Cloud Point Extraction Methodology for Separation and Microamounts Determination of Lead(11)and Cadmium(11)Ions

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Abstract

A Cloud point extraction procedure was presented for preconcentration of lead(11)and cadmium(11)ions in various samples after complexation by 2-[(Benzo thiazolyl)azo]-4-benzyl phenol (BTABP) with lead and 2-[(3-Bromo phenyl)azo]-4,5-diphenylimidazole (BPADPI) with cadmium ions are quantitatively extracted in Triton-x-100 Following separation ,5ml of 1,2Dichloroethane (1,2-DCE) was added to surfactant -rich phase of lead and 5ml ethanol added for surfactant rich phase of cadmium prior to its analysis by UV-Vis Spectrometry. The experimental conditions such as pH, concentration of Triton-x-100, temperature, time of heating ,organic solvent effect, stoichiometry for complex extracted, synergism, when evaluated in the proposed method was applied for the determination of lead(II) and cadmium(II) in different samples .

Keywords: Cloud point extraction, lead, cadmium.

الخلاصة

استعملت طريقة استخلاص نقطة الغيمة في تقدير وفصل أيونات الرصاص pb^{+2} والكادميوم Cd^{+2} من نماذج مختلفة بعد أجراء عملية التعقيد لهذه الأيونات مع الكواشف العضوية -2-[(Benzothiazolyl)azo] 4-benzylphenole (BTABP) لأيون الرصاص و 2-[(3-Bromo phenyl)azo]-4,5-diphenyl imidazole (BPADPI) لأيون الكادميوم وقد استخلصت هذه الأيونات قيد الدراسة كمياً إلى Triton-x-100 وبعد فصل نقطة الغيمة تذاب في 5ml من مذيب2,1- ثنائي كلوروأيثان 1,2-DCE للرصاص والميثانول للكادميوم قبل أجراء التحليل الكمي لها وفق تقنية مطيافية فوق البنفسجية – المرئية وقد حددت كافة الشروط التجريبية الخاصة مثل الدالة الحامضية pH وتركيز Triton-x-100 ودرجة حرارة الحمام المائي وزمن التسخين والمذيب العضوي مع دراسة تركيب المعقد المستخلص إلى نقطة الغيمة وتأثير توليف المذيب على عملية الاستخلاص وقيم نسب التوزيع D إضافة إلى تطبيقات لتقدير عنصري الرصاصPb^{+2} والكادميوم Cd^{+2} في نماذج مختلفة.

الكلمات المفتاحية: استخلاص نقطة القيمة، الرصاص، الكادميوم.

Introduction

Cloud point extraction (CPE) is based on the phase behavior of non-ionic surfactants in aqueous solution , which exhibit phase separation after an increase in temperature or the addition of a salting out agent . Separation and preconcentration based on (CPE) are becoming an important and practical application of surfactant in analytical chemistry[1,2].Cloud point extraction has been used for pre-Concentration of Pb(II) after Complex with 1-(2-pyridylazo)-2 naphthal (PAN) , then determination of pb (II) by FAAS method . The analyst is extracted to the phase rich in the Surfactant Triton-x-114[3]. A cloud point extraction procedure was presented for the preconcentration of copper , nickel , zinc and iron in various samples , after complexation by 2-(6-(1H benzo [d] imidazol-2-yl) pyridin -2-yl)-1H-benzo[d] imidazole -(BIYPYBI)[4]. In this present work a simple , selection and sensitive CPE method for preconcentration and determination of Pb^{+2} and Cd^{+2} ions in various real sample using BTABP and BPADPI as selective and sensitive complexing agents in basic media was established . Cloud point extraction procedure was presented for preconcentration of lead(II)and cadmium(II)ions in various samples after complexation by 2-[(Benzo thiazolyl)azo]-4-benzyl phenol (BTABP) with lead and 2-[(3-Bromo phenyl)azo]-4,5-diphenylimidazole (BPADPI) with cadmium ions are quantitatively extracted in Triton-x-100.

