

***Spectrophotometric determination for microamount of mercury (II) and zinc(II) from HCl media by Rhodamine 6G**

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Rhodamine 6G used as anion exchanger in organic phase for extraction and spectrophotometric determination of Hg^{2+} and Zn^{2+} ions from HCl aqueous media after conversion metal ions into chlorol complexes anion .The study include limitation optimum condition for extraction such as , HCl concentration , metal ion concentration shaking time as well as stoichiometry of ion pair complex extracted , organic solvent effect , thermodynamic studies about extraction was endothermic for both metal ions ; in addition to another studies and applications for determination analyte metal in different samples .

Introduction

This study to rely on used liquid anion exchange method for extraction and spectrophotometric determination of Hg^{2+} as $HgCl_3^-$ or $HgCl_4^{2-}$ and Zn^{2+} as $ZnCl_4^{2-}$ by used Rhodamine 6G (R6G) as ion exchanger in solution . Cd^{2+} and Hg^{2+} was extracted from hydrochloric acid media with α -Naphthyl amine 4-Amino benzoic acid , 2-[(4-carboxy methyl phenol)azo] -4,5-diphenyl imidazole and Cryptand (C₂₂₂) and definition of all parameters effect on extraction method [1]. Extraction of Ni (II) from H_2SO_4 media by use sodium Diethyl dithio carbamat (SDDT) with organic solvents as well definition optimum conditions for extraction and determination in environmental and vital samples [2]. Spectrophotometric determination of mercury with Iodide and RhodamineB by formation ion association complex $[(Rhodamine\ B)^+_2(HgI_4)^-]$ in highly acidic solution [3]. Trace amount of toxic such as(cadmium) was determine of spectrophotometer method by using 2- dihydroxy anthraquinone -3- sulphonic acid , sodium salt .(Alizarin red 5) as anew spectrophotometer reagent in acid solution H_2SO_4 [4]. Bis (salicylaldehyde) ortho phenyleuediamin (BSOPD) has been proposed as new analytical reagent for the direct spectrophotometric determination chromium (VI) in acidic media (0.1-0.3)M H_2SO_4 with presence Tritonx-100 [5]. Extraction of Mn(II) from sulphate - acetato medium by bis (2,4,4 - tri methyl phenol) phosphoric acid dissolved in distilled aliphatic kerosene has been investigated , the equilibration time more than 5min [6]. Norfloxacin using to form yellow colored complex at pH= 6 with maximum absorbance

***The Research is apart of on MSC. Thesis in the case of the second researcher**

430nm ,molar absorbtivity $2 \times 10^4 \text{L.mol}^{-1} \text{cm}^{-1}$ [7]. Baking - Leaching - Solvent extraction provcen was investigated to recover metal values from waste petroleum catalyst . Baking of(Mo -Ni/AL₂O₃) spent catalyst with H₂SO₄ followed by leaching of the baking man concentrate [8]. N,N,N',N'-tetra octyldiglycolamide was applied for the extraction and separation of Zr(IV) and Hf(IV) from nitric acid solution [9]. Measurements of the partitioning of various alkali eather cations between solutions of hydrochloric acid and a series of 1,3- dialkylimidazolium liquid (ILs) with a crown ether has added have revealed substancial differences in extraction be haviiov [10]. Phosphonium ionic liquid are frequently used for separation of metals ions ,Zn(II) and Iron from chloride solution in classical liquid-liquid extraction and polymer inclusion membranes[11]. Synthesis and extraction properties of new lactam ionoporees . these lactam derivative were easily synthesized via aminolysis of 2,2'-methylene bis (4-chlorophenol) dimethylester with corresponding diamine compounds in methanol – dichloromethane solvent systems at one step [12]. Solvent extraction of trivalent lanthanoids with 4-benzoyl-3-phenyl-5-isoxazolone and tert-ButylCalix(4)arene Tetrakis(N,N-Dimethylacetamid) [13]. The diamide N,N,N',N'-tetraoctyldiglycolamide was applied for extraction of Ce(III) from nitric acid solutions , the equilibrium studies included the dependencies of Cerium distribution ratio on nitric acid [14]. Extraction behavior U(VI) and Th(VI) from nitric acid medium is investigated by using organo-phosphoran extractant .The effect of diluents, nitric acid concentration as well as extractant concentration of U(VI) and Th(VI) are evaluated [15]. A novel automated liquid/liquid extraction system was developed for the determination of trace contaminants in unalloyed , alloyed , highly alloyed steel and super alloys . In the presented batch extraction System the aqueous phase and the non-water miscible organic phase were brought into close phase contact by high-speed stirring with a magnetic stir bar [16]. The gol of this study to determination mercury (II) and zinc (II) in different sample by use R6G as complexion reagent by liquid ion exchange affect determination the condition of formation stable ion pair complex .

