

ONIUM METHOD FOR EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF ZN (II) AND CO (II)

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ABSTRACT

UV-Vis. spectrum for complexes of Zn (II) and Co (II) extracted according to onium system from acidic HCL solution by use 2,4-dimethylpentan-3-one (2,4-DMP) as onium complex was (262nm) for Zn(II) but onium complex for Co(II) was (243nm), this method show need 0.5M HCL for extraction Zn^{2+} and 0.8M HCL for Co^{2+} , as well giving obey to Beer-Lambert relation at the (1-20 μ g) for Zn^{2+} and (1-50 μ g) for Co^{2+} . The onium complex extracted have structure $H(H_2O)(2,4-DMP)_3^+;HZnCl_4^-$, $H(H_2O)(2,4-DMP)_3^+;HCoCl_4^-$. This method obey to Beer-Lambert relation at the range (1-20 μ g) for Zn^{2+} $\epsilon=16893.56L.mol^{-1}.cm^{-1}$, D.L= $6.33 \times 10^{-6} \mu$ g/ML, RSD%=0.0069 μ g/ML, Sandell's sensitivity= $3.87 \times 10^{-9} \mu$ g/cm² and (5-50 μ g) for Co^{2+} , $\epsilon=8918.77L.mol^{-1}.cm^{-1}$, D.L= $3.38 \times 10^{-5} \mu$ g/ML, RSD%=0.00664 μ g/ML, Sandell's sensitivity= $7.33 \times 10^{-9} \mu$ g/cm². As well as this research involved many studies and apply for determination Zn^{2+} and Co^{2+} in different samples.

KEYWORDS: Onium Species, Zinc, Cobalt, Spectrophotometric Determination

INTRODUCTION

Onium method is an application of simple coordination and ion association solvent extraction method, this application extracted acidic halo metallic complex, whereas hydrated hydrogen ion is the cation participate to form ion association complex, this complex partition in water but when substituted three water molecules in the hydration shell of proton with organic compound then the complex partition to organic phase^[1]. Extraction of Bi(III) with n-octylaniline in chloroform from HCL and HBR media. The optimum conditions were evaluated such as acidity, n-octylaniline concentration, equilibration time and diluents, and extracted species was $(RNH_3^+)_2BiCl_5^-$ ^[2]. Extraction and separation of SN, As, Cu, PB and Zn from HCL solution by using TBP as an extractant, studies all optimum conditions^[3]. Determination Co(II) spectrophotometrically by using 3,5-dicl-PADAT(5-[3,5-dichloro-2-pyridyl azo]-2,4-diamino toluene at pH=3 form complex which is very stable^[4]. CPE methodology applied for extraction of Ni(II) as chloroanion by using crown ether DB18C6, ion pair association complex extracted having $\lambda_{max}=295$ nm, in presence 0.5M HCl and 0.25M NaCl and 1% Triton X-100 as surfactant. The extracted complex has the structure 1:1[NaDB18C6]⁺;NiCl₃⁻, [NaDB18C6]⁺;HNiCl₄⁻^[5]. By used organic reagent 1-(2-pyridylazo)-4-Benzene naphthol as reagent for the determination of Mg(II) in different samples after conversion Mg^{2+} cation to anion complex by reaction with oxine. The study show 0.5M NaOH favorite to produce oxine anion, the organic reagent PABN primary react with Ni(II) to form large cation produce ion association complex with $Mg(OX)_3^-$ ^[6]. Used 1-(2-pyridylazo)-2-naphthol for determination of Pd(II) in real samples by CPE method in presence TritonX-114 and CPL was diluted with HNO₃ (65%w/w) after phase separation, then the concentrations of Pd were determined by GFAAS^[7]. Solvent extraction of Ga (III) from HCL using 2-octylaminopyridine dissolved in chloroform.

Study all parameters effect on extraction efficiency. From slope analysis method extracted species was $[\text{RR}'\text{NH}_2^+; \text{GaCl}_4^-]$ ^[8]. CPE method for extraction Cr(VI) by using 2-[benzene thiazolyl azo]-4-benzene naphtholas reagent. The CPE efficiency is optimized by one-factor at a time^[9].