Experimental

Reagents

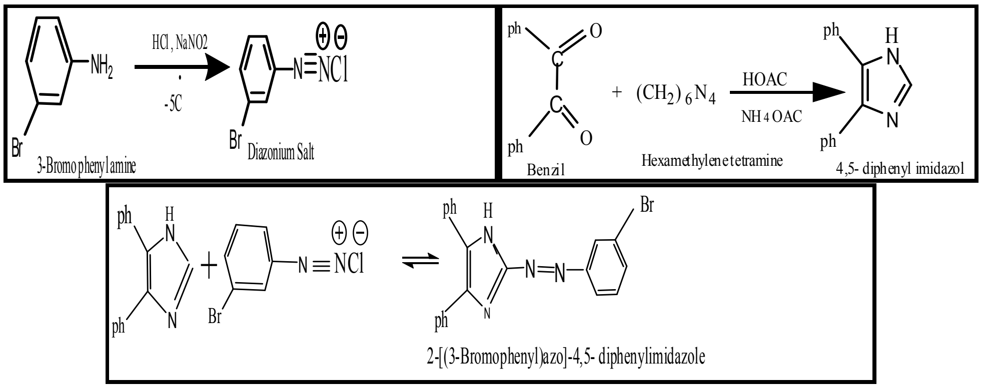
All solutions were prepared with distilled water, analytical grade used in this study were obtained from international companies and used as received without more purification.The ligand2-[(Benzothiazolyl)azo]-4-benzyl phenol(BTABP) synthesized according to thesis[5], but the ligand 2-[(3-Bromophenyl)azo]-4,5- diphenyl imidazole (BPADPI) as anew ligand synthesized according to general procedure [6]. The Calibration Curve for Pb^{+2} and Cd^{+2} ions was established using standard solutions prepared at optimum Conditions for each ion.$Pb(NO_3)_2$ in purity 99.99% from (B.H.D),$Cd(NO_3)_2$,in purity 99.99% from (Merk),Triton-X-100 purity Analer from (B.H.D),1,2-DCE, in purity 98% from (G.C .C), ethanol in purity 99% from (B.H.D) all other salts used in this research was in purity 99.8% from (B.H.D).

Instruments

Shimadzu double beam UV-Vis spectrophotometer UV-1700 (Japan) , shimadzu single beam UV-Vis spectrophotometer UV-1000-02 (Japan) , shimadzu Testscan FTIR 8400 series , shimadzu AA6300 (Italy), pH- meter WTW, E163694 CE Germany .

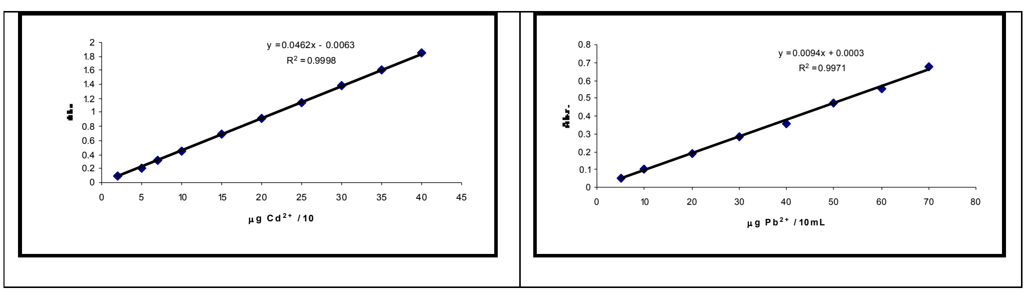
Preparation of BPADPI

Organic reagent which is used as complexation agent 2-[(3-Bromophenyl)azo]-4,5- diphenyl imidazol was prepared according to mechanism below.This organic reagent was prepared by the general Shibata procedure by the condensation azo deravitive with 4,5-diphenyl imidazole. Azo deravitive prepared by reaction of 3-bromo phenyl amine with $NaNO_2$ at -5˚C in HCl media and the product was diazonium salt and 4,5-diphenyl imidazole prepared by reaction of benzil with hexa athylene diamine in buffer of acetic acid and ammoium acetate after that the solution of diazonium salt at -5˚C added drop by drop to coling solution of 4,5-diphenyl imidazole with shaking and after complet the addition stand by the solution for hour and addition 400mL distilled water and leave the solution over night after that filter the solution and washing the reagent with distilled water and recrystallization in prydin to get very pure organic reagent used for spectrophotometric determination of elements. (m.p.155C°-164C°)