Experimental

Apparatus

Shimadzn UV- 1700 spectrophotometer (Japan) was used for absorbance measurements , for shaking used HY- 4 vibrator with AD just about speed multiple (Italy) .

Materials and Solutions

All chemical materials received from commercial sources with high purity and used as received , Hg(II) 1mg/ml aqueous solution was prepared by dissolving 0.1713gm of Hg (NO₃)₂- H₂O in 10 ml distilled water contain 0.5ml concentrated nitric acid in 100ml volumetric flask , all another working solution prepared by dilution with distilled water Rhodamine 6G solution in concentration $1 \times 10^{-2} \text{M}$ prepare by dissolved 0.0479gm in 10ml chloroform and 10ml volumetric flask, and all another working solutions prepared by dilution with chloroform Dithizone in solution $1 \times 10^{-2} \text{M}$ prepared by dissolved 0.0256gm of Dithizone in 10ml CCl₄ and volumetric flask and other solution prepared by dilution with CCl₄ aqueous solution of Zinc (II) prepared by

dissolved 0.1gm of Zinc metal in 15ml hydrochloric acid HCl (1:1) and then complete the solution into 100ml with distilled water by use 100ml volumetric flask.

Adoption procedure

The ion pair complex of Hg (II) and Zn (II) with (R6G) prepare at optimum condition giving maximum absorbance at $\lambda_{max} = 481\text{nm}$ for mercury(II) and $\lambda_{max} = 548\text{nm}$ for zinc(II) with molar absorptive $\epsilon = 10798.5 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ for Hg(II) but $\epsilon = 9403 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ for Zn (II). for determination of Hg(II) and Zn (II) in environmental and vital samples digest by moist method [17], after complete the aqueous solution to 25ml, for 5ml portion of sample solution added masking agent, as well as added fixed concentration of hydrochloric acid HCl to conversion metal ion into anion chlorol complexes and then added 5ml of R6G solution in chloroform at $1 \times 10^{-4} \text{ M}$ and shaking to optimum time. after that separated aqueous layer from organic layer take absorbance of organic phase at $\lambda_{max} = 481\text{nm}$ for Hg(II) and phase at $\lambda_{max} = 548\text{nm}$ for Zn(II) vis organic solution of R6G as blank after resort of calibration curve Fig(1) determine amount of Hg(II) and Zn(II) in the sample. and to the aqueous phase determine remainder quantity Hg(II) or Zn(II) according to Dithizone method [18] as well calculate distribution ratio(D) depended calibration curve Fig (2). according to results at Fig(1) show the method have.

Metal	%RSD	DL mol.L ⁻¹	S $\mu\text{g}\cdot\text{cm}^{-2}$
Mercury(II)	% 7.078×10^{-3}	2.117×10^{-6}	1.860×10^{-2}
Zinc(II)	% 8.037×10^{-3}	7.373×10^{-6}	5.909×10^{-3}

