Application Cloud Point Extraction Method Joined with Liquid Ion Exchange for Selective Determination of Fe^{3+} and Hg^{2+} in Real Samples

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Abstract: By using two approaches cloud point extraction technology CPE and liquid ion exchange to separate and extracted Fe(III) and Hg(II) ions from acidic HCl media as ion pair association complexes by using new laboratory prepared 2-(4-hydroxy phenyl azo)-4-benzene naphthol (HPBN) whereas the spectrophotometric studies show the new organic reagent (HPBN) have a wave length for maximum absorbance was $\lambda_{max} = 450$ nm, the ion pair association complex of Fe^{3+} $\lambda_{max} = 477$ nm but for Hg^{2+} $\lambda_{max} = 476$ nm, so that, the optimum condition for high extraction efficiency was 0.5M HCl for both ions ,100 µg metal ions in 10 mL aqueous solution 1×10^{-4} M of HPBN and necessary to heating the solution at 90°C for 20 min to Fe^{3+} ion and 15 min. For Hg^{2+} ion and in presence of 0.5 mL Triton X-100 for Fe^{3+} and 0.8 mL Triton X-100 for Hg^{2+} ion. As well as the research involved other studies such as electrolyte effect interferences effect, stoichiometry, application and determination of trace amounts of Fe(III) and Hg(II) in environmental sample by spectrophotometry.

Key words: Cloud point extraction, liquid ion exchange, 2-(4-hydroxy phenyl azo)-4-benzene naphthol (HPBN), mercury, iron, Hg(II)

INTRODUCTION

Cloud Point Extraction (CPE) is sensitive, simple method to determine many of the micro amount elements from various chemical and biological systems (Tokalioglu *et al.*, 2000; Samaddar and Sen, 2014). The system depend on using surfactants and that too at low concentrations at specific temperatures to form clouds that separate out from the aqueous solution (Jawad and Azooz, 2014, 2015a, b; Jawad and Hayder, 2015). Liquid ion exchange method consider as indirect method for extraction metal ions as oxyanions or hallo anion complexes after formation ion pair association complexes by using suitable reagent in acidic medium this method very sensitively to extraction Cd^{2+} and Hg^{2+} ions by using many organic reagent (Jawad and Hameed, 2017). By joined liquid ion exchange and CPE as extracted Pt(II) ion from acidic HCl media as ion pair association complexes by using Janus green B(JG) 1×10^{-4} M and 0.5 mL TritonX-100 after heating at 75°C for 15 min. The complex extracted was $[JG^{+}; HptCl_{4}^{-}]$ (Jawad and Salih, 2015). Use crown ether DB18C6 and from Hcl media extracted Fe^{3+} ion by CPL after change Fe^{3+} into $FeCl_{4}$-TritonX-100 was necessary to obtained higher extraction efficiency, there are another empirical application for this study in real sample. By using new reagent 3-[(2-pyridyl azo)]-1-nitroso-2-naphthol (PANN)

from acidic media of 1M HCl as a liquid ion exchanger for extraction Zn^{2+} by application CPL with presence 0.6 mL TritonX-100 and determination Zn^{2+}in different samples (Jawad and Azooz, 2015a, b). For extraction and determination of $Fe^{3+}$and Hg^{2+}ions from aqueous solution using onium system coupled with CPE in presence of BAEE from HCl aqueous solution and TritonX-100 as surfactant. As well as the research involved other studies such as electrolyte effect interferences effect, application for determination of Fe^{3+} ion and Hg^{2+}ion in biologic samples (Jawad *et al.*, 2017).

MATERIALS AND METHODS

Experimental: For spectroscopic studies and absorbance measurements used double beam spectrophotometer Biochrom Model (80-7000-11) Libra S60 Cambridge CB40FJ with 1.00 cm quartz cell and FTIR spectrophotometer Shimadzu FTIR 8400 series (Japan), so that, used Electrostatic water bath (WNB7-45) (England) for heating to CPT as well as all experiments needed balance (A & D Company, Limited, Dool, CE, HR 200, Japan) (±0.0001g).