Cloud -point extraction procedure

Atypical Cloud point experiment required the following steps :10mL solution contain analyte ions, 0.6 % Triton -X-100 for Pb^{+2} ions and $4*10^{-4}$ M BTABP was adjusted to related pH 8.0 , but 0.8 % Triton-X-100 for Cd^{2+} and $2*10^{-4}$ M BPADPI was adjusted to related pH 10.0 , the mixture shaken for 1min and left to stand in a thermostated bath at 90C°for 20 min to pb^{2+} ion and 80C°for 20 min to Cd^{2+}ion, high viscosity Cloud point formed ,the bulk aqueous phase was easily decanted .The remaining micellar phase was dissolved in 5ml 1,2-DCE for Pb^{+2} ion and ethanol for Cd^{2+} ion and then the ions content was readily evaluated by UV-Vis spectrophotometry at λ_{max} for complex λ = 393nm for pb^{2+}ion and λ=516nm for Cd^{2+},as well as calculated distribution ratio D values by spectrophotometric dithizone method [7]. With dependance on Calibration Curve Fig(1).

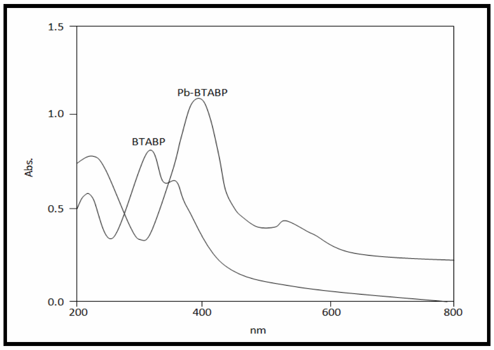


(b) (a)

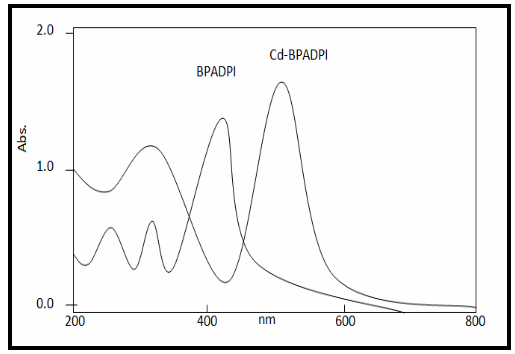
Fig (1): Calibration Curve by dithizone method (a):for pb^{2+} ion (b)for Cd^{2+} ion

Results and Discussion

Absorption spectra



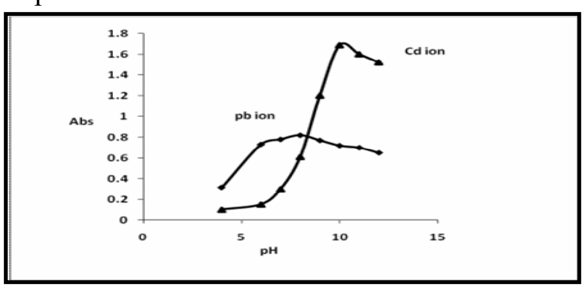
Fig(2): UV-Vis. Spectrum for ligand BTABP & its complex Pb-BTABP as cloud point



Fig(3): UV-Vis. Spectrum for ligand BPADPI & its complex Cd- BPADPI as cloud point

Effect of PH

Cloud point extraction Yield depends on the pH at which complex formation occurs. pH play a unique role on metal - complex formation and subsequent extraction . CPE of lead and cadmium ions was performed in solution of pH ranging form 4 to 12 Fig (4)

