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CLOUD POINT EXTRACTION METHOD FOR SEPARATION AND PRE

CONCENTRATION OF MG (II) AS ANION COUPLED WITH SPECTRO PHOTO METRIC APPLICATIONS

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ABSTRACT

Cloud point extraction methodology used as qualified procedure for separation Magnesium (II)as anion after combination with Oxine as well as for spectrophotometric determination The method involved the formation ion pair association complex between Rhodamin–B⁺ and Oxine anion complex of magnesium [Mg(OX)3⁻] in basic media, and this complex extracted to surfactant Triton X-100 at optimum conditions The cloud point layer which is contain ion pair complex extracted mediated with ethanol solvent and spectrophotometrically measured at λ_{max} =648nm ,also by adoption on Eriochrom Black-T method spectrophotometrically determination ,the remaining Mg²⁺ in aqueous phase after extraction and calculate distribution ratio D. This study demonstrates all optimum conditions for high efficiency of extraction as well illustrated all factors affect on extraction, in addition to applicable this method.

KEYWORDS: Cloud Point Extraction, Preconcentration, Magnesium

INTRODUCTION

Magnesium is an important element has numerous physiological functions in the body in health as in disease, so appear relation with muscle function. As well magnesium affects oxygen uptake, energy production and electrolyte balance Magnesium is re-distributed within the body to accommodate altered metabolic needs. When restricting or reducing diets to maintain or reduce body weight using chloranilate as suitable chelating agent for determination Magnesium by cloud point extraction(CPE) methodology fallowed flame atomic absorption (FAAS)¹.CPE methodology has been successfully used for the preconcentration of trace amounts of Mg²⁺ as a prior step to their determination by flame atomic absorption spectrometry (FAAS) at a solution pHof10,Quanizarin1,2 and Triton X-114 were used as hydrophobic ligand and nonionic surfactant, respectively the chemical variables affecting the preconcentration process were optimized, the proposed method was successfully applied to the determination of magnesium in fruits and vegetables samples². Extraction and coupled with spectrophotometric determination of Cu2+, Co2+andAg+bycloud point extraction methodology with high efficiency³. As sensitive method used cloud point extraction for separation Pd²⁺, Co2⁺ and Cu²⁺ in different vital samples after complex formation with 1-phenyl thiosemicarbazide and extracted on TritonX-114 coupled with flame atomic absorption (FAAS) for determination⁴. Cloud point extraction coupled with flame atomic absorption for separation and determination Ag+ in water samples by usedithizone as complex agent and Triton X-114 with detection limit 0.7µg L⁻¹⁵. In sensitive application of cloud point extraction methodology extracted and spectrophotometric determination Ni²⁺,Cd²⁺ and Pb²⁺ by two complexing agent 2-[(Benzothiazolyl)azo]-4-benzyl phenol and 2-[(3-Bromo phenyl)azo]-4,5-diphenyl

imidazole in different environmental and vital samples⁶. Effective separation for Cu²⁺, Zn²⁺, Pb²⁺, Ni²⁺, Co²⁺ and Cd²⁺ from water samples by CPE method with using 8-hydroxy quinoline coupled with inductive coupled plasma⁷. Used psulfornateo calix [4] arene as complexing agent with TritonX-100 for separation Cu2+ and La3+ by cloud point extraction methodology from weak acidic media8. Dependence on CPE method and bromothymol blue in acetate buffer media with used TritonX-114 extracted codeine from drugs and biological samples, and measure absorbance of cloud point after dissolved in ethanol with detection limit 2.6µgL⁻¹⁹.Ag⁺extracted and determination in water samples by CPE coupled with flame atomic absorption in presence of TritonX-114 at pH=10 with D.L=6.3µgL⁻¹¹⁰. Another worker appliance CPE method coupled with flame atomic absorption to preconcentration as well determination of Pb2+in different soil and water samples by use 1-(2-pyridyl azo)-2-naphthol and Triton X -114 at pH=8 11. By used methyl trioctyl ammonium as complex agent with CPE method coupled with flow injection make separation and determination of Cd2+as CdI4 formation ion association complex with TritonX-114 giving detection limit 0.3µgL-1 12. By followed CPE method and used BHIS as complexing agent with Triton X -114 extracted small amount of Ag⁺at pH=8 with detection limit 1.9µgL⁻¹¹³. Some worker followed CPE method and FAAS by used Triton X-114 at pH=5 and N,N-[2,2(ethane-1,2-diyl bis(oxy)bis(ethane-2,1diyl)bis(2-chloroacetamide) as complexing agent for determination Iron in different sandy soil samples with detection limit 1.22µgL⁻¹¹⁴.Using micelle-mediated extraction was developed for separation and spectrophotometric determination of manganese as MnO₄ by brilliant green in acidic solution and the ion pair complex was extracted into surfactant Triton X-100 at optimum condition with detection limit $0.086\mu g \text{ mL}^{-115}$.

