UV-Vis) spectrophotometer TRIUP international CORP-TRUV 745 (Italy) were used for scanning the absorption spectra of the complex formed and absorbance measurements of all analytes respectively .The operating conditions were those recommended by the manufacturer, unless specified otherwise .A Galvanothermy thermostatic bath(G, Gerhardt, Germany) was used to control the desired temperature so as to achieve the phase separation.

Reagents and Solutions

All the chemicals used were of analytical reagent grade, and were used without further purification. Doubled distilled water was used for diluting the reagents and samples. The nonionic surfactant (Triton X-100) whose chemical structure is $\text{C}_8\text{H}_{17}\text{C}_6\text{H}_4(\text{OC}_2\text{H}_4)_n$ with n equal to 9-10 and an average molecular weight of 625 g/mol, was purchased from Sigma (Sigma Ultra , >99.6%). (UK) and used without further purification. A crystal violet reagent was obtained from Sigma Ultra (UK).

A solution of 1% (w/v) of Triton X-100 was prepared by diluting 1 g of reagent in 100 mL water. A 1×10^{-2} M of CV was prepared by dissolving of 0.4079 g in water. A stock solution of $1000 \mu\text{g mL}^{-1}$ of cadmium ion was prepared by dissolving an appropriate amount of high purity compounds of CdCl_2 in water. The working Cd^{2+} standard solutions were obtained by appropriate dilution of the stock standard with water. All glassware were soaked in 4M HNO_3 overnight and cleaned with doubled distilled water prior use.

Recommended Procedure

For cloud point extraction, aliquots of 10 mL of the standard or sample solution containing the analyte in 1M HCl ,crystal violet (1×10^{-3} M) and Triton X-100 (0.8 mL of 0.1% w/v) were allowed to stand for 10 min in a thermostated bath at 80°C . Separation of the two phases were

occurred immediately where the surfactant-rich phase became a highly viscous (without need of centrifugation and cooling) and settled down at the bottom of the tube making the aqueous phase easily discarded by simply inverting the tube. Later, the surfactant-rich phase in the tube was dissolved in 5 mL of ethanol and the absorbance of the resulting solution was measured at 449 nm in a 1-cm cell against a reagent blank.

Preparation of Samples

A duplicate sample (soil or plant) solution was prepared by transferring approximately 5 g of dried sample into a 50 mL conical flask and adding 10 mL of concentrated HNO₃. The contents of the flask were heated on an electric hotplate until the volume was reduced to 2-3 mL. After cooling, a further of 10 mL of concentrated HNO₃, 5 mL of concentration H₂SO₄ and 4 mL H₂O₂ were added and the content reheated to boiling until the volume became 2-3 mL, then 10 mL of water were added until colorless solution was obtained indicating of the oxidation of organic matter. The content was cooled and transferred into 100 mL volumetric flask and diluted to the mark with distilled water.

An aliquot of 5 mL of sample solution was pipetted into 25 mL conical flask and treated with 1 mL of 20% potassium sodium tartarate solution with continuous shaking and then filtered. The filtrate was transferred into 10 mL volumetric flask and diluted to the mark with water. The cadmium content was determined according to the recommended procedure. The blank solution was prepared in the same manner without analyte.

Statistical Analysis

All statistical calculations, such as basic statistics, significance tests, regression equations and correlation coefficients for the calibration curves, were implemented using Minitab version 14 (Minitab Inc., State College, PA, USA) and Excel 2007 (Microsoft Office®).

Results and Discussion

Absorption Spectra

UV-Vis spectra of crystal violet cation (CV⁺) solution and its ion-association complex with cadmium chloro anion after addition of surfactant according to the recommended procedure were recorded using Shimadzu model UV1700 equipped with 1-cm matched quartz cell. To verify the formation of ion pair complex and assess its optimum wavelength, the concentration level of Cd²⁺ at 3 μg ml⁻¹ Cd²⁺ (in 0.5 M HCl) standard solution was chosen. It was shown (**Figure 1**) that the λ_{max} for absorption CV⁺ in 1 M HCl without surfactant was of 430 nm and λ_{max} for absorption of ion pair complex [CV]⁺¹[HCdCl]⁻¹ with CPE procedure was of 449 nm.