Materials and solution:s For preparing all the solutions needing in experiment used high purity materials received from commercial sources without further purification and

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used doubly distilled water with set of suitable glassware, stock solution 1 mg/mL of Fe^{3+} ion prepared by dissolving 0.2880 g of $FeCl_3$ in 100 mL and for Hg^{2+} ion dissolved 0.1353g of $HgCl_2$ in 100 mL of distilled water other working solutions preparing by dilution with distilled water in suitable volumetric flask, so, $1 \times 10^{-2}M$ of HPBN was prepared by dissolving 0.0850 g in 25 mL distilled water contain TritonX-100. Other working solutions were prepared by dilution method with distilled water.

Comprehensive method: Aqueous solutions 10 mL in volume contain 100 µg of Fe^{3+} or Hg^{2+} with optimum concentration HCl and $1 \times 10^{-4}M$ HPBN in the presence optimum volume of surfactant 1% TritonX-100. Heating the solution in electrostatic water bath for suitable temperature and time until formation Cloud Point Layer then separated CPL from aqueous solution and dissolved CPL in 5 mL ethanol. The absorbance of alcoholic solution is measured at $\lambda_{max} = 477$ nm for Fe^{3+} and $\lambda_{max} = 476$ nm for Hg^{2+} ion against blank prepared in the same manner without metal ions. But aqueous solution for Fe^{3+} ion treated according to thiocyanate method but Hg^{2+} ion treated according to Dithizone spectrophotometric method (Marczenko and Balcerzak, 2000) to determine the remainder quantity of metal ions in aqueous solution after extraction and subtraction this quantity from original quantity 100 µg to determine the transferred quantity to CPL to formation ion pair association complex extracted then calculated Distribution ratio (D) according to relation Eq. 1:

$$D = \frac{[M^{n+}]_{CPL}}{[M^{n+}]_{aq}} \quad (1)$$

Whereas:

$$M^{+n} = Fe^{3+} \text{ or } Hg^2$$
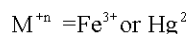
RESULTS AND DISCUSSION

The laboratory preparing of the new organic reagent HPBN (Shibata *et al.*, 1976) demonstrate according to mechanism (Fig. 1).
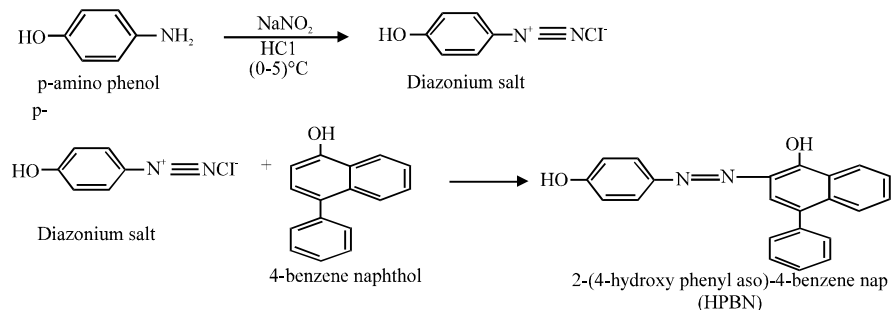
Spectrophotometric studies: The spectrum of new organic reagent HPBN dissolved in aqueous solution contain some drops of TritonX-100 shows wave length of maximum absorbance was $\lambda_{max} = 450$ nm as in Fig. 1. FTIR for this reagent appear as in Fig. 2. So that, to determining the wave length of maximum absorbance of ion pair association complex extracted for each metal ion under study, taking 10 mL aqueous solutions contain 100 µg of metal ion Fe^{3+} or Hg^{2+} in the existence of 0.5 mL HCL, $1 \times 10^{-4}M$ (HPBN), 0.5 mL of TritonX-100. Heating the solution at 90°C for 15 min until formation Cloud Point Layer CPL, separating CPL and dissolved in 5 mL of ethanol and then taking UV-VIS. Absorption spectrum to the alcoholic solution the results demonstrate in Fig. 2-5