The CPE method for extracted Cd(II) as chloro anion with crystal violet dye by using nonionic surfactant Triton X-100 to form ion association complex which having $\lambda_{\text{max}}=449\text{nm}$ ^[10]. Used 3,5-Dimethoxy-4-hydroxy benzaldehyde isonicotinoyl hydrazone as reagent for Pb(II), the complex extracted has $\lambda_{\text{max}}=430\text{nm}$ with $\epsilon=1.82 \times 10^4 \text{ L.mol}^{-1}.\text{cm}^{-1}$, the stoichiometry show the complex extracted was 1:1 with stability constant $8.99 \times 10^{6[11]}$. CPE methodology used to separation and extraction Co^{2+} ion by using 2-[4-antybyrenzolyazo]-1,2-dihydroxy-9,10-anthracene-dione as complexing agent and non-ionic surfactant 1% Tritonx-100 at pH=8, study involved determination optimum conditions, thermodynamic, synergism and spectrophotometric determination of Co(II) in different samples with D.L= $1.6559 \times 10^{-5} \mu\text{g.mL}^{-1}$, Sandell's sensitivity = $7.99 \times 10^{-5} \text{mg.cm}^{-2}$, $\epsilon=7374.12 \text{L.mol}^{-1}.\text{cm}^{-1}$ and RSD% =0.0065.^[12] Extraction of Zn(II) according to CPE method by using new organic agent 2-(4-amino-N-5-methylisoxazol-3-yl)benzene sulfonamideazo-1-Naphthol-Benzen at pH=9 and by using Triton X-100 as surfactant, extracted complex having $\lambda_{\text{max}}=380\text{nm}$. Addition to study effective parameters such as thermodynamic, time of heating, interferences, electrolyte, stoichiometry shows that the complex extracted was $[\text{Zn}(\text{AIBSNB})]^+; \text{Cl}^-$ or $[\text{Zn}(\text{AIBSNB}(\text{Cl}))]$. The method applied to determination of Zn(II) in different samples with $\epsilon=13067 \text{L.mol}^{-1}.\text{cm}^{-1}$, R.S.D=0.0068, D.L= 1.55×10^{-5} and Sandell's sensitivity= $0.0005 \mu\text{gcm}^{-2[13]}$.

Experimental

- **Apparatus**

The spectrophotometric measurements were made by double beam UV-Vis. spectrophotometer, (Biochrom Libra S60) (UK) is used by 1cm quartz cells. For shaking used HY-4 vibrator with AD Just about speed multiple (Italy). For thermodynamic study used shaking water bath (Galvanothermy thermostatic water bath(G, Gerhardt, Germany))

- **Reagent and Materials**

Astock solutions of Zn (II) in (1mg/mL) prepared by dissolved 0.1gm of Zn (II) element in small quantity of 1:1 hydrochloric acid solution and complete the solution to 100mL with distilled water in volumetric flask, as well as Co (II) solution in (1mg/mL) prepared by dissolved 4.780gm of $\text{CoCl}_2.\text{H}_2\text{O}$ in distilled water contain 2mL of concentrated HCl then dilute the solution with distilled water to 1L in a volumetric flask. Other working solution for Zn (II) and Co (II) prepared by dilution with distilled water, where all chemical used in experiments are of analytical grade and were used without further purification.

- **The Fundamental Method for Extraction**

Taken 5mL aqueous solution contain a fixed quantity of Zn^{2+} or Co^{2+} ion and suitable concentration of hydrochloric acid shaking this solution for 5min., afterward add 5mL of 2,4-dimethylpentan-3-one dissolved in chloroform at $1 \times 10^{-4} \text{M}$ and shaking these two phases for 10min. at latter separate organic phase from aqueous phase, determine the absorbance of organic phase at maximum absorbance wavelength for onium species against blank prepared at the same manner without analyte metal ion, but the aqueous phase treated according to spectrophotometric determination for each ion (dithizone method for Zn^{2+} and 1-nitroso-2-naphthol for Co^{2+})^[14] and after return to calibration curves for each ion to determine reminder quantity of metal ion after extraction, afterward subtraction this quantity from origin quantity of metal

ion in aqueous solution before extraction to determine transfer quantity of metal ion into organic phase as onium species, and from these two quantities calculate distribution ratio (D). As well as we are founded the transferred quantity of metal ion to organic phase determined by stripping method after shaking organic phase with two portions of 5mL concentrated NH_4OH was equal to the same quantity determined by subtraction remaining quantity, then we are using the subtraction method for determining the distribution ratio (D) because faster and easier.

RESULTS AND DISCUSSIONS

Spectroscopy

In spite of determine maximum absorbance wavelength for onium species extracted into organic phase for Zn^{2+} and Co^{2+} , UV-Vis. spectrum in Figure 1 show $\lambda_{\text{max}}=262\text{nm}$ for Zn^{2+} and $\lambda_{\text{max}}=243\text{nm}$ for Co^{2+} .