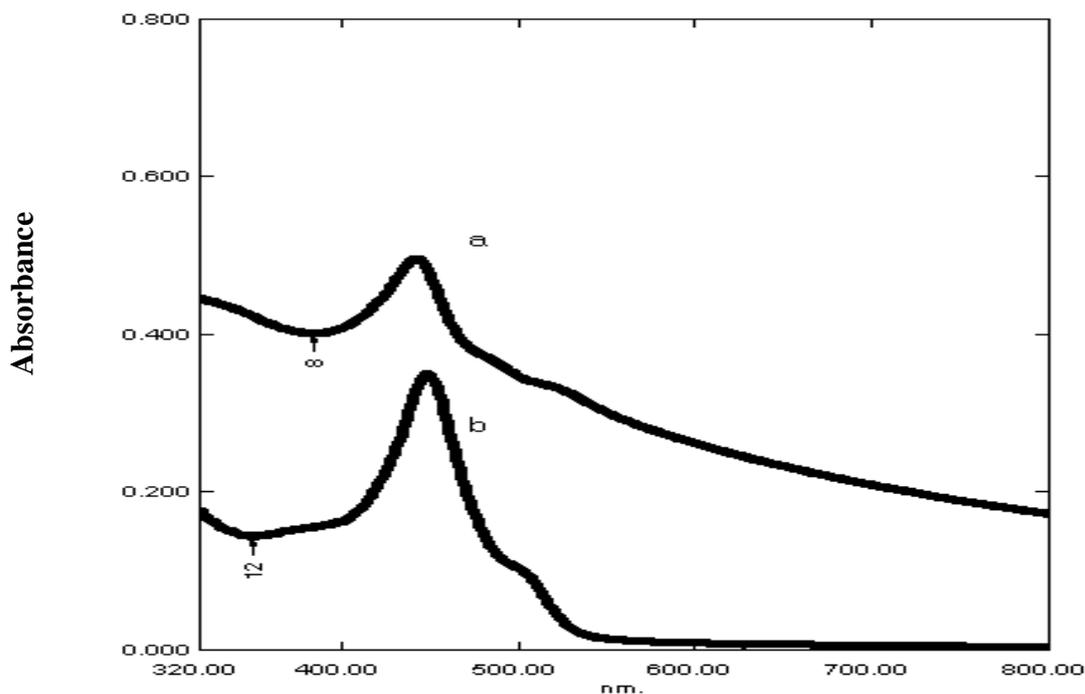


Fig. 1: The Molecular Absorption Spectra of (A) Crystal Violet Cation 1M HCl (B) $[\text{Hcdcl}]^- [\text{CV}]^+$ Complex in Micelle Dissolved in Ethanol (Conditions: 0.5M HCl, 0.8 mL 1% TX-100, 5×10^{-4} M CV and $3 \mu\text{g Cd mL}^{-1}$)

Optimization of Variables of CPE Methodology

Effect of Triton X-100 Concentration: A successful cloud point extraction procedure should maximize the extraction efficiency by minimizing the phase volume ratio, which improve its concentrating ability [27]. The effect of Triton X-100 concentration was investigated between (0.5 to 2 mL) of 1% (w/v) in 10 mL aqueous solution containing $3 \mu\text{g mL}^{-1} \text{Cd}^{2+}$, 0.5 M HCl and 5×10^{-4} M crystal violet. The results are shown in **Figure 2**. Triton X-100 was chosen for the surfactant-rich phase among the other selected surfactants in this study, due to its high extraction efficiency, adequate cloud-point temperature, and high viscosity of the surfactant-rich phase, which easing the phases separation without need of centrifugation and cooling steps. The results have shown that the maximal absorbance signal were achieved when the volume of 1% (w/v) Triton X-100 at 0.8 mL (**Figure 2**) and the absorbance subsequently decreased sharply because of the increment in the overall analyte volumes and viscosity of surfactant phase leading to poor sensitivity. Consequently, the optimum volume of 1% (w/v) Triton X-100 at 0.8 mL was selected for optimal absorbance to achieve the highest possible extraction efficiency and pre-concentration factor.

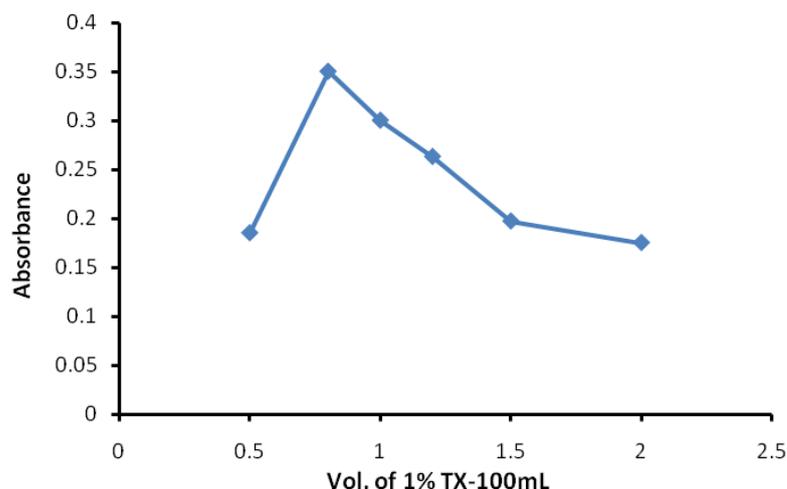


Fig. 2: Effect Of Triton X-100 on The Absorbance of CdCl_4^{2-} Complex Formation with CV By CPE(Conditions: $3\mu\text{g MI}^{-1}$ Cd^{2+} , 0.5 M HCl and 5×10^{-4} M Crystal Violet)

Effect of HCl Concentration on CPE: Because the HCl concentration plays an important role in metal anion CdCl_4^{2-} complex formation with crystal violet and subsequent extraction, the effect of HCl concentration was studied by measuring the absorbance of solutions containing $3\mu\text{g mL}^{-1}$ cadmium as CdCl_4^{2-} with various concentrations of hydrochloric acid (0.1– 3M), 5×10^{-4} M crystal violet and 0.8 ml of 1% (w/v) Triton X-100 as shown in **Figure 3**.

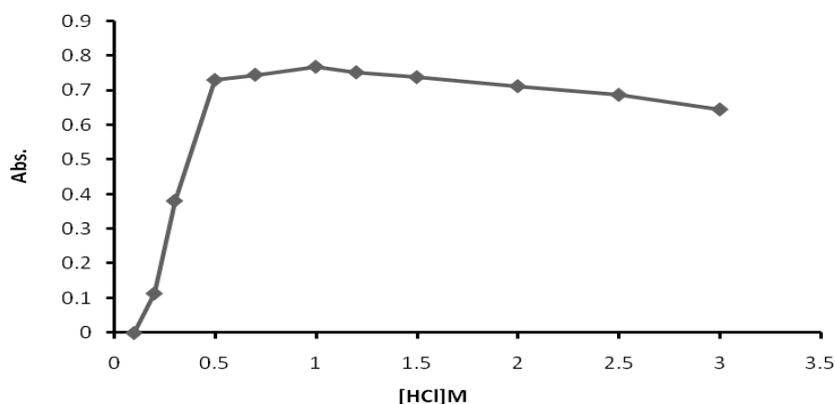


Fig. 3: Effect of HCl Concentration on CdCl_4^{2-} Complex Formation with CV^+ By CPE(Condition: $3\mu\text{g MI}^{-1}$ Cd^{2+} , 5×10^{-4} M Crystal Violet and 0.8 MI Of 1% (W/V) Triton X-100).