Experiment

A shimadzu double beam UV-visible spectrophotometer model uv-1700 (Japan) equipped with 1cm cell path length for study absorption spectra of complexes formed. But absorbance measurement were performed with shimadzu single beam UV-visible model 100.02 spectrophotometer (Japan).

Reagent and Material

All analytical grade reagents were used a received from different company without further purification. doubled distilled water was used for diluting the standard reagents and samples surfactant TritonX-100 consider as nonionic surfactant which is having a structure C_8H_{17} $C_6H_4(C_2H_4O)_n$ and an equal to 9-10 with average molecular weight of 625gmol⁻¹was ready from Sigma (purity>99.610). The stock solution of Mg^{2+} at 1mg/mL was prepared by dissolved of 0.2877gm of $MgSO_4.7H_2O$ dried at $110^{\circ}C$ for 10minutes in 100mL of doubled distilled water in volumetric flask. Rhodamin-B at 1×10^{-2} Mconcentration prepared by dissolved 0.4790gm in water by used volumetric flask. Buffer solution pH=9.6 prepared by dissolved 6.0gm of NH₄Cl in water then added 12mL of concentrated ammonia and complete the solution to 100mL in volumetric flask 0.02% Eriochrom black T prepared by dissolved in water with fixed volume. 0.2M 8-hydroxy quinoline prepared by dissolved fixed quantity in moderate basicsolution.

General CPE Procedure

10mL aqueous phase contain defined quantity of magnesium and 0.5mL of 1% Triton X-100,so 1×10⁻⁴M Rhodamin-B with 0.02M 8-hydroxyl quinoline as well 0.5M sodium hydroxide NaOH, after mixing the solution very well heating in water bath at 90°C for suitable time until formation high density smaller volume cloud point layer ,at latter separate cloud point layer from large aqueous solution, measure the absorbance of cloud point layer after dissolved in 5mL

ethanol at fixed wave length λ_{max} as well as determine distribution ratio D by measurement remainder quantity of Mg^{2+} in aqueous solution ,and transferred quantity into cloud point layer by spectrophotometric method published elsewhere 16.

Samples Preparation

To 5gm of any sample in 250mL conical flask add 10mL of concentrated nitric acid HNO₃ and heating for boiling point on electrical hotplate to minimize the volume into 2mL after cooling the samples add once more 10mL concentrated nitric acid and 5mLconcentrated sulfuric acid H_2SO_4 with 4mL of hydrogen peroxide H_2O_2 , then heating on electrical hotplate for 10minutes ,at latter added 10mLdouble distilled water and heating to suitable time for emphasis liberation all acids ,at last filtered the solution and complete the solution to 100mL by double distilled water. An aliquot of 5mL of each samples solution pipette into 10mLconical flask added 0.1mL of 1×10^{-2} M potassium cyanide solution as masking agent to the filtered. Filtratedtransferred into 10mL volumetric flask and treated according to general CPE procedure and measured absorbance of cloud point formed at λ_{max} of 648nm against blank prepared at the same manner without magnesium.