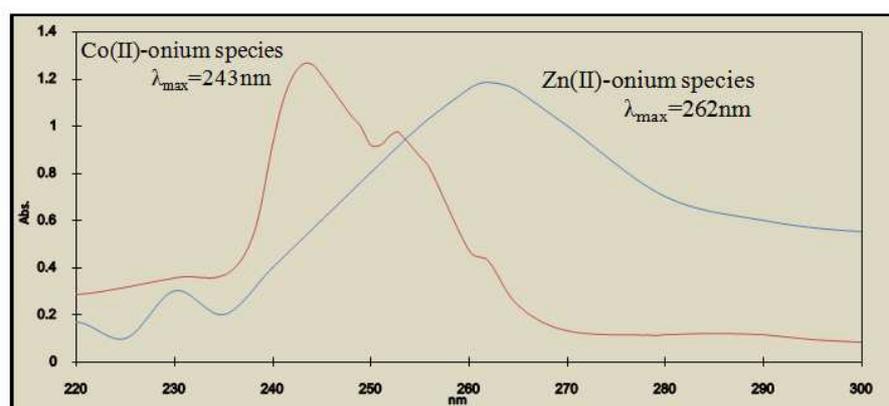


Figure 1: UV-Vis-Spectrum for Zn^{2+} and Co^{2+} Onium Species

Variation of Hydrochloric Acid Concentration

Aqueous solutions 5mL in volume contain $20\mu\text{g Zn}^{2+}$ or $50\mu\text{g Co}^{2+}$ with different concentrations of HCl in the range (0.05-1.0M), shaking these solutions for 5min., then adding 5mL of $1 \times 10^{-4}\text{M}$ solution of (2,4-DMP) dissolved in chloroform and shaking these two layers for 10min. at latter separate the organic phase from the aqueous phase and determine the absorbance of organic phase at 462nm for Zn^{2+} and 243nm for Co^{2+} against blank prepared at the same manner in absence of analyte metal ion as well as treated the aqueous phase according to spectrophotometric methods^[14] for each metal ion as detailed in the main method to calculate distribution ratio (D) values after return to calibration curve in Figures (2,3) and the results were as in Figures (4,5).

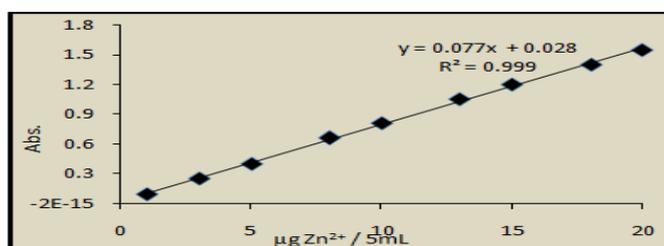


Figure 2: Calibration Curve for Zn^{2+} Ion by Dithizone Method

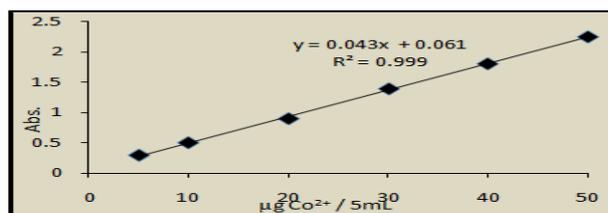


Figure 3: Calibration Curve for Co^{2+} ion by 1-Nitroso-2-Naphthol Method

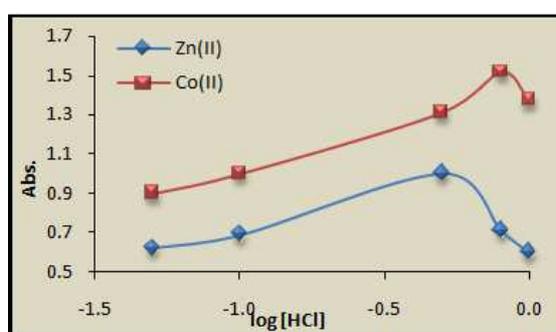


Figure 4: Effect of HCL Concentration on Onium Species for Mation and Extraction

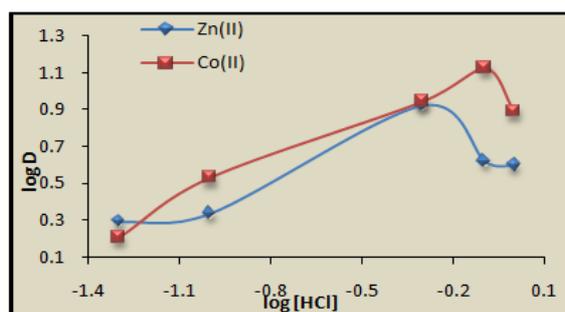


Figure 5: F (Log [HCL])

The results show an optimum HCl concentration was 0.5M for Zn^{2+} but for Co^{2+} was 0.8M, at these concentrations reach to favorable thermodynamic equilibrium for formation onium complex with three molecules of (2, 4-DMP) replaced water molecules in the hydrated hydrogen ion as cation, any concentration less than optimum value not enough to reach equilibrium for formation and extraction onium species. As well as HCl concentration more than optimum value causing decline extraction efficiency by effect of the Le chatlier principle and mass action law and increase dissociation and decrease formation of onium species as well increase formation stable compounds ZnCl_2 and CoCl_2 .