The results reveal that the absorbance is almost constant in the HCl concentration range of 0.5-1.5 M. At lower than 0.5 M HCl, the absorbance reduction occurs due to incomplete ion pair complex formation between CdCl_4^{2-} and CV^+ , while the above 1.5 M HCl the absorbance slightly decreases because of the instability of ion pair complex and less micelles formation with surfactant Triton X-100. Thus 1M of HCl was selected as optimum value throughout the experiment.

Effect of CV Concentration: The effect of the amount of crystal violet(CV) was investigated by measuring the absorbance signal (at $\lambda_{\max}=449$ nm) of 10 mL solutions containing $3 \mu\text{g mL}^{-1}$ as CdCl_4^{2-} and various amounts of CV (1×10^{-5} - 5×10^{-3} M) and kept other conditions constant. The results are depicted in **Figure 4**.

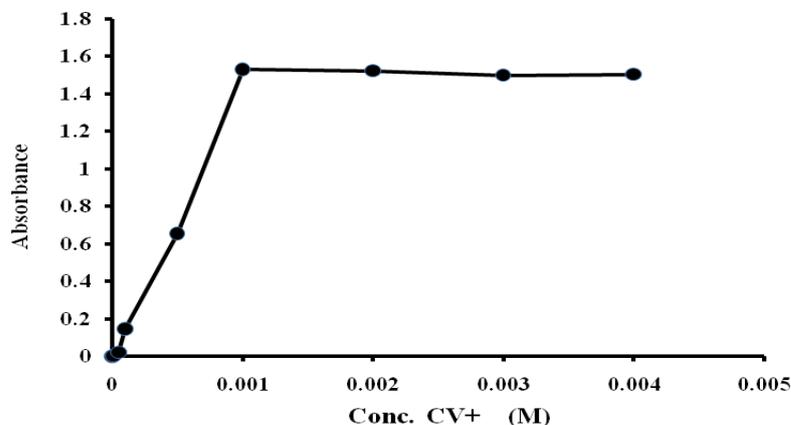


Fig. 4: Effect Of CV Concentration on Extracted of CdCl_4^{2-} Complex By CPE (Condition: $3 \mu\text{g mL}^{-1}$ Cd^{+2} , 0.8 ml of 1% (W/V) Triton X-100).

The absorbance increased linearly with an increase in CV^+ concentration up to 1×10^{-3} M which was sufficient for ion-association complex formation in the extracted medium. Beyond this concentration the absorbance remained constant indicating that the extraction of the complex in micelles medium was independent of further increase in the concentration of CV^+ . Therefore, a concentration of 1×10^{-3} M of CV^+ was decided to be used as optimum. This experiment was also conducted to obtain the distribution ratio (D) from the remainder quantity cadmium as CdCl_4^{2-} by spectrophotometric method (dithizone method) [28] and amount of transferred cadmium as CdCl_4^{2-} to form ion-pair complex as $[\text{CV}^+][\text{HCdCl}^-]$ into surfactant as shown in **Figure 5**.

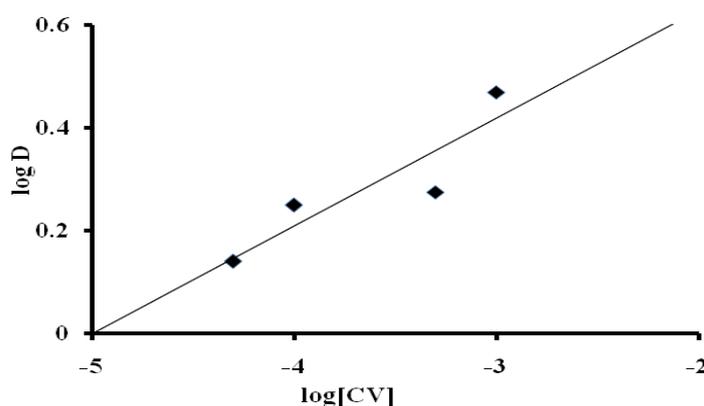


Fig. 5: Effect of CV Concentration on D Values (Condition: 10ml of Aqueous Solution Have The Residual of Cd^{2+} Ion At $\text{pH}=2$ and 1×10^{-4} M D_2H Reagent in CCl_4)

The results have shown that the concentration of 1×10^{-3} M CV provides a high distribution ratio (D) with highly stable ion pair complex formation extractable into surfactant, whereas at 5×10^{-3} M gave complete extraction. At lower than 1×10^{-3} M CV, unstable ion-pair complex was formed which led to depress the extraction into surfactant. Whilst, at higher than of 1×10^{-3} M more dissociation of complex might occur resulting in a negative deviation in the absorbance values because of mass action effect as shown in equilibrium below:



Effect of the Equilibration Temperature and Time: To ensure phase separation and preconcentration of an analyte efficiently, optimal equilibration temperature and time are very crucial parameters for complete reaction. Figure 6 shows the effect of temperature in the range of 80-110 °C at 10 min as a function of absorption signal. Preliminary experiments indicated that at temperature below 80 °C, no concrete phase separation (i.e. two phases weren't formed) was observed due to very low number of micelles formed with the ion-pair association complex stability at this temperature which led to decrease the distinguish organic phase.

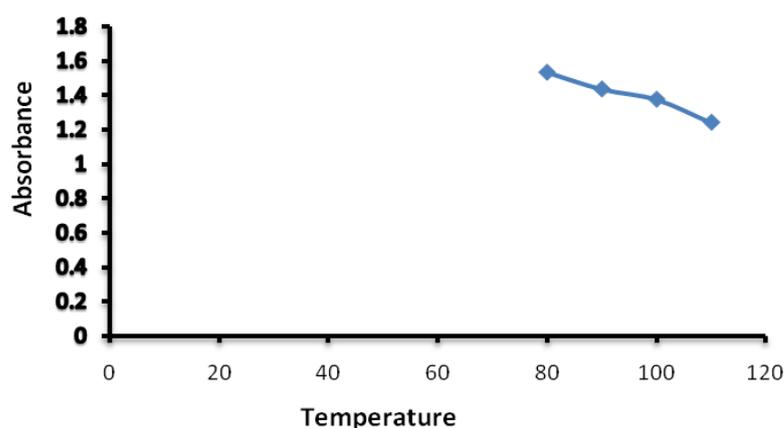


Fig. 6: Effect of Temperature on Ion Pair Complex Formation By CPE
(Condition: $3 \mu\text{g ml}^{-1}$ Cd^{+2} , 1×10^{-3} M CV, 0.8 ml of 1% (W/V) Triton X-100. Heating Time 10 Min. at 80°C and $1\text{M}[\text{HCl}]$).