RESULTS AND DISCUSSIONS

Absorption Spectra

Absorption spectra in Figure 1 demonstrate Absorption spectra for reagent Rhodamin-B and ion pair complex $[Rhb^+][Mg(OX)_3^-]$ which separated in surfactant rich phase against blank prepared at the same manner were recorded using shimadzuUV1700 equipped with 1cm cell path length quartz cell. It was appeared that the absorption maximum λ_{max} =570 nm, therefore λ_{max} =648 nm for ion pair complex was used throughout this work.

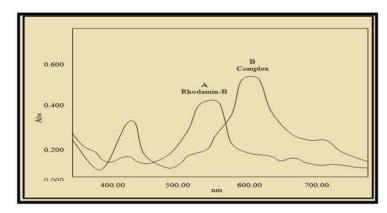


Figure 1: Absorption Spectra for Reagent Rhodam in-B and Ion Pair Complex [RHB⁺][Mg(OX)₃-]

Effective Parameter on CPE Method

Several experimental parameters which impact the CPE efficiency were carried out by classical optimization we observe the effect of one factor at a time on an experimental response.

Effect of Metal Ion Concentration

Several aqueous solutions contain rising quantity of metal ion $1\mu g$ - $50\mu g$ in 10mL and 0.5M NaOH, $1\times10^{-4}M$ Rhodamin-B as well $2\times10^{-2}M$ 8-hydroxy quinoline in addition to 0.5mL of 1% Triton X-100. Heating the solution in

electrical water bathat 90° C for 20minutes until cloudpoint formation with high density smaller volume, then separate micelles rich phase layer from aqueous solution, and dissolve micelles rich phase in 5mL absolute ethanol and measure absorbance at λ max=648 nm against blank prepared at the same manner in absence metal ion Mg^{2+} . As well deal with aqueous solution according to spectrophotometric method 16, to seek the help of Figure 2 to determination remainder quantity of Mg^{2+} in aqueous solution after CPEmethod and transferred quantity to micelle rich phase to calculate distribution ratio D .

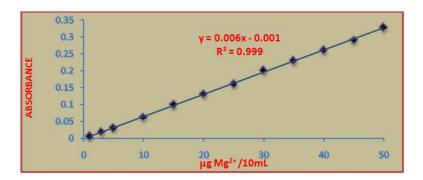


Figure 2: Calibration Curve for Method

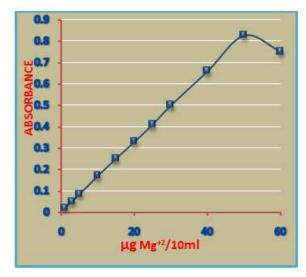


Figure 3: Variation Complex Formation as Function of Metal Ion Concentration

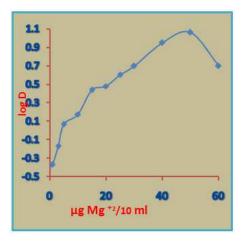


Figure 4: The Dependence Log D =F [Mg2+]

The results in Figures 3,4 demonstrate maximum complex formation and stability at 50µg/10mL consideration the concentration of metal ion is thermodynamic value effect on thermodynamic quilibrium of complex formation and stability as well as extraction behavior according to CPE method ,the results appear increasing in complex formation and distribution ratio with increasing metal ion concentration, whereas concentration of metal ion less than optimum value not allow to reach thermodynamic equilibrium. So metal ion concentration more than optimum value effect to decreasing complex formation and extraction efficiency according to lechatelier principle

Effect of 8- Hydroxyl Quinoline Concentration

Aqueous solution 10mL in volume contain $50\mu g~Mg^{2+}$ with rising concentration of 8-hydroxy quinoline $5\times10^{-3}M$ to $1.8\times10^{-1}M$ and 0.5 m NaOH as well 0.5 m L of 1% Triton X-100 in addition to $1\times10^{-4}M$ Rhb+Cl heating the solution at 90° C for 20minutes in thermo stated bath until isolation micelles rich phase as cloud point layer, separate cloud point layer from aqueous solution. then dissolve micelles rich phase in 5mL absolute ethanol and measure absorbance at higher absorbance wave length λ_{max} =648nm against blank prepared at the same manner in absence metal ion Mg^{2+} from other hand aqueous solution treated according to spectrophotometric method16 to determine remainder quantity of Mg^{2+} in aqueous phase to seek the help of Figure 2 as well transferred quantity of Mg^{2+} to micelles rich phase as complex and calculate distribution ratio D.