Variation of Metal ion Concentration

Aqueous solutions 5mL in volume contain different quantities of under study metal ions in the range ($1\text{-}22\mu\text{g Zn}^{2+}$) and ($5\text{-}60\mu\text{g Co}^{2+}$) and 0.5M HCl for Zn^{2+} and 0.8M for Co^{2+} , after shaking these solutions for 5min. added 5mL of $1 \times 10^{-4}\text{M}$ solution of (2,4-DMP) dissolved in chloroform and shaking these two layers for 10min. at latter separate the organic phase from the aqueous phase and determine the absorbance and the distribution ratio (D) values at each concentration of metal ion. The results were as in Figures (6, 7):

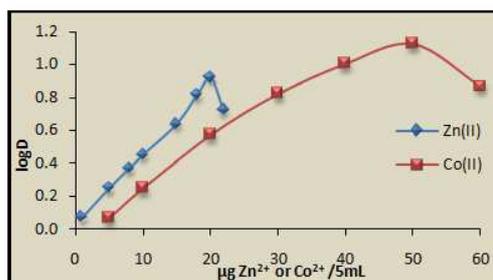


Figure 6: Effect of Metal ion Concentration on Onium Complex Formation and Extraction

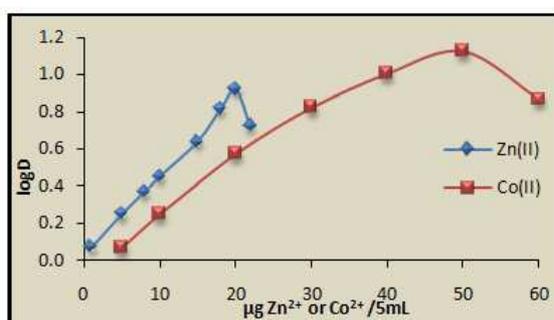
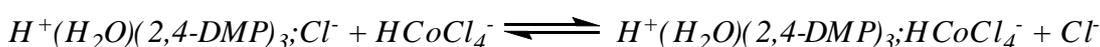
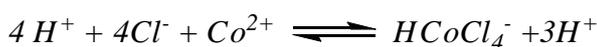
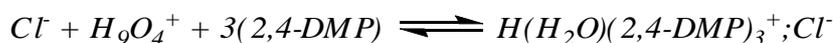


Figure 7: D= F[Metal Ion]

The results show the optimum concentration was 20µgZn²⁺ and 50µg Co²⁺, these concentrations suitable to reach thermodynamic equilibrium:



Whereas metal ion concentration inter to thermodynamic equilibrium for formation acidic halo metallic complex, which is given by thermodynamic equilibrium for exchange onium ion pair complex extracted into the organic phase, any concentration not enough to reach favorable equilibrium and decreased absorbance and the distribution ratio (D) values. Of concentration more than optimum effect to increase the rate of backward reaction and increase dissociation of the acidic halometallic complex, according to mass action law and Le chatlier principle.

Variation of 2,4-DMP Concentration

Extracted metal ions Zn²⁺ and Co²⁺ from 5mL aqueous solutions contain 20µgZn²⁺ or 50µg Co²⁺, and 0.5M HCl for Zn²⁺ and 0.8M for Co²⁺, shaking for 5min. and then added 5mL of (2,4-DMP) dissolved in chloroform at different concentration (1×10⁻⁵-3×10⁻¹M) and shaking the two layers for 10min. at latter separate the organic phase from the aqueous

phase and determine the absorbance and the distribution ratio (D) values according to the fundamental method at each concentration of 2,4-DMP. The results were as in Figures (8, 9).

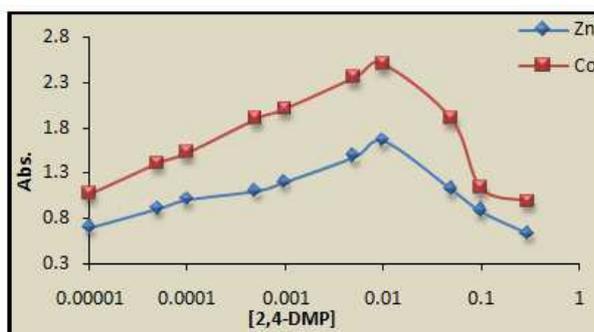


Figure 8: Effect of (2,4-MP) Concentration on Onium Complex Formation and Extraction

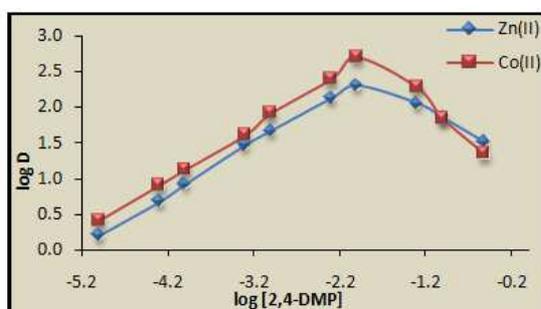


Figure 9: D= F [2, 4-DMP]

The results show absorbance as well distribution ratio increasing as a straight line with increasing 2,4-DMP 1×10^{-2} M for both metal ions, thus increasing in absorbance and distribution ratio values reflect the increasing in onium species formation, but the concentration more than optimum value at constant other variables effect to increase the rate of dissociation and decrease absorbance and distribution ratio values according to Le chatlier principle.