But, at 80°C excellent phase separation has taken place because of high number of micelles formed at CPT leading the entire transfer of the hydrophobic complex into surfactant-rich phase that maximize the sensitivity. Over 80°C , thermal decomposition of ion-association complex might occur thus decreasing of separation efficiency dramatically as shown in **Figure 6**. So, an equilibrium temperature of 80°C was used in all experiments.

Figure 7 depicts the effect of incubation time on extraction efficiency of ion association complex in the range of 5-40 min at 80°C . It showed that the maximum time of incubation observed at 10 min and beyond this value resulted in poor quantitative extraction probably

due to thermal instability of the complex. Therefore, an incubation time at 10 min was selected as optimal.

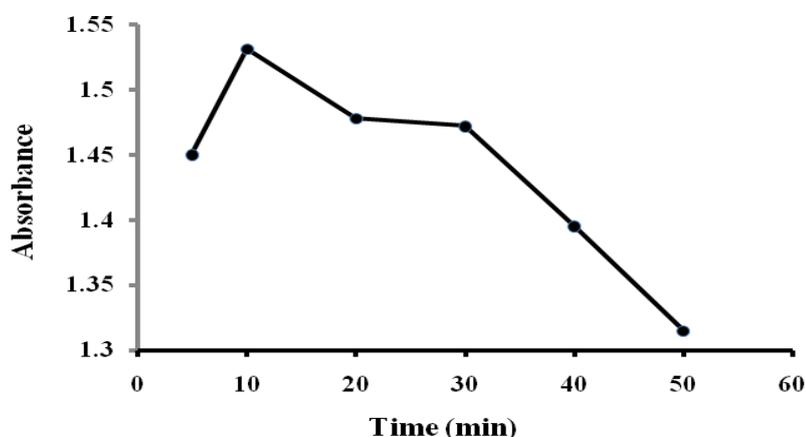


Fig. 7: Effect of Time on CdCl_4^{2-} Complex Formation By CPE(Condition: $3\mu\text{g MI}^{-1} \text{Cd}^{2+}$, 0.8 MI Of 1% (W/V) Triton X-100. Heating at 80c^0 and 1M [Hcl])

Thermodynamic Study: The equilibrium extraction constants (K_{ex}) and thermodynamic parameters for the extraction of $[\text{CV}^+ ; \text{HCdCl}_4^-]$ complex during the cloud point using Triton X-100 as a mediated extracting agent at various temperatures were determined. The equilibrium constants (K_{ex}) at the selected temperature were calculated from equation below and the results are shown in Table 1 and **Figure 8**.

$$K_{\text{ex}} = \frac{D}{[\text{Cd}^{+2}]_{\text{aq.}}[\text{CV}]}$$

Table 1: Variation of equilibrium constant with temperature during CPE

$T^{\circ}\text{C}$	85	90	100	110
$T^{\circ}\text{K}$	358	363	373	383
$1/T$	2.79×10^{-3}	2.755×10^{-3}	2.68×10^{-3}	2.61×10^{-3}
K_{ex}	1.13×10^8	7.68×10^7	3.188×10^7	2.065×10^7

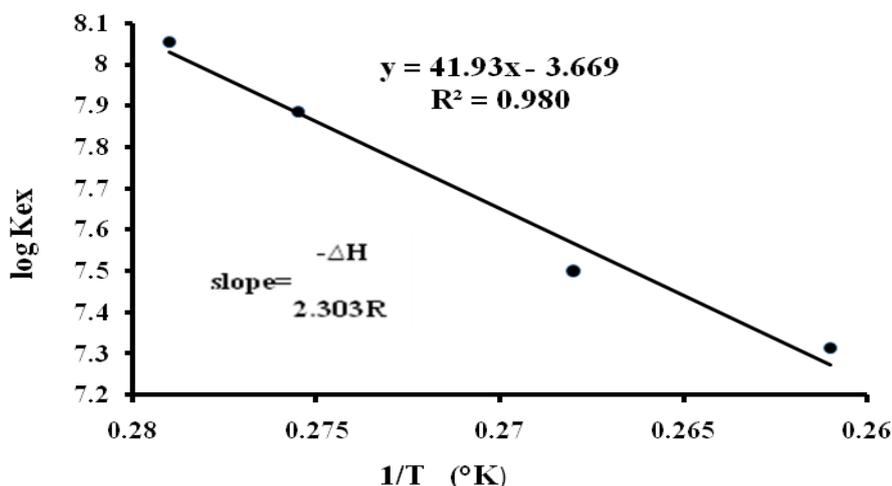


Fig. 8: Effect of The Equilibration Extraction Temperature on Ion Pair Complex Formation By CPE (Condition: $3\mu\text{g ML}^{-1}$ Cd^{2+} , $1 \times 10^{-3}\text{M}$ CV, 0.8 ML Of 1% (W/V) Triton X-100. Heating Time is for 40 Min. at 80C^0 and $1\text{M}[\text{HCl}]$).

Thermodynamic parameters were also calculated from the relationships mentioned elsewhere [29]. The results are summarized in **Table 2**.