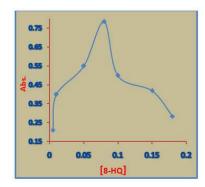


Figure 5: Complex Extracted Formations Vary a Function (8- HQ) Concentration

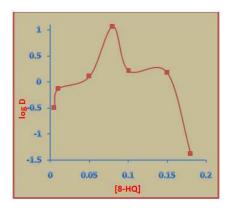
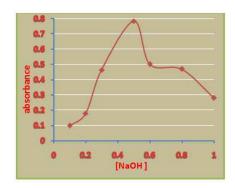


Figure 6: Effect Of [8-HQ] on Distribution Ratio D Value in CPE Method

The result in Figure 5,6 show increasing absorbance of alcoholic solution of cloud point layer and distribution ratio D, with increasing 8-hydroxyquinoline rising to better equilibrium of complex formation and higher extraction efficiency at optimum value of 8-hydroxy quinoline which was 8×10^{-2} M, any concentration less than optimum value not allow to reach thermodynamic equilibrium in complex formation and extraction, 8-hydroxy quinoline concentration more than optimum value effect to increasing dissociation step of complex which is effect to decrease complex extracted into micelles rich phase layer giving decline in absorbance and distribution ratio D value.

Effect of NAOH Concentration

Basic media play an effective rule for changing 8-hydroxy quinoline to oxine and reacting with magnesium metal cation to from anion complex can be extracted with Rhodam in-B as ion pair complex this operation submitted to thermodynamic equilibrium and concentration of basic media is very effective parameter play to limitation, the bestequilibrium and highest extraction, to quittance this optimum concentration of Basic media taken several aqueous solution 10mL in volume contain $50\mu\text{g}$ Mg²⁺, 0.5mL 1% Triton X-100, $1\times10^{-4}\text{M}$ Rhb⁺;Cl⁻, 0.08M, 8-hydroxy quinoline, and rising concentration of NaOH 0.1M to 1.0M, after heating the solution at 90°C for 20minutes in electrical water bath until formation cloud point layer, separate micelles rich phase layer from aqueous solution, and dissolved in 5mLethanol and measured the absorbance at λ max=648 nm against blank prepared at the same manner in absence metal ionMg²⁺, as well aqueous solution treated according to spectrophotometric method16 to seek the help Figure 2 for determination remainder quantity of Mg²⁺in aqueous phase as well transferred quantity of Mg²⁺to micelles rich phase layer and calculate distribution ratio D.



1.5 1 - 0.5 - 0.5 -1 - 1.5 - 2 0 0.5 1 [NaOH]

Figure 7: Ion Pair Complex Formation as A Function of [NAOH]

Figure 8: Distribution Ratio D Change with [NAOH]

The results in Figures 7, 8 shows effective optimum concentration of NaOH in aqueous solution giving higher absorbance for complex transferred to micelles rich phase and distribution ratio D was 0.5M NaOH, any concentration of NaOH less than optimum value not favorable for extraction according to CPE method, as well as concentrations more than 0.5M appear decline in extraction efficiency by reason of increasing dissociation equilibrium according to the lechatelier principle.