The spectra shows wave length of maximum absorption of HPBN was $\lambda_{max} = 450$ nm, IR spectrum show peak at wave number 3400 cm^{-1} belong to stretching vibration -OH group for naphthol but aromatic C-H appear at 3061-2973 cm^{-1}, Bending vibration for phenolic C-O giving peak at 1303 cm^{-1}, also, peak at 1585 cm^{-1} for C = C aromatic as well as the weak peaks at 1450-1350 cm^{-1} belong to N = N also the region 1510-1100 cm^{-1} belong to all the peaks for vibration of bridge azo group also the peak at 762 cm^{-1} for naphthol ring in finger print region. As well as the wave length of maximum absorbance for ion pair complex of Fe^{3+} was $\lambda_{max} = 477$ nm but ion pair association complex of Hg^{2+} was $\lambda_{max} = 476$ nm using these wave length to measurement the absorbance of CPL solutions whereas the absorbance appear as a function to the concentration of ion pair complex extracted into CPL.

Effect of hydrochloric acid concentration: The 10 mL aqueous solutions contain 100 µg of Fe^{3+} or Hg^{2+} with different concentration of HCL and 0.5 mL of 1% TritonX-100 and 1×10^{-4} M HPBN. Heating these solutions in electrostatic water bath at suitable temperature and time to produce CPL with good properties then separated CPL from aqueous solution and complete the procedure according to comprehensive method. The results were as in Fig. 6 and 7.

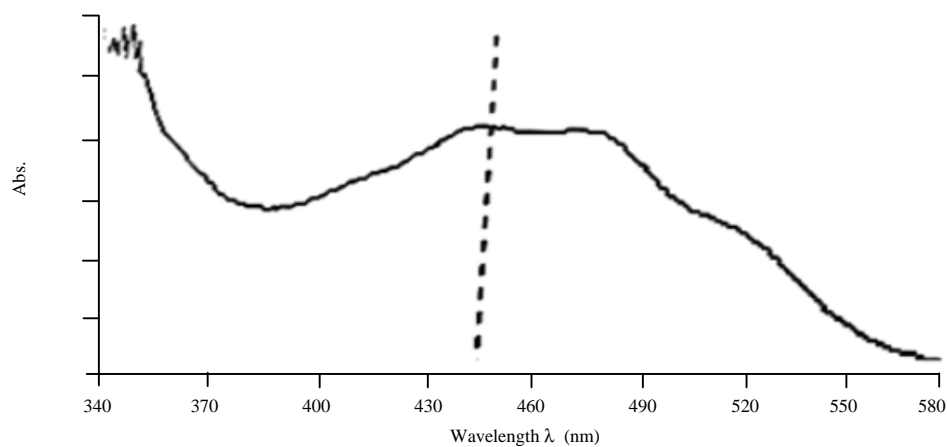Fig. 1: Wave length of maxmimum absorbance

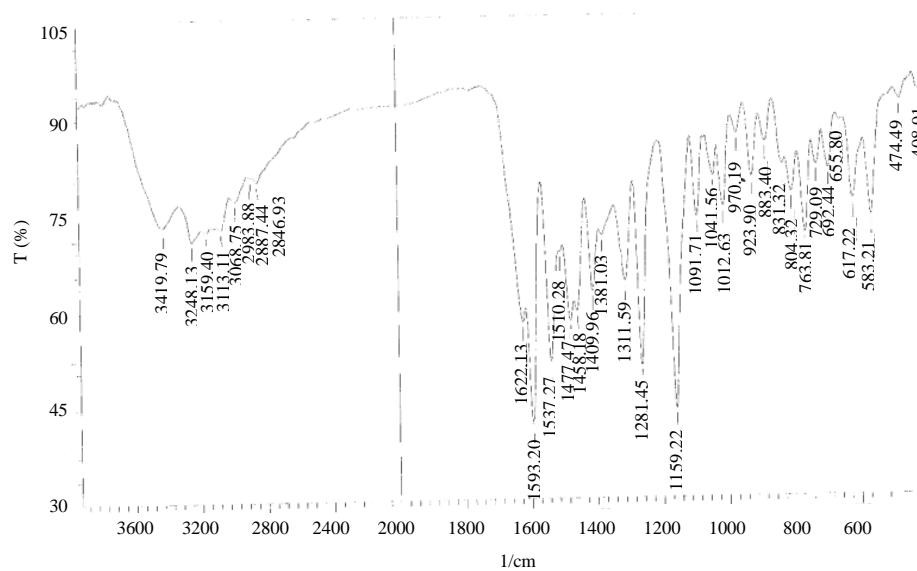Fig. 2: UV-VIS absorption spectrum of organic reagent HPBN (λ 450.0 nm)