Shaking Time Effect

Extracted $20 \mu\text{g Zn}^{2+}$ or $50 \mu\text{g Co}^{2+}$ in 5mL aqueous solutions in presence 0.5M HCl for Zn^{2+} and 0.8M for Co^{2+} , shaking for 5min. afterward added 5mL of (2, 4-DMP) dissolved in chloroform at 1×10^{-4} M and shaking these two layers for different shaking time (2-20min.), as well as determined absorbance and distribution ratio values at each shaking time according to the main method detailed. The results obtained were as in Figures (10, 11).

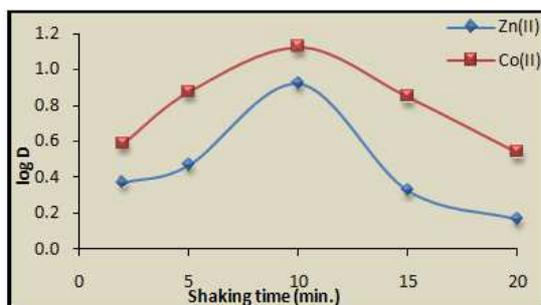


Figure 10: Complex Formation and Extraction=F [Shaking Time]

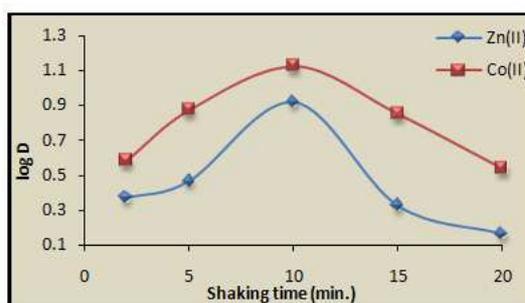


Figure 11: D= f [Shaking Time]

The results demonstrate onium complex formed and extracted increase with shaking time increasing till reached the optimum shaking time 10min. for both metal ions, at this time reached favorable thermodynamic equilibrium and giving a maximum concentration of onium species extracted, whereas shaking time reflect the kinetic side of extraction to complete reached for higher extraction efficiency any shaking time less than optimum not allow to reach equilibrium of extraction so that shaking time more than optimum causing increase rate of back ward direction of equilibrium.

Effect of Organic Solvent

Aqueous solutions 5mL in volumetric flask contain 20µg Zn²⁺ or 50µg Co²⁺ at optimum conditions shaking for 5min. afterward added 5mL solution of 2,4-DMP dissolved in different organic solvents at 1×10⁻⁴M concentration and shaking for 10min., then separate organic phase from aqueous phase, and taken UV-Vis. spectrum for organic phase against blank prepared at the same manner without metal ion, as well as treated aqueous phases according to spectrophotometric method for each metal ion^[14]. The results were in Figure (12a, 12b) and Tables (1, 2).

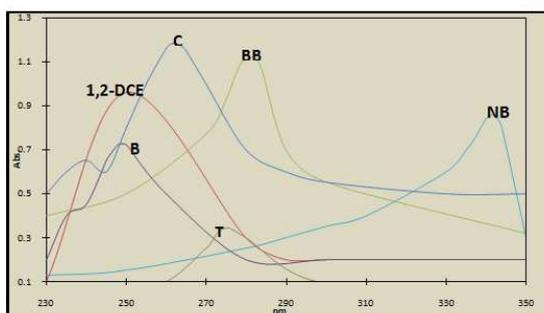


Figure 12a: UV-Vis Spectrum for Organic Solvent Effect on Extraction Activity of Zn (II)

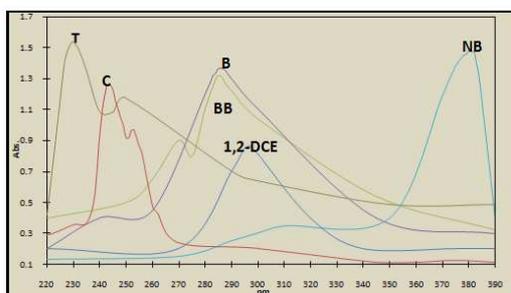


Figure 12b: UV-Vis Spectrum for Organic Solvent Effect on Extraction Activity of Co (II)