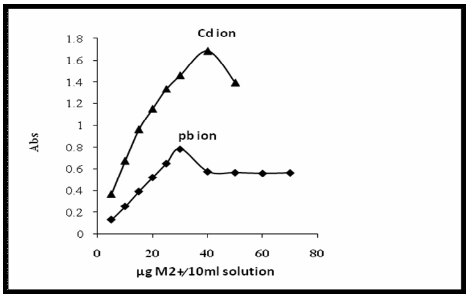


Fig(4): Effect of pH on Micelles formed

shows the effect of pH on the absorbance and sensitivity of method also distribution ratio D values . It was found that in the pH of 8.0 maximum extraction for Pb^{+2} ion but in the pH of 10 for cd^{+2} ion . At lower pH the ligand is protonated and its ionic characteristics increase and lead to decrease in Complex and micelles formation . At higher pH due to formation stable hydroxide compounds such as $M(OH)_2$ or $M(OH)^+$ also decrease micelles formation .

Effect of ions concentration

According to thermodynamic laws , concentration of metal ion play important major parameter on formation and stability of complex and micelles . CPE of lead and cadmium ions studied for solutions contain range of concentration for each ion from 5µg to 70µg in 10 mL solution, Fig (5)

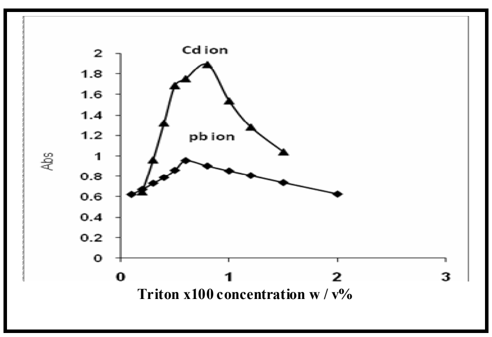


Fig(5): Effect of metal ion Concentration on complex formation by CPE

shows more sensitive and clear cloud point at 30µg Pb^{+2} and 40µg cd^{+2},the lower concentration of metal ion not allow to reaching best thermodynamic equilibrium to form complex and micelles with high stability . At higher concentration, the thermodynamic equilibrium inverse to dissociation of complex and increases ionic from according to mass action law and lechatlier principle.

Effect of Triton x-100 Concentration

The non-ionic surfactant Triton x-100 was chosen because of its commerical availability in a high purified homogeneous form , low toxicological properties . Also, the high density of the surfactant rich phase easily separation . Additionally the cloud point of Triton x-100 permits its use in the extraction and /or pre-concentration of a large number of molecules and complex [8, 9].To limitation optimum concentration of Triton x-100 using ranging from 0.1% → 2% (w/v) Fig (6)

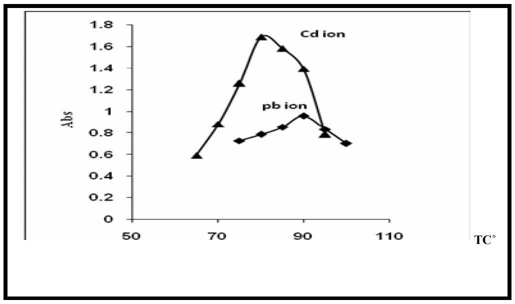


Fig(6): Effect of Triton x-100 Concentration cloud point formation and extraction

shows optimum concentration for Triton x-100 was 0.6% for Pb^{+2} ion and 0.8% for cd^{+2} ion . Lower concentration Triton x-100, reduce the cloud point layer formation probably due to assemblies that were in adequate to quantitatively entrap the hydrophobic complex [10]. The high concentration of Triton x-100 resulting in an increase in the volume of the surfactant -rich phase . In addition the viscosity of the surfactant -rich phase increase leading to poor sensitivity [11,12].

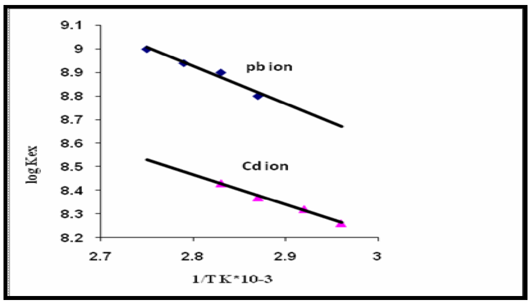
Effect of Temperature

Cloud point formation obey to thermodynamic law with Optimum Temperature. Extraction performed with temperature ranging from 60C° to 100C° Fig (7).