Fig. 3: FTIR spectrum for new organic reagent HPBN (λ 477.0 nm)
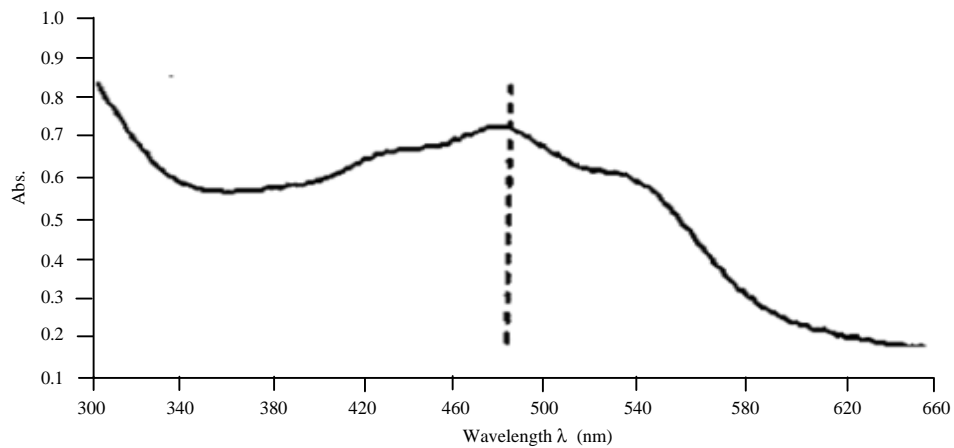

Fig. 4: UV-VIS absorption spectrum of ion pair association complex of Fe^{3+} extracted (λ 476.0 nm)
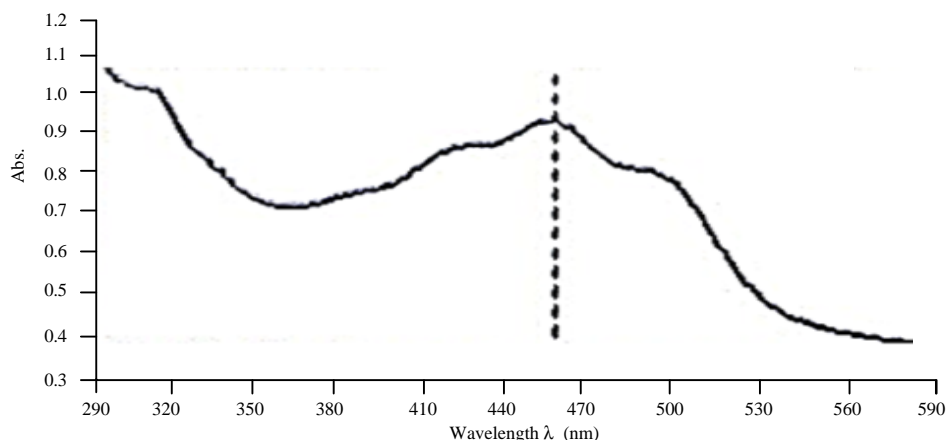
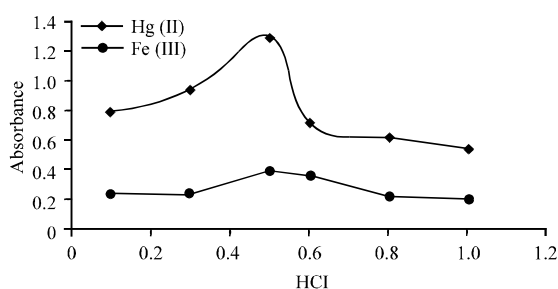Fig. 5: UV-VIS absorption spectrum of ion pair association complex of Hg^{2+} extracted