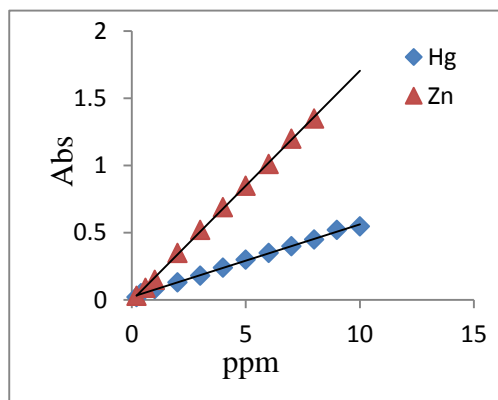


Fig (1) Calibration curve of Hg^{2+} and Zn^{2+} with R6G in CHCl_3

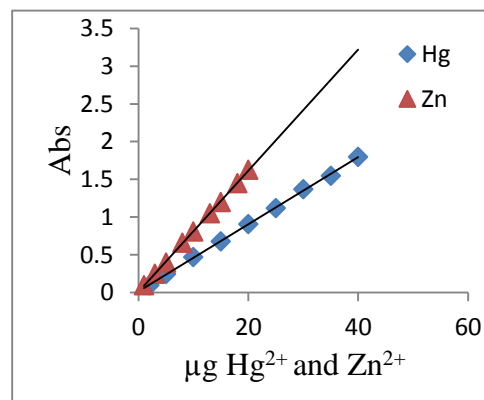


Fig (2) Calibration curve of Hg^{2+} and Zn^{2+} with Dithizone

Results and Discussion

Effect of HCl concentration

5ml aqueous solution contain $60\mu\text{g}$ Hg^{2+} or $30\mu\text{g}$ Zn^{2+} with different concentration of HCl at range (0.1-1)M after shaking for 5 minutes then added 5ml R6G solution at 1×10^{-4} M, shaking the two layers for 10 minutes organic phase at from aqueous phase, measure the absorbance of organic phase at $\lambda_{\text{max}}=481\text{nm}$ for Hg^{2+} and $\lambda_{\text{max}}=548\text{nm}$ for Zn^{2+} vis R6G solution as blank, but for aqueous phase determine remainder quantity of Hg(II) or Zn(II) as well as calculate distribution ratio (D) according to Dithizone method [18] obtained the results in Fig (3,4). The results demonstrate optimum HCl concentration was 0.8M for Hg(II) extraction but 1M for Zn(II) extraction, which is play to conversion metal ion into anion chlorol complex reached to equilibrium for formation, from other hand giving the equilibrium for the anion exchange.

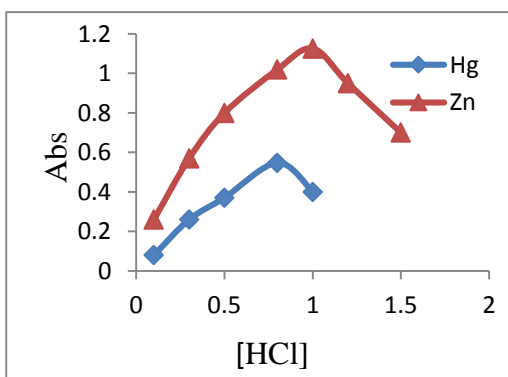


Fig (3): Effect of Hydrochloric acid concentration on ion pair complex formation

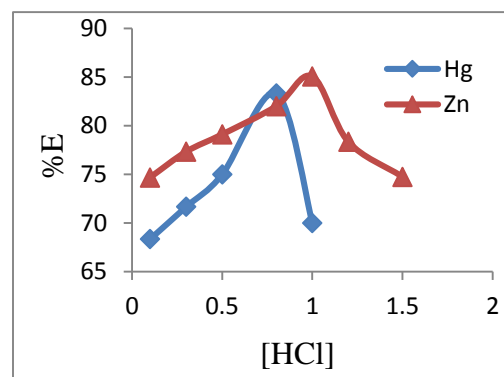


Fig (4): Effect of Hydrochloric acid concentration on efficiency of extraction

Effect of metal ion concentration

5ml aqueous solution contain range of metal ion (5-70) μg with 0.8M HCl and 1M HCl for Hg(II) and Zn(II) respectively after shaking for 5minutes added 5ml of R6G solution dissolved in chloroform at 1×10^{-4} M, after shaking the two layres for 10 minutes separate organic phase from aqueous phase, determine absorbance of organic phase at $\lambda_{\text{max}}=481\text{nm}$ for Hg(II) and at $\lambda_{\text{max}}=548\text{nm}$ for Zn(II) vis R6G solution as blank, determine remainder quantity of metal ion by dithizone method [18]. after that calculate distribution ratio (D), as the results $50\mu\text{g}$ Hg^{2+} and $40\mu\text{g}$ Zn^{2+} which is giving more favorable equilibrium and more stable ion pair complex formation according to thermodynamic behavior of extraction method, metal ion concentration less than optimum value not allow to reach thermodynamic, equilibrium but when the concentration more than optimum value that is effect to increase dissociation equilibrium according to the lechatelier principle, and mass action law.