Fig(7): Effect of Temperature on Cloud point formation and extraction method

shows 90C° was suitable for Cloud point Formation with higher viscosity and easily separated for Pb^{+2} ion but for cd^{+2} ion was 80C° with obtaining maximum sensitivity . Higher temperature lead to decomposition of ion complex and reduction of extraction and micelles formation. At lower temperature the separation of two phases is not complete . After calculate extraction constant k_{ex}. Fig (8)



Fig(8): Effect of Temperature on k_{ex}

shows the linear relation help to determine thermodynamic data from relation below giving ΔH_{ex} = 0.0351k J mol^{-1} , ΔG_{ex} = -62.57 k J mol^{-1} , ΔS_{ex} =172.5 J k^{-1} mol^{-1} as well as complex and micelles formation was endothermic to optimum temperature , that is for pb^{+2} ion but for cd^{+2} ion thermodynamic data was ΔH_{ex} = 0.025 K J mol^{-1} ΔG_{ex} = -53.06 K J mol^{-1} ΔS_{ex} = 150.38 J K^{-1} mol^{-1} with endothermic relation

$$Kex = \frac{D}{[M^{2+}]_{aq}.[Ligand]_{org}}$$

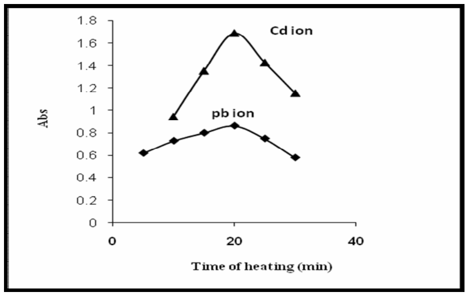
$$\Delta G_{ex} = - R\, T \ln K_{ex}$$

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

$$slope = \frac{-\Delta H_{ex}}{2.303R}$$

Effect of time for heating

Extraction each ion by CPE method at optimum temperature at various time of heating ranging from 5min to 30min was studied . Fig(9)



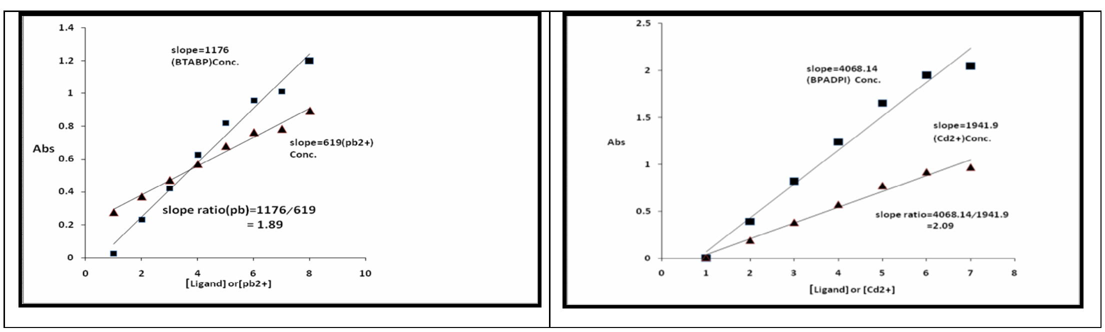
Fig(9): (a) Effect of time of heating on cloud point formation and extraction method

shows 20 minutes was favorable time for heating to form cloud point layer with high viscosity , at lower time the separation of the two phases is not complete, but more than optimum time leading to diffusion cloud point layer and reduction absorption of micelles formation and distribution ratio D .