Table 2: Thermodynamic Parameters for The Extraction of Ion-Pair Complex By CPE

T(°K)	ΔH_{ex} (KJ mole ⁻¹)	ΔG_{ex} (KJ mole ⁻¹)	ΔS_{ex} (J mole ⁻¹)
353	-0.06283	-53.243	150.6
363		-53.610	147.5
373		-52.419	140.36
383		-52.465	136.682

The value of enthalpy change (ΔH_{ex}) was obtained from the plot of $\log K_{\text{ex}}$ versus $1/T$ (**Figure 8**) and found to be $-0.06283 \text{ kJ mol}^{-1}$ while the values of Gibb's free energy (ΔG_{ex}) were obtained at different temperatures. Once these two parameters are obtained, the values of entropy change (ΔS_{ex}) were also calculated and all data are shown in Table 2. The results revealed that the extraction of ion-pair complex is easy and thermodynamically favorable due to the negative value of ΔH_{ex} which leads to dehydration of micelles (i.e decrease the value of ΔH_{solv} and increase ΔH_{hyd}) and resulting in increasing the phase-volume ratio thus extraction efficiency enhancement.

$$\Delta H_{\text{ex.}} = \Delta H_{\text{solv.}} - \Delta H_{\text{hyd.}}$$

It was also noted from **Table 2** that the values of ΔG_{ex} approximately increased with temperature. The negative values of ΔG_{ex} indicate that the ion-pair complex solubilization process is also spontaneous and thermodynamically favorable [30]. The reaction of extraction by CPE is exothermic reaction and positive value of ΔS_{ex} mean the reaction is entropic inregine.

Selection of Diluents for the Surfactant Rich Phase: Since the surfactant-rich phase obtained after the cloud point preconcentration is a highly viscous layer containing the complex $[CV^+; HCdCl_4^-]$ extracted, the effect of different organic solvents such as amyl alcohol, methanol, chloroform, acetone and ethanol, on the absorption behavior of $[CV^+; HCdCl_4^-]$ complex in the presence of surfactant was investigated. The results are summarized in **Table 3**.

Table 3: Effect of Organic Solvent on The Absorbance

Organic solvent	λ_{max}	Absorbance	Molar absorptivity ($L mol^{-1} cm^{-1}$)
amyl alcohol	443	1.037	3.989×10^4
methanol	433	1.017	3.912×10^4
chloroform	507	0.850	3.077×10^4
acetone	445	0.640	2.462×10^4
ethanol,	449	1.531	5.884×10^4

All the selected solvents gave a good solubility of $[CV^+; HCdCl_4^-]$ complex in micelles phase, but ethanol was preferred to other solvents because of producing the highest analytical signals. Thus the absorbance and hence the molar absorptivity (ϵ) of the ion-pair complex dissolved in ethanol is approximately 1.5- fold larger than in amyl alcohol and methanol and 2-fold larger than in chloroform and acetone. Therefore, ethanol was chosen as the best solvent for reducing the viscosity and facilitating the sample transportation into a quartz cell.

Selection of the Surfactant: In cloud point extraction, the kind of surfactant plays a significant role in the separation process. Therefore, the experiments were conducted according to general procedure by using other surfactants such as, Tween-80 and Tween-20 and SDS. It has shown that the formation of the separated surfactant-rich phase needs a higher temperature than $80^\circ C$ and 15 min for Tween-20 and Tween-80 except that SDS needs approximately $63^\circ C$ and 15 minute. On the other hand, Triton X-100 gave significantly higher distribution ratio than the remainders as shown in **Figure 7**.

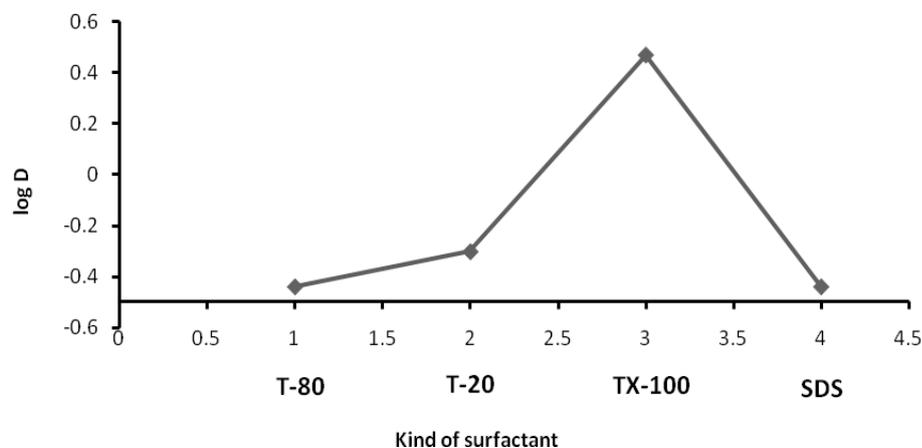


Fig. 7: Effect of The Kind of Surfactant on CPE Efficiency

The presence of ether groups on structure of Triton X-100 is more probable by sharing lone pair electron of which making the hydrogen bonding leading to significant increase of the micelles which reflect higher distribution ratio of the ion-pair complex in Triton X-100 than in the other surfactants studied.

Interferences Effect: Table 4 shows the effect of some salts which contain both cations and metal anions on the extraction of CdCl_4^{2-} by CPE. As a rule cations such as Na^+ , K^+ and NH_4^+ cannot give an evidence for the interfere with CdCl_4^{2-} because they are highly strong acids and thereby cannot form anion complexes capable to compete with interested metal anion complex. Whereas, the anions such as picrate, $\text{C}_2\text{O}_4^{2-}$, ClO_4^- , NO_3^- , $\text{Cr}_2\text{O}_7^{2-}$, WO_4^{2-} and $\text{Mo}_7\text{O}_2^{2-}$ are compete considerably with CdCl_4^{2-} in the formation of ion-pair complexes under the conditions of CPE. It was evident that WO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ anions have the most effect leading to depress the distribution ratio markedly of CdCl_4^{2-} extraction, but NO_3^- had less effect due to its strong affinity toward Na^+ and H^+ ions rather than CdCl_4^{2-} ion in acidic medium (Table 5). Thus this study has proved that the anions according to their mole size and nature in aqueous solutions compete CdCl_4^{2-} ion in the extraction processes by virtue of thermodynamic laws of CPE. However, these anions are not present environmentally therefore no interferences actually exist that affect the CdCl_4^{2-} measurement as shown in Figures 8 and 9.