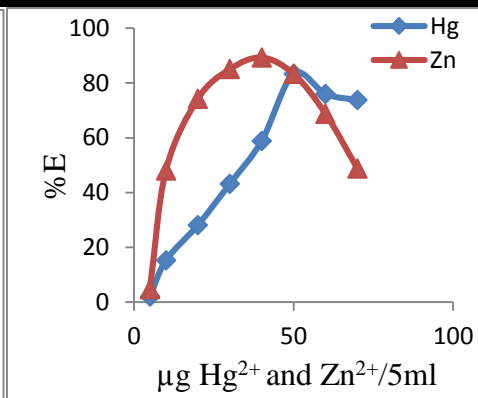
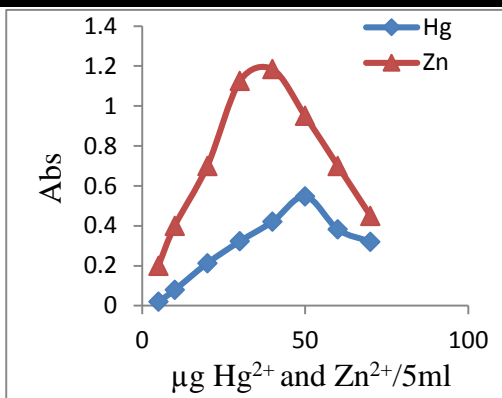


Fig (5): Effect of metal ion concentration on ion pair complex formation

Fig (6): Effect of metal concentration efficiency of extraction

Effect of shaking time

5ml aqueous solution contain 50μg and Hg²⁺ 0.8M HCl , or 40 μg Zn²⁺ and 1M HCl shaking for 5mintes , added 5ml of 1×10⁻⁴ M R6G solution dissolved in chloroform ,after shaking for different time (5-25) min, separate organic phase from aqueous phase , determine absorbance of organic phas at λ_{max} for each metal ion,as well calculate distribution ratio (D) . giving the results as in Figs (7,8) show 10 minutes for extraction Hg²⁺ and 15 minutes for extraction Zn²⁺ was the optimum skaking , shaking time less than optimum not allow to reach thermodynamic equilibrium , but shaking time more than optimum increase dissociation equilibria,and decrease complex formation and distribution ratio.

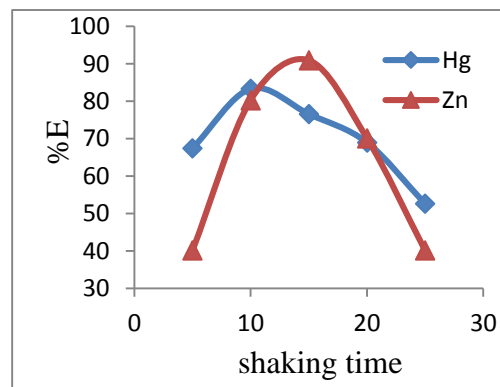
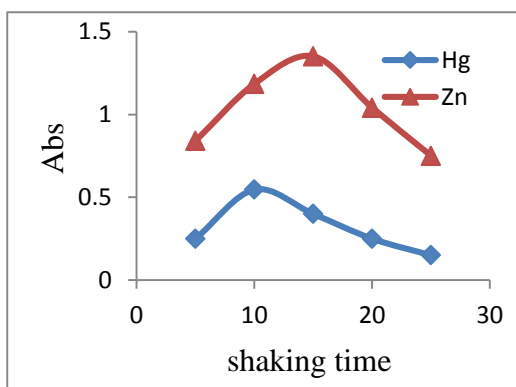