Stoichiometry

Slope ratio method

To limitation more probable structure of chelate complex Pb-BTABP and ion pair complex [Cd-BPADPI] anion performed many methods one of these is slope ratio method , in cloud point extraction of ions at BTABP or BPADPI concentration ranging from $1*10^{-6}$M to $1*10^{-3}$M and extraction at different concentration of each ion ranging from $1*10^{-6}$M to $1*10^{-3}$M Fig (10 a,b)



(a) (b)

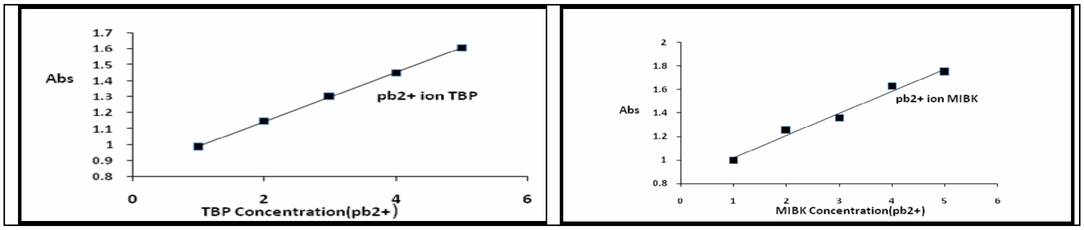
Fig(10): Slope ratio method (a)for pb2+ ion ,(b)for Cd2+ ion

show , the two linear relationship with slope ratio equal to 1.89 for Pb^{+2} ion and 2.09 for cd^{+2}. lead to the structure of complex extracted as cloud point micelles was 1:2 (Metal : ligand) $[pb^{+2}(BTABP^{-})_2]$ and $[Cd(BPAPI)_2]^{+2}$ $2Cl^{-}$.

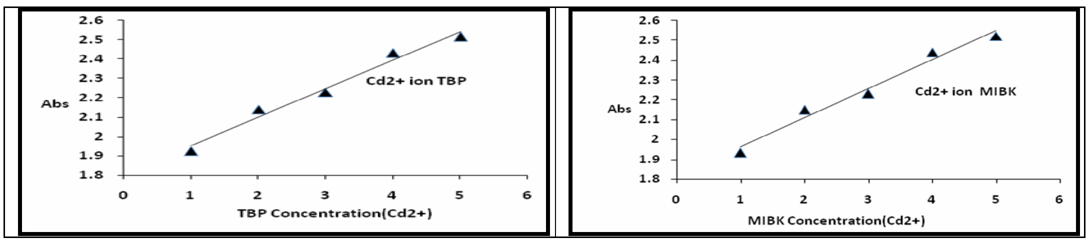
Synergistic effect

Extraction of analyte ions by CPE methodology at experimental conditions in the presence tributylphosphate (TBP) or methylisobutylketone (MIBK) in concentration ranging from $1*10^{-5}$ M to $1*10^{-3}$ M have shown in Fig(11,12),it shows increase in absorbance of micelles formation and distribution ratio D with increasing TBP or MIBK concentration and straight line relation with slope equal to 0.743 for pb^{2+}ion with TBP as well 0.734 with MIBK as well as forCd^{2+}slope 0.52 with TBP and 0.493

with MIBK these slope values demonstrated one molecule of TBP or MIBK was participated in complexes extracted as micelles with CPE Methodology .

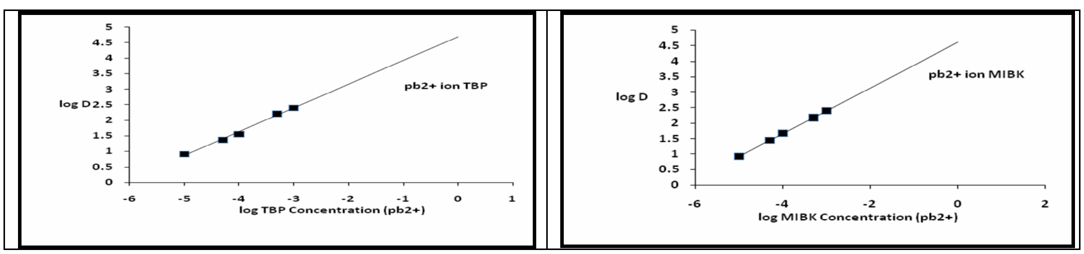


(a)