NB=Nitrobenzene, 1, 2-DCE=1, 2-Dichloroethane, BB=Bromobenzene,

C=Chloroform, B=Benzene, T=Toluene

Table 1: Molar Absorptivity and λ_{MAX} for Spectrums

Organic Solvents	ϵ	λ_{max} nm		Absorbance		Molar absorptivity (ϵ) L.mol ⁻¹ .cm ⁻¹	
		Zn(II)	Co(II)	Zn(II)	Co(II)	Zn(II)	Co(II)
NB	35.74	342	381	0.857	1.48	8570	14800
1,2-DCE	10.65	250	297	0.959	0.864	9590	8640
BB	5.400	281	285	1.121	1.32	11210	13200
C	4.806	262	243	1.187	1.26	11870	12600
B	2.804	249	286	0.728	1.37	7280	13700
T	2.438	275	230	0.342	1.54	3420	15400

Table 2: Effect of Organic solvent on Extraction Efficiency

Organic Solvents	ϵ	D		- ΔG_t		$K_A * 10^4$		K_{ex}		- ΔG_{ex}	
		Zn(II)	Co(II)	Zn(II)	Co(II)	Zn(II)	Co(II)	Zn(II) * 10^9	Co(II) * 10^8	Zn(II)	Co(II)
NB	35.74	2.69	15.67	0.04	0.03	6.04	9.82	1.19	144.38	47.23	52.87
1,2-DCE	10.65	3.76	11.82	0.22	0.20	7.78	7.56	2.31	82.19	48.73	51.59
BB	5.400	4.88	13.97	0.47	0.43	9.61	8.82	3.89	114.80	49.91	52.35
C	4.806	8.30	13.33	0.53	0.49	15.20	8.44	11.26	104.47	52.31	52.14
B	2.804	2.37	14.65	0.93	0.86	5.51	9.21	0.92	125.82	46.65	52.56
T	2.438	1.57	18.23	1.08	0.99	4.21	11.33	0.40	195.51	44.79	53.56

The results demonstrate there is not any linear relation between dielectric constant for organic solvents and distribution ratio (D) as well absorbance of complex extracted into the organic phase, that is mean there is not any effect of polarity and dielectric constant of organic solvent on extraction efficiency, but there is an effect of organic solvent structure on extraction efficiency and participate the ion pair complex extracted.

Effect of Temperature

Extracted 20 μ g Zn²⁺ or 50 μ g Co²⁺ according to onium system at optimum conditions except temperature (5-45°C) and according to the main procedure detailed at each temperature. The results were as in Figures (13, 14):

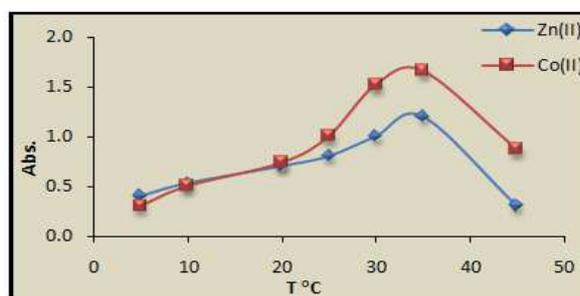


Figure 13: Absorbance=f [T°C]

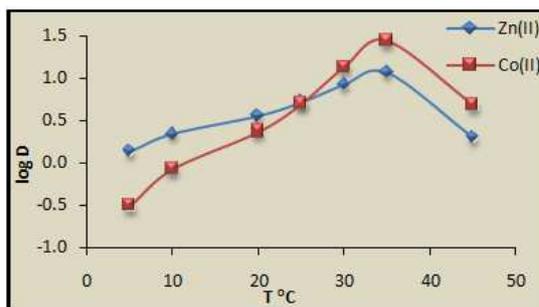


Figure 14: D= f [T°C]

The results in Figures (13, 14) demonstrate that (35°C) was the optimum temperature for each ions. And calculate extraction constant K_{ex} from distribution ratio according to relation below:

$$K_{ex} = \frac{D}{[M^{2+}]_{aq} \cdot [2,4-DMP]_{org.}}$$

Where $M^{2+} = Zn^{2+}, Co^{2+}$

The results were as in Figure 15:

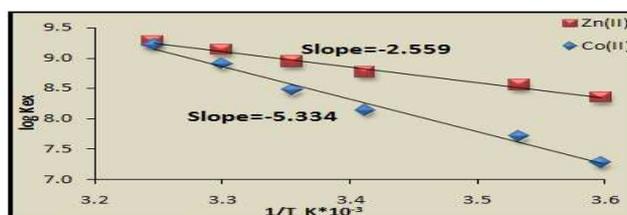


Figure 15: Extraction Constant KEX as a Function of Temperature

From the slope of straight line relations in Figure 15 and mathematical thermodynamic relations determine thermodynamic data:

Table 3: Thermodynamic Data

M^{2+}	ΔH_{ex} KJ.mol ⁻¹	ΔG_{ex} KJ.mol ⁻¹	ΔS_{ex} J.mol ⁻¹ .K ⁻¹
Zn ²⁺	0.049	-53.79	177.68
Co ²⁺	0.102	-53.41	176.60

The results show extraction according to onium system is endothermic behavior as well as the high value of entropy reflect the dependence of onium system method on entropic region to form onium species with high stability extracted to organic phase.