Table 4: Interferences Effect of Salts on CPE Formation and Effect of Foreign Anions

Interferent	Interferent/Cd(II) Ratio	% E_{rel}	Distribution Ratio (D)
KClO_4	12500	-0.038	1.42
$\text{Na}_2\text{C}_2\text{O}_4$	12500	-0.034	1.31
Picric acid	12500	-0.017	1.38
$(\text{NH}_4)_2\text{Mo}_7\text{O}_2$	12500	-0.034	1.38
Na_2WO_4	12500	-0.030	0.97
$\text{K}_2\text{Cr}_2\text{O}_7$	12500	-0.034	0.85
NaNO_3	12500	-0.030	2.26

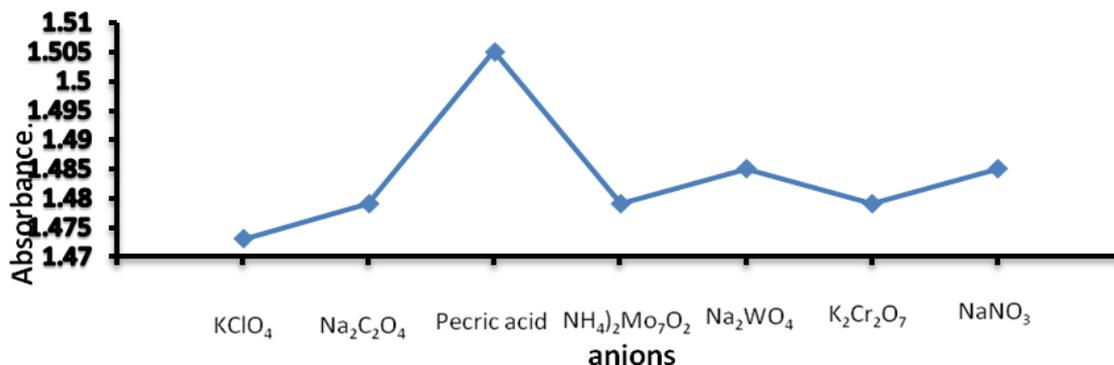


Fig. 8: Interferences Effect of Salts on CPE on CdCl_4^{2-} Complex Formation By CPE (Conditions: $3\mu\text{g ML}^{-1}$ Cd^{+2} , 0.8 ML of 1% (W/V) Triton X-100. Heating at 10 Min., 80C^0 and 1M [Hcl])

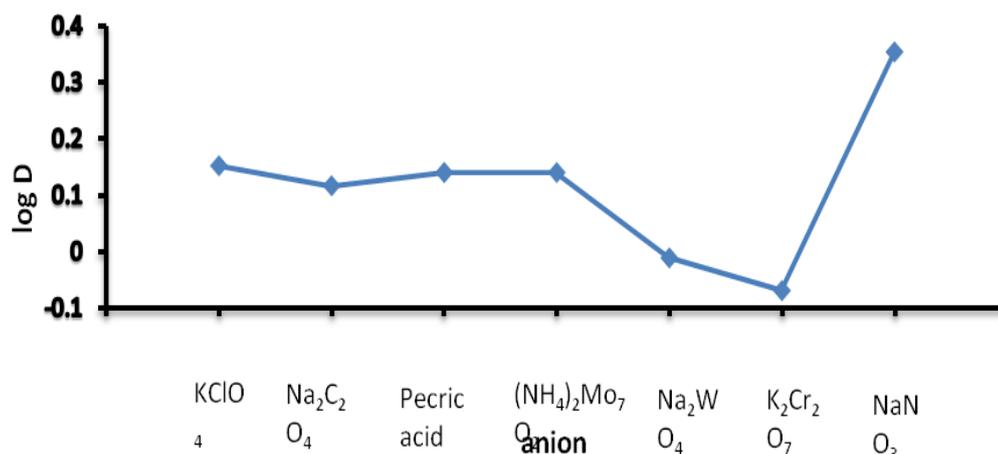


Fig . 9: Interferences Effect on D , Cd- Complex By Dithiazon Method Containing The Residual of Cd^{+2} Ion at pH=2 and 1×10^{-4} M DzH Reagent In CCl_4

Effect of Electrolyte Salts: The effect of the electrolytic solutions like group (I) and (II) metals as chlorides and nitrates were selected on the bases that these anions do not compete the anionic complex under study in the CPE process. However, the presence of such electrolytic salts in aqueous solution somewhat contribute in increasing the ionic activity in solution. Since the solutions used for the extraction of CdCl_4^{2-} were acidic medium at 1 M HCl , the ionic strength played an important role in increasing or decreasing the ionic activity of the anionic complex under study . Therefore, the effect of some of electrolytic solutions upon the extraction of CdCl_4^{2-} complex anion by CPE was investigated.

As shown in Figure 10, there is a little influence for the most electrolyte solutions at different concentrations on the micelles phase containing CdCl_4^{2-} complex through the extraction process but the absorbance has somewhat decreased i.e. most of these electrolytic solutions will decrease the ionic activity of the complex anion under study expect sodium nitrate which

has a significant influence at concentration of 0.2 M. This might be ascribed due to the electrophoretic effect of potassium ion. However, in all cases, the effect of presence of electrolytic salts was explicit on the extraction of CdCl_4^{2-} . Inasmuch as CdCl_4^{2-} anion formed in acidic medium, the electrolyte will probably hinder, to some extent, the formation of anion under study by reducing its thermodynamic formation constant.