Effect of Rhodamin-B Concentration

Extraction efficiency depend on ion pair complex formation so that extracted into micelles rich phase layer, but ion pair complex need fixed concentration of complexing agent Rhodam in-B to giving best extraction, and this concentration define experimentally by taken Several 10mL aqueous solutions each one contain $50\mu g \, Mg^{2+}$, $0.5M \, NaOH$, $8\times10^{-2}M \, 8$ -hydroxy quinoline in addition to 0.5mL of 1% Triton X-100 with different concentration of Rhodamin-B $1\times10^{-6}M$ to $1\times10^{-3}M$, heating these solution in electrical water bath at $90^{\circ}C$ for 20minutes until cloud point layer formation, separate micelles rich phase layer from aqueous solution and dissolved in 5mL absolute ethanol and measure absorbance at λ_{max} =648 nm against blank prepared at the same manner in absence metal ion Mg^{2+} , from other hand aqueous solution treating according to spectrophotometric method 16 , And Figure 2 to determination remainder quantity of Mg2+in aqueous solution after CPE method and transferred quantity to micelle rich phase and calculate distribution ratio D the results obtained as in Figures 9,10

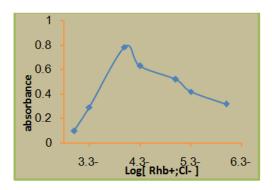


Figure 9: Change of Complex Absorbance with Concentration RHB+; CL-

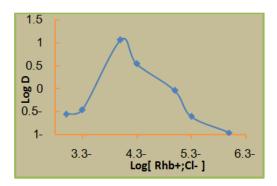


Figure 10: Function Relation=F [RHB+; CL].

The results in Figures 9, 10 demonstrate 1×10^{-4} M was the optimum concentration giving the best thermodynamic equilibrium for complex formation and extraction into micelles rich phase layer which is appear as higher absorbance and distribution ratio D. Any concentration of Rhodamin-B less or more than 1×10^{-4} M not realize effective extraction because the concentration of Rhodamin-B was not suitable for extraction.

Effect of Triton X-100 Concentration

Whereas extraction according to CPE methodology depend on surfactant used with constitution of micelles which is extracted complex formed in cloud point layer formation ,as well as concentration of this surfactant in aqueous solution effect on efficiency of extraction ,an experiment about this purport,10mL aqueous solution contain 50 μ g Mg²⁺, 0.5M NaOH ,1×10⁻⁴M Rhodamin-B ,as well 8×10⁻²M 8-hydroxy quinoline with changeable volume of 1% TritonX-100 0.1mL to 0.8mL heating the solution in a thermo stated bath at 90°C for 20minutes. Then separate cloud point layer from aqueous solution .and dissolved in 5 mL absolute ethanol and measure the absorbance at λ_{max} =648 nm vies against blank prepared at the same manner in absence metal ion Mg²⁺as well as calculate distribution ratio D by followed spectrophotometric method¹⁶getting the results in Figures 11,12.

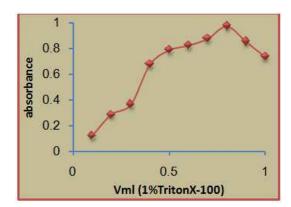


Figure 11: Effect of Triton X-100 Concentration on Extraction Ability

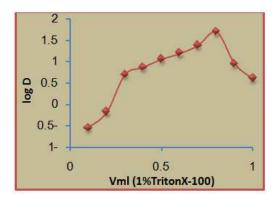


Figure 12: Effect of Triton X-100 Concentration on Distribution Ratio

The results shows optimum volume of 1% Triton X-100 giving higher efficiency of extraction appear from high absorbance of alcoholic cloud point layer and distribution ratio was 0.8mL, this quantity of Triton X-100 enough to extracted all ion pair complex formed but any quantity less not enough to that and this aggregation of micelles and extraction on it to submit to thermodynamic equilibrium then Triton X-100 more than 0.8mL effect to increase diffusion in aqueous solution and decrease extraction ability.

Thermodynamic study

Generally CPE method is an endothermic behavior appear increasing aggregation of micelles in smallest volume and higher density to giving favorable cloud point layer extracted ion pair complex formed, but there is fixed temperature shows excellent state make an experiment at all conditions defined at previous experiment but heating for different temperatures 70°C to 90°C for 20minutes giving the results as in Figures 13, 14.