Fig (7): Effect of shaking time on ion pair complex formation

Fig (8): Effect of shaking time efficiency of extraction

Organic solvent effect

5ml aqueous solution contain 50 μ g Hg²⁺ and 0.8M HCl or 40 μ g Zn²⁺ and 1M HCl shaking for 5 minutes , add 5ml of R6G solution dissolved in different organic solvents differ in dielectric constant , after shaking for 10 minutes to Hg²⁺ and 15 minutes to Zn²⁺ separate organic phase from aqueous phase and determine absorbance of organic phase at λ_{max} for each analyt metal ion ,as well calculate distribution ratio (D) giving the results as in Table (1) . the results illustrate there is not any linear relation between absorbance of organic phase or distribution ratio (D) with dielectric constants but there is an effect for organic solvent structure.

Table (1) : Effect of organic solvent on extraction method

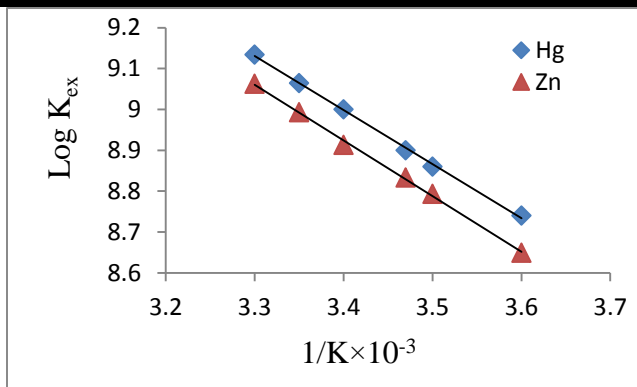
Organic solvents	ϵ L.mol ⁻¹ .cm ⁻¹	Hg ²⁺		Zn ²⁺	
		Abs λ_{max} = 481nm	D	Abs λ_{max} = 548nm	D
Nitro benzene	35.74	1.666	10.66	1.893	16.40
Amyl alcohol	15.8	1.659	10.43	1.818	14.38
1,2-DCE	10.65	1.895	13.32	1.606	13.29
DCM	9.08	1.875	12.19	1.740	14.69
Chloro benzene	5.708	1.275	8.27	1.122	8.90
Bromo benzene	5.4	0.885	7.88	1.244	9.50
Chloroform	4.806	0.547	5	1.350	10
Benzene	2.804	0.306	3.75	1.530	12.80
Toluene	2.438	0.331	4.22	1.320	9.80

Thermodynamic study

Extraction analyte metal ion at optimum condition at different temperature (5-30)C^o(278-303)K , after determine distribution ratio (D) calculate extraction constant K_{ex} according to relation.

$$K_{ex} = D/[M^{2+}][R6G]$$

The relation between K_{ex} and temperature was endothermic for Hg²⁺ and Zn²⁺ as in Fig(9) , and thermodynamic data was $\Delta H = 0.02485$ K J mol⁻¹ , $\Delta G_{ex} = -52.890$ K J mol⁻¹ and $\Delta S = 174.637$ J mol⁻¹K⁻¹ for Hg²⁺ but for Zn²⁺ was $\Delta H = 0.02638$ K J mol⁻¹ ; $\Delta G_{ex} = -52.479$ K J mol⁻¹ and $\Delta S = 173.286$ J mol⁻¹K⁻¹.