Effect of Interferences

Extraction Zn²⁺ and Co²⁺ at optimum conditions and in presence of many anions as interferences according to the main method detailed, the results were as in Table 4:

Table 4: Interferences Effect

Electrolyte salt	Zn(II)			Co(II)		
	D	%E	Abs.	D	%E	Abs.
KMnO ₄	2.70	73.00	0.069	3.03	75.20	0.76
Na ₂ C ₂ O ₄	1.94	66.00	0.031	3.17	76.04	0.87

KH ₂ PO ₄	1.53	60.50	0.045	2.45	71.00	0.72
tartrate	2.70	73.00	0.081	3.17	76.00	0.801
picrate	3.08	75.50	0.033	1.87	65.20	0.55
K ₂ Cr ₂ O ₂	4.13	80.50	0.070	2.01	66.80	0.68

The results demonstrate there is interference for all anions used in different activity.

Effect of Electrolyte

Extraction Zn²⁺ and Co²⁺ at optimum conditions for each analyze metal ion in presence different electrolytes, according to the main procedure detailed, the results were in Table 5:

Table 5: Effect of Electrolyte

Electrolyte salt	Zn(II)			Co(II)		
	D	%E	Abs.	D	%E	Abs.
LiCl	99.00	99.00	0.282	61.50	98.40	1.34
NaCl	22.81	95.80	0.193	58.52	98.32	1.25
KCl	19.20	95.05	0.123	49.51	98.02	1.11
RbCl	13.29	93.00	0.155	34.71	97.20	0.86
CsCl	10.56	91.35	0.131	27.90	96.54	0.75
MgCl ₂	27.57	96.50	0.142	50.02	98.04	1.2
CaCl ₂	18.05	94.75	0.126	46.62	97.90	0.903
SrCl ₂	12.16	92.40	0.112	31.89	96.96	0.82
BaCl ₂	9.58	90.55	0.101	25.45	96.22	0.74

The results show presence electrolyte salts in aqueous solution effect to increase extraction efficiency and this increasing appear as a function to the ionic diameter and charge density of cation and according to this phenomena LiCl giving higher extraction because Li⁺ has smaller ionic diameter and higher charge density, which is effect to more destroyed hydration shell of Zn²⁺ or Co²⁺ by pulling more water molecules to its hydration shell.

Effect of Methanol

Extracted 20µg Zn²⁺ or 50µg Co²⁺ each one alone from aqueous solutions, contain optimum concentration of HCl and in presence different percentage of methanol (5%-50%) and shaking these solutions for 5min. and then added 5mL organic solution of 2,4-DMP dissolved in chloroform at 1×10⁻⁴M concentration and shaking for 10min., afterward separate aqueous phase from organic phase, then measure the absorbance of organic phase at λ_{max}=262nm for Zn²⁺ and λ_{max}=243nm for Co²⁺ against blank prepared at the same manner without metal ion, but aqueous phase treated by spectrophotometric method^[14] for each ion and calculate distribution ratio D values for each ion according to procedure detailed in the main method. The results were as in Figures (16, 17).

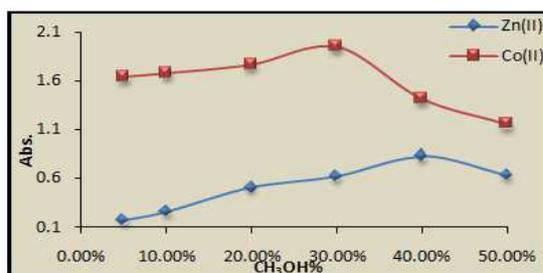


Figure 16: Effect of Methanol on Extraction Efficiency

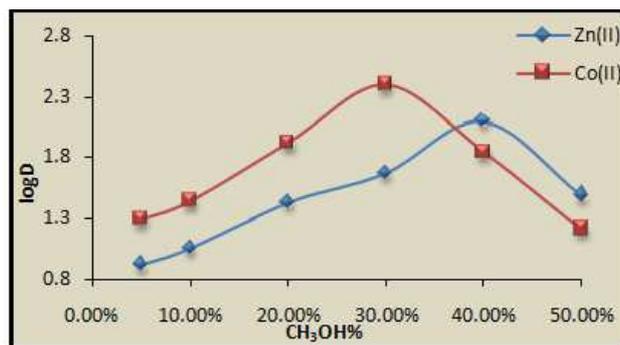
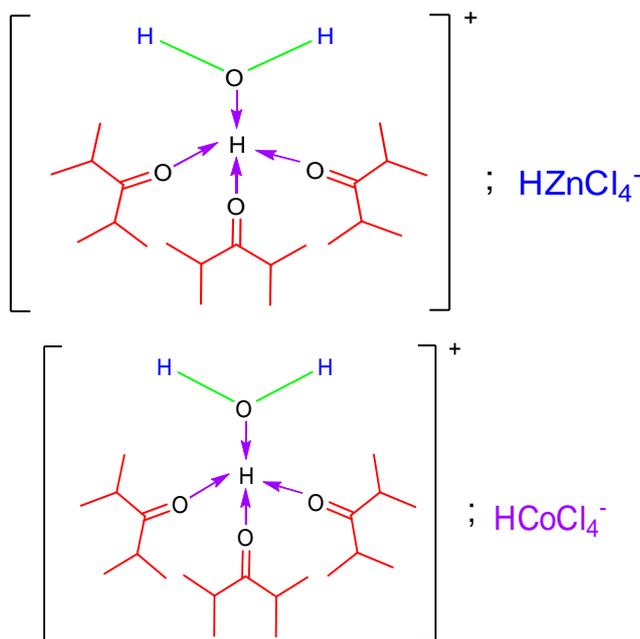