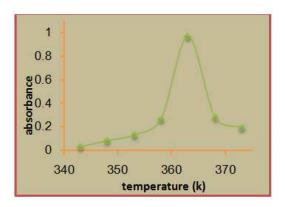


Figure 13: Absorbance Increasing with T K.

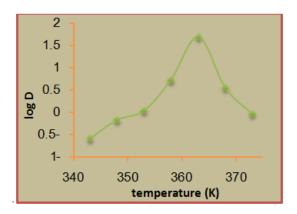


Figure 14: D= F (TK)

The results shows increasing absorbance and distribution ratio D with increasing temperature TK to optimum 90°C and decreasing in absorbance and D values at temperature more than 90°C because increasing temperature help to increasing of cloud point layer formation by increasing dehydration and increase density of this layer with smallest volume to giving good extraction, for determine thermodynamic data calculated extraction constant from the relation.

$$K_{ex} = \frac{D}{[Mg^{+2}][Rhb^+;Cl^-]}$$

And form the linear relation $Log K_{ex}$ and 1/T K, Figure 15 calculate thermodynamic date from the relation.

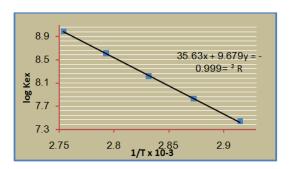


Figure 15: KEX = F(T K)

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

 $\Delta Gex = -RTLn Kex$

 $\Delta Gex = \Delta Hex - T\Delta Sex$

Table 1

ΔHex K.J.Mole-1	ΔGEX K.J.Mole-1	ΔSexj.Mole-1 S-1
0.4201	-61.09	169.4

High value of entropy ΔS exreflect the behavior of this method in extraction and appear is entropic region by

increase dehydration attitudes with increasing temperature and creation anew system in solution which is cloud point layer, all temperature more than optimum effect to increase micelles diffusion in large solution and missing extraction ability.

Effect of Heating Time

Another factor effect on extraction ability according to CPE method is the time of heating ,to demonstrate that ,make an experiment for extraction at optimum conditions but heating for different times from (10–30)minutes. The results appear in Figures 16, 17.

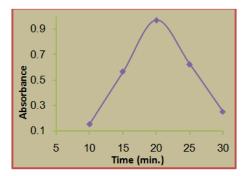


Figure 16: Effect of Heating Time on Extraction Ability

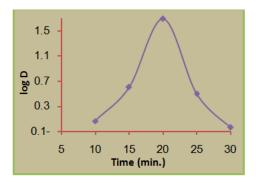


Figure 17: Effect of Heating Time on D Values

The results shows 20minutes was the optimum heating time giving higher absorbance and distribution ratio because the time of heating illustrate the kinetic energy behavior of aqueous solution to aggregate micelles in smaller volume and high density and any time less than 20minutes not ensure that, so as heating time more than 20minutes effect of increase diffusion micelles in aqueous solution and decrease extraction efficiency.

Stoichiometry

Two methods used for define ion pair complex extracted to cloud point layer according to CPE method:

Slope Analysis Method

Extracted ${\rm Mg}^{2+}$ according to CPE methodology under optimum conditions and distribution ratio values at different concentration of Rhodamin-B show straight line relation as in Figure 18 with slope value equal to (1.007).

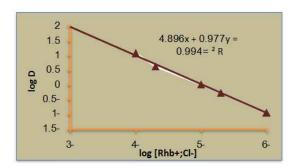


Figure 18: Slope Analysis Method

The results demonstrate the structure of ion pair complex extracted was 1:1 Rhb⁺; Mg (OX)₃.

2- Slope Ratio Method

Performance two experiments the first extraction according to CPE method at optimum condition with different concentration of metal ion Mg^{2+} , then experiment giving straight line relation between absorbance of alcoholic solution of cloud point and molar concentration of metal ion Mg^{2+} with slope equal to 3792.190 as in Figure 19A, the second experiment extraction Mg^{2+} according to CPE method at optimum condition and different concentration of Rhodamin-B , this experiment giving linear relation also between absorbance and molar concentration of Rhodamin-B with slope equal 4575 as in Figure 19B .