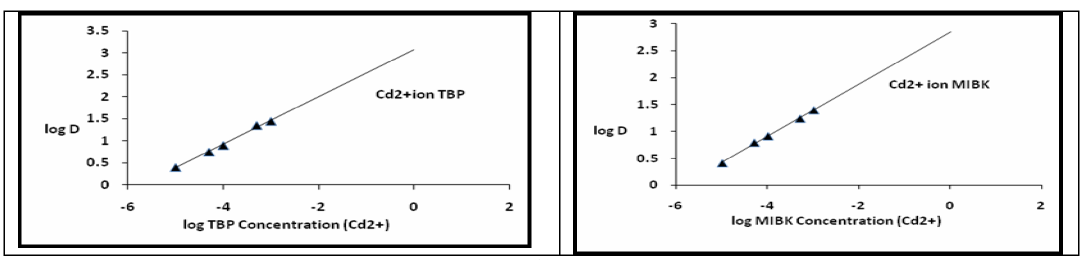


(b)

Fig(11)Synergistic effect on absorbance of micelles formation (a)pb^{2+} and (b)Cd^{2+} ions



(a)



(b)

Fig(12): Synergistic effect on D values (a)pb^{2+} (b)Cd^{2+}ions

Interferences

Preconcentration procedures for heavy metal ions determination at high salt content samples can by strongly affected by the matrix constituents of the samples [13-17] .To perform this study , 10 mL of solution containing analyte ions and interferon's ion ($1*10^{-4}$ M)in a constant analyte mass ratio in the presence Triton x-100 at optimum concentration and experimental conditions . Table (1) shows interferences results .The results shows all anions effect to decrean absorbance of complex in micelles also distribution ratio by reagan of Masking metal cation to form complex except thiucyanate anion SCN^- giving increase in complex formation and D value by destroy the hydration shell of metal cation and the same effect for cation and$C_2O_4^=$,ClO_3^- with Cd^{2+} ion.

Table(1).Effects of the interferences ions

Interference ion	Pb^{+2}		Cd^{+2}	
	Abs micelles	D	Abs micelles	D
Na^+	-	-	- - -	-
K^+	+	++	+	+
NH_4^+	-	-	- - -	-
Mg^{2+}	++	+++	- - -	-
Ca^{2+}	+	++	- -	-
Sn^{2+}	-	-	- -	-
Fe^{3+}	-	-	- - -	-
CH_3COO^-	-	-	-	-
SO_4^{--}	-	-	-	-
SCN^-	+	+	-	-
$C_2O_4^{--}$	-	-	+	+
CrO_4^{--}	-	-	-	-
$Cr_2O_7^{--}$	-	-	-	-
ClO_3^-	-	-	+	+
F^-	-	-	-	-

- = D-1, -- = D-2, --- =D-3, +=D+1, ++=D+2, +++=D+3

Effect of organic solvent

Micelles cloud point layer dissolved in different organic solvent differ in polarity. Table(2) shows absorbance and deviation . in wave length

Table(2) :Effect of organic solvent on absorbance of micelles

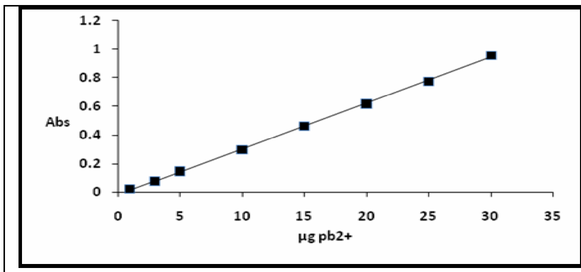
Organic solvent	Dielectric constant(ε)	Pb^{2+}		Cd^{2+}	
		λ(nm)	Abs.	λ(nm)	Abs.
Ethanol	25	428	0.428	576	0.6
Amyl	15.8	431	0.367	481	1.864
alcohol	10.65	393	0.825	469	1.585
1,2-DCE	9.08	361	0.209	438.5	0.784
DCM	5.708	363	0.386	448	0.622
Chloro	2.804	361	0.646	441	0.656
benzene	2.438	363	0.152	432	0.656
Benzene	2.38	-	-	432	0.656
Toluene					
CCl_4					