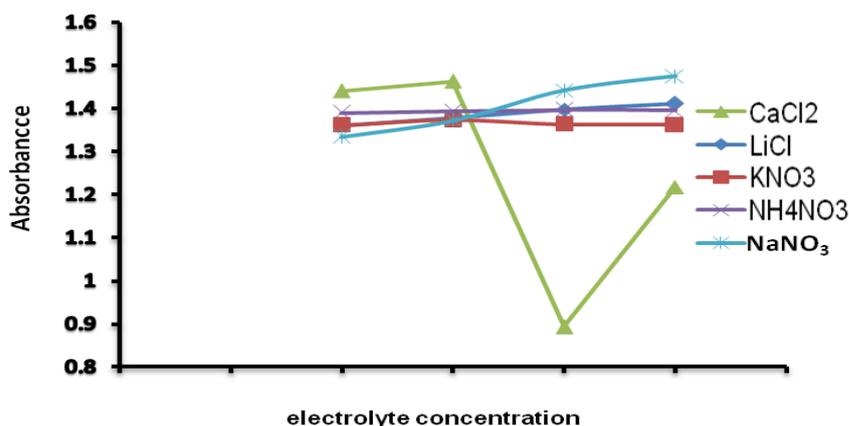


Fig. 10: Effect of Electrolyte Salts on CPE

Analytical Figures of Merit: Calibration curve was obtained by plotting the absorbance versus the concentration of Cd^{2+} via the processing 10 mL standard aqueous solutions containing $(0.2-5) \mu\text{g mL}^{-1}$ of Cd^{2+} as CdCl_4^{2-} under the established optimized conditions. The figures of merit which statistically obtained were summarized in **Table 5**.

Table 5: Figures of Merit for The Determination of Cd By The Proposed Methods

Parameter	Cd (II)
λ_{max} (nm)	449
Regression equation	$y=0.243 x+ 0.013$
Correlation coefficient(r)	0.9995
Coefficient of determination (R^2)	99.9%
C.L. for the slope ($b \pm \text{tsb}$) at 95%	0.243 ± 0.00409
C.L. for the intercept ($a \pm \text{tsb}$) at 95%	0.013 ± 0.010555
Concentration range ($\mu\text{g mL}^{-1}$)	0.25-5.0
Limit of Detection ($\mu\text{g mL}^{-1}$)	0.042
Limit of Quantitation ($\mu\text{g mL}^{-1}$)	0.14
Sandell's sensitivity ($\mu\text{g.cm}^{-2}/0.001\text{A.U}$)	1.1×10^{-4}
Molar absorptivity ($\text{L.mol}^{-1}.\text{cm}^{-1}$)	5.884×10^4
Composition of complex (M: L)*	1:1
RSD% (n=7) at $3 \mu\text{g mL}^{-1}\text{Cd}^{2+}$	2.68%
Preconcentration factor	125
Enrichment factor	150

*obtained by slope ratio method

Very good linearity was obtained in concentration range of 0.2-5.0 $\mu\text{g mL}^{-1}$ for Cd with coefficient of determination (R^2) of 99.9% which suggests a statistically valid fit. Analysis of variance (ANOVA) for the regression line was also carried out as shown in **Table 6**. ANOVA analysis supports that there is a strong significant relationship between the concentration of the analyte and absorbance units as $F_{\text{tab}} = F_{1,9} = 7.209 \ll 17827.08$

Table 6: Analysis of Variance of Regression Line

Source	DF	SS	MS	F
Regression	1	1.5739	1.5739	17827.08
Residual Error	9	0.0008	0.0001	
Total	10	1.5747		

DF=degrees of freedom, SS: sum of squares, MS: mean of squares, F(Fisher F-test)

The regression line was used to estimate the analyte concentration in the samples selected which appears justified on statistical basis. The detection and quantification limits were determined directly from regression model and found to be of 0.042 and 0.14 $\mu\text{g mL}^{-1}$ respectively. This low value of LOD allows working with the smallest concentration range of lowers than 0.25 $\mu\text{g mL}^{-1}$. However, the limit of detection obtained by the proposed method was generally worse than that obtained by FAAS coupled with flow injection analysis and CPE [19]. This is obviously due to the detection limitations of UV-Vis spectrophotometry compared to the above sophisticated methodology. The enhancement factor, calculated as the ratio of slope of calibration curve obtained by preconcentration of sample to that obtained without preconcentration was found to be 150. The proposed method was applied for the determination of cadmium(II) in various samples including soils, plants (vegetable and leaves) and water selected randomly from different areas of the Najaf City (middle of Iraq) in order to test its applicability and reliability. For this purpose, an aliquot of each sample prepared according to (2-4) was preconcentrated following CPE recommended procedure and cadmium determined spectrophotometry. The results of the proposed method for each type of the selected samples were compared with flame atomic absorption spectrometry (FAAS) in our laboratory. The results are summarized from **Table 7** to **11**.

Table 7: Concentrations of Cd ($\mu\text{g G}^{-1}$) in The Non-Agriculture Soil Samples (Roadsides) of The Najaf City (Middle of Iraq).

Sample No.	Proposed method	AAS method	\bar{X}_d	S_d	$t_{\text{cal}} (n=6)$	$t_{\text{crit.at}} 95\% \text{DF}=5$	P-value
1	1.68±0.01	1.61±0.05	0.038333	0.041191	2.27	2.57	0.072
2	1.61±0.27	1.54±0.31					
3	1.14±0.37	1.11±0.23					
4	2.30±0.14	2.25±0.50					
5	0.52±0.11	0.47±0.07					
6	1.23±0.04	1.27±0.40					

Table 8: Concentrations of Cd ($\mu\text{g G}^{-1}$) in The Agriculture Soil Samples (Most of Near of The Rivers) of The Najaf City (Middle of Iraq)

Sample No.	Proposed Method	AAS Method	\bar{X}_d	S_d	T_{cal} (N=6)	$T_{crit. at}$ 95% DF=5	P-Value
1	1.05±0.35	0.98±0.33	0.060000	0.069857	2.10	2.57	0.089
2	1.25±0.03	1.16±0.02					
3	1.53±0.49	1.40±0.50					
4	0.38±0.05	0.42±0.01					
5	0.35±0.04	0.36±0.02					
6	1.15±0.04	1.03±0.05					

Table 9: Concentrations of Cd ($\mu\text{g G}^{-1}$) In The Vegetable Samples of The Najaf City (Middle of Iraq).