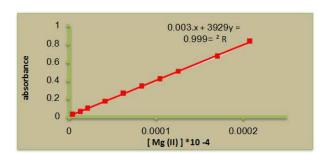


Figure 19 A: Absorbance = F [Mg2+]

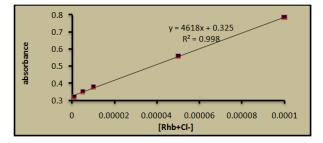


Figure 19 B: Absorbance = F [RHB+; CL-]

Dividing slope value of Figure 19B over slope value for Figure 19A giving the value equal to 1.2 that is mean the ion pair complex extracted was 1:1 [Rhb]⁺; [Mg(OX)₃]⁻

Effect Kind of Surfactant

10mL aqueous solution contain $50\mu g$ Mg²⁺under optimum conditions pin point at all experiments makes but differ in surfactant used $1\times10^{-4}M$ Tween 20 ,Tween 40, Tween 80, SDS, when all previous experiments used Triton X-100 after heating these solutions in electrical water bath at $90^{\circ}C$ for 20minutes to produce cloud point layer which is Separate and treated the aqueous solution according to spectrophotometric method 16 and calculate distribution ratio D. The results as in Figure 20.

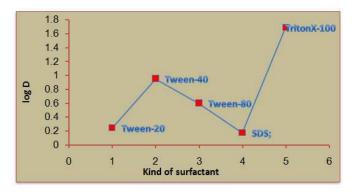


Figure 20: Effect of Surfactant Kind

The results shows Triton X-100 was the best surfactant for extraction under optimum conditions used and may be other surfactant need limitation optimum conditions for each one because each surfactant having different ability for formation micelles rich phase in addition to differ in the nature and behavior as surfactant for separation.

Effect of Electrolyte Salt

Hydrated inorganic salts play a major rule in CPE method because effect toincrease dehydration and micelles rich phase produce with higher density smallest volume in addition to different effect with different electrolyte salt and to see that aqueous solutions 10mL in volume contain optimum values as well 1×10^{-2} M of differ electrolyte salt, afterwards heating in electrical water bath at 90°C for 20minutes until forming micelles rich phase layer and separated to dissolved in 5mL ethanol and measured the absorbance of this alcoholic solution at λ_{max} =648 nm against blank prepared at the same manner in absence metal ion Mg²⁺, as well aqueous solution treated according to spectrophotometric method16. The results as in Table(1). Without electrolyte salt (abs=0.971) (D=49).

Table 2: Effect of Electrolyte Salt on Extraction Ability of Ion Association Complex

Electrolyte	Absorbance at	Distribution	
Salt	684 Nm	Ratio D	
LICL	1.266	499	
NACL	1.130	165.67	
KCL	1.079	124	
NH4Cl	0.994	82.33	
CaCl2	1.151	165.67	
MgCl2	1.037	99	
NiCl2	0.463	3.76	

Determination of Magnesium in Real Samples

The proposed method was applied to the determination of Magnesium in soil, vegetables, meat and fish samples,

each samples treated according to digestion procedure explained in experimental work and all Magnesium change into ion pair complex extracted separated on micelles rich phase, by measure the absorbance at λ max=648 nm against blank without ion Mg²⁺.

Table 3

Samples	Proposed Method (PPM)	
Agricultural soil	92	
Non-agricultural soil (Al-Salam Valley)	380	
Cow meat (beef)	10	
Farms Fish	3	
Date	6	
Banana (imported)	12	
Orange(imported)	4	
Spinach	8	
Celery	64	
Peppergrass	20	

CONCLUSIONS

This work include new idea for extraction and determination Magnesium in the form of anion after change metal cation Mg²⁺into complex anion with oxine in basic media Mg(OX)₃] and react with Rhodam in-B to form ion pair complex extracted into micelles rich phase ,although thermodynamic study and effect of many parameters gave encouraging results. Also the proposed procedure to increase the popularity of UV–VIS spectrophotometric technique after CPE methodology to reflect high accurate method

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