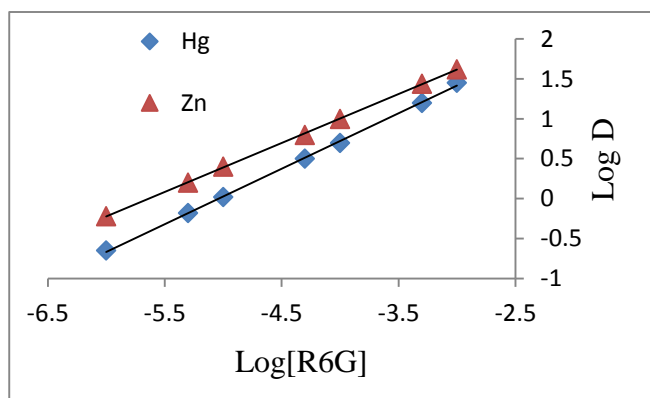


**Fig (9): Effect of temperature on Extraction
Extraction constant K_{ex}**

Stoichiometry

Slop analysis method

At optimum condition extracted Hg(II) and Zn(II) by different concentration of R6G dissolved in chloroform (1×10^{-6} - 1×10^{-3})M. The slope value of straight line relation Fig (10) show the ion pair complex extracted was 1:1 $[\text{R6G}]^+ \text{HHgCl}_4^-$, $[\text{R6G}]^+ \text{HgCl}_3^-$; $[\text{R6G}]\text{HZnCl}_4^-$.



**Fig (10): Effect of R6G concentration on distribution
ratio (D) of extraction**

Slop ratio method

Extraction Hg^{2+} ; Zn^{2+} as chloro anion complex at optimum conditions with constant R6G concentration 1×10^{-4} from different concentration of Hg^{2+} (1×10^{-6} - 1×10^{-3})M, but for Zn^{2+} (1×10^{-6} - 1×10^{-3})M, from other hand constant extracted analyte metal ion at optimum condition and constant metal ion concentration with different R6G concentration 1×10^{-6} M to 1×10^{-5} M, giving the results in Figs (11,12), show the ion pair complex extraction was 1:1 $[\text{R6G}]^+ \text{HgCl}_4^-$; $[\text{R6G}]^+ \text{HgCl}_3^-$; $[\text{R6G}]^+ \text{HZnCl}_4^-$.

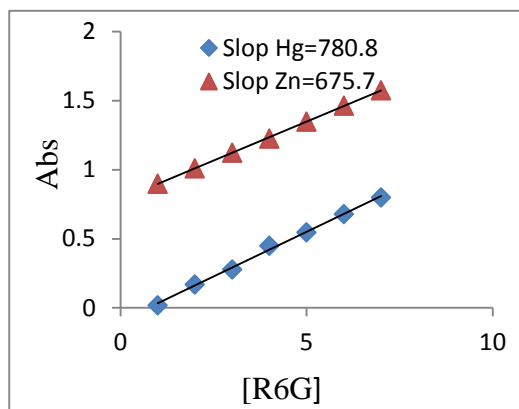


Fig (11): Absorbance as function of R6G concentration

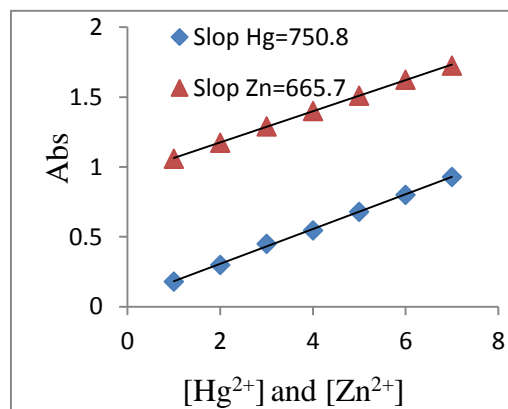


Fig (12): Absorbance as function of mercury and zinc concentration

Methanol effect

Extracted Hg^{2+} and Zn^{2+} at optimum conditions from 5ml aqueous solution contain rang concentration of methanol (1% - 50%) by 1×10^{-4} M R6G dissolved in chloroform giving the result in Figs (13,14), show ethanol effect to enhancement Extraction ion pair with maximum effect at 30% ethanol for Hg^{2+} and 30% ethanol for Zn^{2+} .