Figure 17: Effect of Methanol on Formation and Partition Complex into Organic Phase

The results show enhancement in extraction efficiency in presence methanol in aqueous solution as well as this enhancement increase by increasing methanol, till reached optimum percentage of methanol in aqueous solutions which is 40% with Zn²⁺ and 30% with Co²⁺, the methanol help to destroy hydration shell of metal ion and increase formation sex metal ion which increase formation onium product and this effect increase with increase concentration of CH₃OH till reached optimum any concentration of methanol more than optimum decrease extraction efficiency because effect to partition 2,4-DMP to the aqueous phase by reason of decline polarity of water.

The suggested structure of onium species extracted for Zn²⁺ and Co²⁺ such as below:



Spectrophotometric Determination

For spectrophotometric determination analyte metal ions we are need to preparing calibration curve by application the fundamental method at optimum condition for aqueous solution contain different concentrations of analyte metal ion Zn²⁺, Co²⁺. The results in the Figures (18, 19):

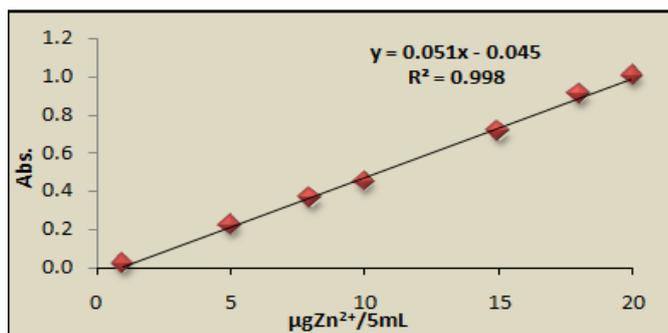


Figure 18: Calibration curve for spectrophotometric determination of Zn^{2+}

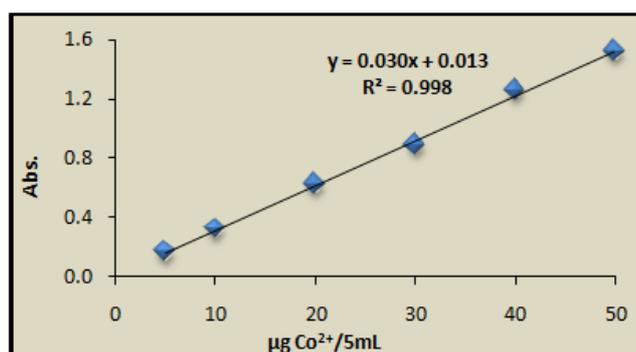


Figure 19: Calibration Curve for Spectrophotometric Determination of Co^{2+}

This method used for spectrophotometric determination of Zn^{2+} , Co^{2+} ions in different samples, where samples solution prepared according to wet digestion method^[15], and aqueous solution of sample treated as fundamental method for extraction and used the suitable masking agent for each ion. The results were as in Table 6:

Table 6: Applications

Sample name	Zn(II) ppm	%RSD	Co(II) ppm	%RSD
<i>Al-Salam Valley</i>	112.11	0.63	45.62	0.15
<i>Agriculture soil Al-Shwati</i>	182.23	0.39	26.00	0.27
<i>Agriculture soil Al-Mishkhab</i>	175.09	0.40	30.47	0.23
<i>Non agriculture soil Al-Mishkhab</i>	135.00	0.52	55.77	0.13
<i>White meat of chicken (breast)</i>	26.60	0.27	0.08	0.12
<i>Cow meat (beef)</i>	35.24	0.20	0.07	0.14
<i>Chicken Livers</i>	21.33	0.34	0.52	0.19
<i>Farms Fish</i>	42.91	0.17	0.43	0.23
<i>Garden cress</i>	22.01	0.32	0.02	0.50
<i>Leek</i>	20.00	0.35	0.09	0.11
<i>Celery</i>	51.16	0.14	0.11	0.09

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