Sample No.	Proposed method	AAS method	\bar{X}_d	S_d	t_{cal} (n=6)	$t_{crit. at}$ 95% DF=5	P-value
1	0.080±0.04	0.096±0.03	0.00400	0.011027	0.89	2.57	0.415
2	0.044±0.05	0.048±0.04					
3	0.070±0.01	0.074±0.02					
4	0.068±0.03	0.072±0.02					
5	0.066±0.05	0.078±0.05					
6	0.076±0.05	0.060±0.01					

Table 10: Concentrations of Cd ($\mu\text{g G}^{-1}$) in The Plant Leaves Samples of The Najaf City (Middle of Iraq)

Sample No.	Proposed method	AAS method	\bar{X}_d	S_d	t_{cal} (n=6)	$t_{crit. at}$ 95% DF=5	P-value
1	0.24±0.18	0.25±0.03	0.006667	0.023381	0.70	2.57	0.516
2	0.16±0.02	0.18±0.07					
3	0.15±0.03	0.13±0.02					
4	0.16±0.01	0.14±0.02					
5	0.26±0.12	0.22±0.15					
6	0.13±0.03	0.14±0.02					

Table 11: Concentrations of Cd ($\mu\text{g mL}^{-1}$) in The Water (River and Well) Samples of The Najaf City (Middle of Iraq).

Sample No.	Proposed method	AAS method	\bar{X}_d	S_d	t_{cal} (n=6)	$t_{\text{crit. at 95\% DF=5}}$	P-value
1	0.031±0.008	0.038±0.004	0.017000	0.025954	1.60	2.57	0.170
2	0.027±0.008	0.024±0.005					
3	0.340±0.035	0.360±0.025					
4	0.130±0.495	0.190±0.500					
5	0.220±0.042	0.250±0.020					
6	0.025±0.035	0.013±0.054					

All statistical results performed by the paired t- test for comparison of means between the proposed and AAS methods for all samples (**Tables 7 to 11**) have revealed that all p values [P(T<t) two tailed] based on the 5% critical values of 2.57 (t critical two tailed) were more than the t calculated values indicating acceptance of null hypothesis (H_0) which specified that there appears insufficient evidence to suggest the accuracy of the established (CPE-Spectrophotometry) methodology differs with that of AAS measurements.

From the environmental point of view, the means (and range) concentration of cadmium in both non agriculture and agriculture soils were of 1.41(0.52-2.30) and 0.95(0.35-1.53) as $\mu\text{g g}^{-1}$ respectively, indicating that the extent of cadmium pollution of soil in some places selected in the Kufa city is slightly high (Tables 7 and 8) but appears naturally more significant in non-agriculture soil due to its location in the vicinity to the roadsides which might be polluted by congestion of the traffic. In fact, there are no guideline levels for cadmium in agricultural soils approved by Iraqi body, but literature data show that in the world, the range of cadmium concentration recorded in soil varies between 0.2-1.05 $\mu\text{g g}^{-1}$, but generally does not exceed 0.5 $\mu\text{g g}^{-1}$ [31]. However, the international and/or national guidelines regarding cadmium in soil are not firmly established so far and varied from country to the others, for example, the quality guidelines for cadmium in Canadian soil are 1.4 $\mu\text{g g}^{-1}$ and Australia and New Zealand are 0.04 - 2 $\mu\text{g g}^{-1}$, while in India the permissible level is 2.5 $\mu\text{g g}^{-1}$ for agricultural soil levels [32-34]. Cadmium levels in the vegetable and plant leaves in addition to water (river and well) samples of the Kufa city were also determined by the proposed method (**Tables 9 to 11**). The results have shown that the concentration of Cd in vegetables (mean value=0.067 $\mu\text{g g}^{-1}$) was just less than the maximum permissible concentration (2 $\mu\text{g g}^{-1}$) as recommended by FAO/WHO-Codex Alimentarius Commission [35], while in plant leaves (mean value 0.18 $\mu\text{g g}^{-1}$) was within or slightly above FAO/WHO guideline. The mean value of Cd in river and well water was of 0.15 $\mu\text{g mL}^{-1}$ (range; 0.025-0.34 $\mu\text{g mL}^{-1}$) indicating that all water samples were mostly above the maximum permitted concentration (0.003 $\mu\text{g mL}^{-1}$) for protection of aquatic life and drinking water as reported by WHO[36].

Conclusions

To the best of our knowledge, the separation and pre-concentration of inorganic anions as ion-association complex into surfactant rich phase in a single-step extraction compared to metal chelates is very rare and just one article [19] was appeared in the chemical literatures since establishing of CPE. We think, the present work will contribute to open a new route to the researchers to widen the theoretical characteristics and analytical applicability of CPE for inorganic anions analysis rather than that of common metal ions. Although, thermodynamic study and effect of such parameters gave encourage results, but more works are needed to investigate the behavior of solubilization of inorganic anions in the micelle phase. However, the present study provides simple, reliable and accurate determination of Cd ion as ion-pair $[\text{HCdCl}_4^- \text{CV}^+]$ increasing the popularity of UV-Vis spectrophotometry after CPE beside the solvent-free extraction of toxic metals from its matrix. The proposed method was successfully applied for the determination of Cd ion in various matrices which proved, no significant difference compared to FAAS technique and it can be considered as an alternative to other spectrometric techniques such as FAAS, ETAAS, ICP-OES etc.

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