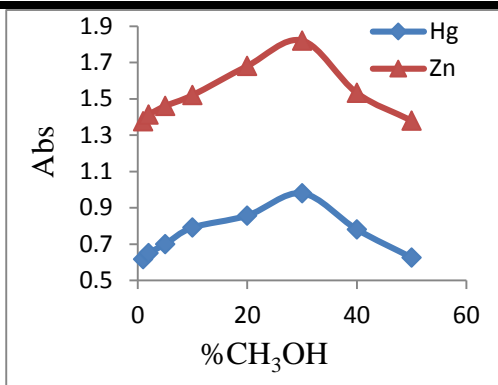


Fig (13): Effect of methanol on ion pair complex formation and stability

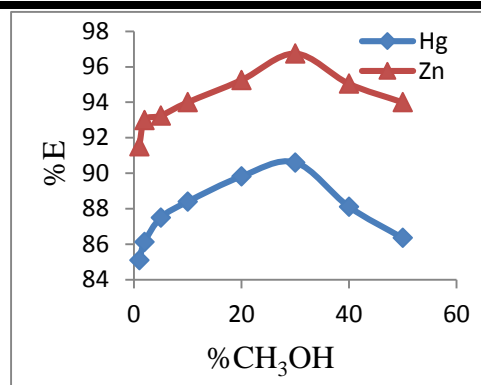


Fig (14): Effect of methanol on efficiency of extraction

Effect of anion

Extraction Hg²⁺ and Zn²⁺ from 5ml aqueous at optimum conditions contain different anion of electrolyte solutions with 1×10⁻⁴M R6G dissolved in chloroform the results as in Table (2) , show all electrolyte salts effected to increase extraction as well stability of ion pair complex with different degree.

Table (2): Effect of anion or extraction method

Anion	Hg ²⁺		Zn ²⁺	
	Abs λ _{max} = 481nm	D	Abs λ _{max} = 548nm	D
SO ₄ ⁼	0.617	8.8	1.36	11.4
NO ₃ ⁻	0.644	20.95	1.48	16.3
CrO ₄ ⁼	0.653	24	1.38	13.7
ClO ₃ ⁻	0.639	15.7	1.42	14.6
I ⁻	0.667	29	1.77	24.4
C ₂ O ₄ ⁼	0.631	13.3	1.62	20.2
HPO ₄ ⁻	0.626	10.9	1.56	18.8

Applications about determination of Hg²⁺ and Zn²⁺ in different samples

By used R6G dissolved in chloroform as spectrophotometric reagent determined Hg²⁺ and Zn²⁺ in environmental and vital samples , After digested the sample according to moist method [17] . after that dealing the sample as evident in adoption method , the results demonstrated at Table (3).

Table (3): Concentration (ppm) of Hg²⁺ and Zn²⁺ in samples environment

Sample	Hg ²⁺	Zn ²⁺
Agricultural soil	0.460	36
Non Agricultural soil	1.040	12
Meat beef	0.056	4.100
Meat fish	1.300	3.200
Meat chicken	0.017	2.400
Brinjal	0.006	5.500
Banana	0.068	4.300
Apples	0.092	2.200
Water river	0.610	1.040
Water tap	0.007	0.780

All the results was identical to the results in aperiom study and by checking the amount of elements in this samples by (AAB) obtained the same values which prove the accuracy of this method for determination was very high and good.

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***التقدير الطيفي لكميات مايكروية من الزئبق (II) والخاصين (II) من وسط حامض
HCl بواسطة R6G**

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شوكت كاظم جواد - نادية مهدي مسلم
جامعة الكوفة - كلية التربية للبنات - قسم الكيمياء

الخلاصة

استخدمت تقنية التبادل الأيوني السائل في الاستخلاص والتقدير الطيفي للزئبق (II) والخاصين (II) ومن خلال استخدام Rhodamine 6G بعد تحويله الى مبادل أيوني سالب وتحويل الأيونات الفلزية الموجبة قيد الدراسة الى معقدات كلور سالبة في وسط حامض الهيدروكلوريك $HgCl_4^{2-}$, $HgCl_3^-$, $ZnCl_4^{2-}$ وقد تضمنت الدراسة تحديد كافة الظروف المثلى والعوامل المؤثرة على عملية الاستخلاص وفق تقنية مثل تركيز حامض الهيدروكلوريك HCl وتركيز الأيون الفلزي وزمن الرج وكذلك دراسة تركيب المعقد المستخلص إضافة الى دراسة تأثير المذيب العضوي ودراسة ثرموديناميكية لعملية الاستخلاص وتطبيق التقنية في التقدير الطيفي للعنصرين قيد الدراسة في نماذج بيئية وحياتية .

***البحث مستل من رسالة ماجستير للباحث الثاني**