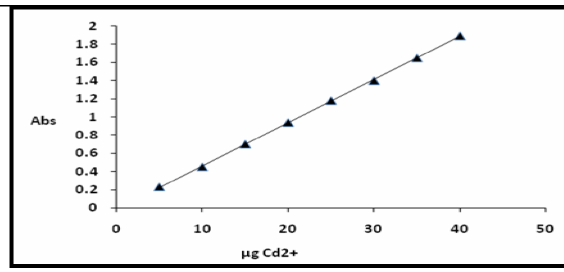
Characteristics of Method

Calibration graphs in Fig(13)were obtained by pre-Concentration 10ml of a sample containing known amounts of analyte ions under the experimental conditions . Under the specified experimental Conditions the calibration curves for Pb was linear from0.1to 3µg ml^{-1} and for Cd was linear from 0.1 to 4µg ml^{-1}.

Parameters	Pb^{2+}	Cd^{2+}
Slope	0.01	0.046
intercept	0.0065	0.006
Correlation Coefficient	0.999	0.998
linearity	0.137	0.238
Sandell's sensitivity	$3*10^{-8}$ $mgcm^{-2}$	$2.1*10^{-8}$$mgcm^{-2}$
Detection limit	$7.47*10^{-7}$ $mgcm^{-2}$	$8.25*10^{-6}$ $mgcm^{-2}$

The preconcentration factor for all ions ware calculated by dividing the aqueous phase volume to the find volume of preconcentrated phase in 50, while the enhancement factor as the ratio of slope of calibration curve of the analyte after preconcentration of the prior preconcentration for pb^{2+} and Cd^{2+}ions was 50, 144 respectively . The results Table 3: for determination pb^{2+} and Cd^{2+} ions in different samples according to CPE methodology.





Fig(13): Calibration curve for micelles formation

Table (3): determination of Microamount pb^{2+} and Cd^{2+} in different Samples

Sample	Pb^{2+}			Cd^{2+}		
	$\mu g.g^{-1}$	AAs	RSD % n = 3	$\mu g.g^{-1}$	AAs	RSD% n = 3
Un agriculture soils						
Sample (Al-Millad quarter)	2.1	2.0	0.3	2.2	2.3	0.4
(Al-Muthana street)	2.4	2.5	0.8	1.8	2.0	0.6
(al-Rowan street)	3.0	3.1	0.3	2.5	2.3	0.7
Agriculture soils						
Sample (Al-Buhidari)	0.95	0.97	0.9	1.9	1.8	0.7
(Al-Mishkhab)	1.01	1.02	0.3	2.6	2.5	0.3
(Al-Hira)	1.22	1.24	0.4	2.44	2.5	0.6
Water samples						
(Al-Kufa bridge)	0.074	0.072	0.4	0.07	0.08	0.4
(ground water)	0.033	0.034	0.8	0.05	0.06	0.8
(Al-Hafar)	0.251	0.250	0.2	0.25	0.30	0.2
Plant leaves in Different location						
(Al-Kufa street)	2.5	2.48	0.6	0.12	0.13	0.5
(Al-Phikah College)	1.8	1.78	0.7	0.08	0.09	0.6
(Al-Amir quarter)	2.3	2.34	0.3	0.11	0.12	0.7
Sheet wool	3.9	3.8	0.8	2.5	2.7	0.4

From the used of t-test method demonstrate the spectrophotometric determination with our procedure by cloud point method there is more sensitive than AAS and recovery procedure of each ion in the sample by our procedure show the ability of this procedure to determine microamount of each ion less than AAS procedure.

Conclusions

The micellar extraction of pb^{2+} and Cd^{2+} ions with BTABP and BPADPI into the phase of non-ionic surfactant Tritonx-100 has been investigated .The sensitivity, metrological characteristics , ecological safety , simplicity and convenience of the suggested procedure are competitive with respect to the methods based on the extraction with organic solvents . The results presented have confirmed its applicability to the separation and preconcentration of lead and cadmium which due its high stability constant and high pH dependency with high selectivity loading and has been carried out . In a view glance to the results one can notice that present method is superior to those previously reported in term of some characteristics performances [18-20].

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