Fig. 6: Effect of HCl concentration on formation and stability of ion pair association complex extracted
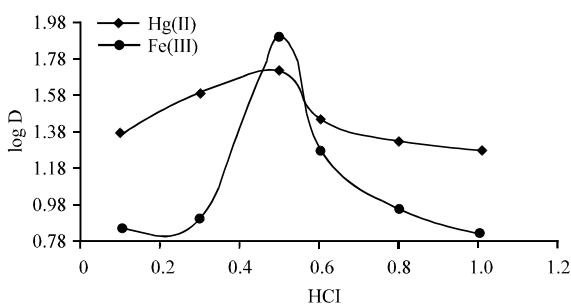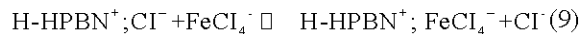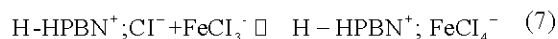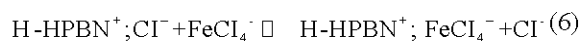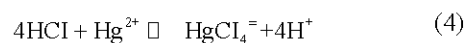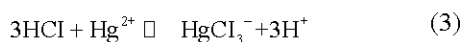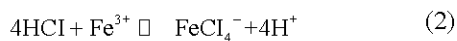

Fig. 7: Effect of HCl concentration on extraction efficiency and D values

The results shows 0.5M HCl was the optimum concentration of HCl for extraction both metal ions at this HCl concentration reached to favorable equilibrium of formation ion pair association complex and extraction the mechanism of extraction were as equilibria:

$$4HCl + Fe^{3+} \rightleftharpoons FeCl_4^- + 4H^+ \qquad (2)$$

$$3HCl + Hg^{2+} \rightleftharpoons HgCl_3^- + 3H^+ \qquad (3)$$

$$4HCl + Hg^{2+} \rightleftharpoons HgCl_4^= + 4H^+ \qquad (4)$$

$$HPBN + HCl \rightleftharpoons H\_HPBN^+; Cl^- \qquad (5)$$

$$H\text{-}HPBN^+; Cl^- + FeCl_4^- \rightleftharpoons H\text{-}HPBN^+; FeCl_4^- + Cl^- \qquad (6)$$

$$H\text{-}HPBN^+; Cl^- + FeCl_3^- \rightleftharpoons H - HPBN^+; FeCl_4^- \qquad (7)$$

$$H\text{-}HPBN^+; Cl^- + FeCl_3^- \rightleftharpoons H\text{-}HPBN^+; HgCl_3^- + Cl^- \qquad (8)$$

$$H\text{-}HPBN^+; Cl^- + FeCl_4^- \rightleftharpoons H\text{-}HPBN^+; FeCl_4^- + Cl^- \qquad (9)$$

Any concentration of HCl less then optimum not enough to reached equilibrium and effect to decrease the concentration of anion chloro complex and ion exchanger H-HPBN$^+$, Cl$^-$ and decrease in extraction efficiency, so that, any concentration of HCl more than optimum effect to decrease extraction efficiency also because effect to decrease concentration of anion chloro complex formation according to mass action low and by formation stable compound for metal ion not extracted.

Effect of metal ions concentration: Preparing two set of 10 mL aqueous solutions, the first set contain different concentration of Fe^{3+} but the second set contain rising concentration of Hg^{2+} and each solution of the two sets exist 0.5 M HCl and 0.5 mL TritonX-100 and 1×10^{-4} M HPBN. Heating all these solutions in electrostatic water bath at suitable temperature and time to produce CPL with good proportion then separated CPL from aqueous solution and complete the working as in comprehensive method. The results were as in Fig. 8 and 9.

The results show there is a straight line relation between absorbance, so, distribution ratio with metal ions
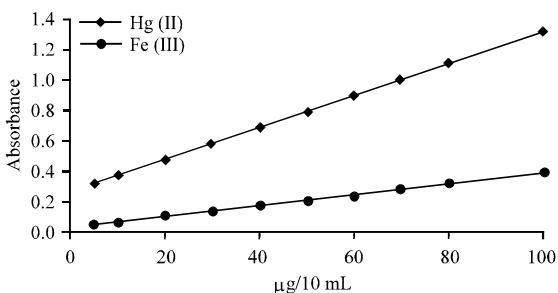
Fig. 8: Effect of metal ions concentration on formation and stability of ion pair complex
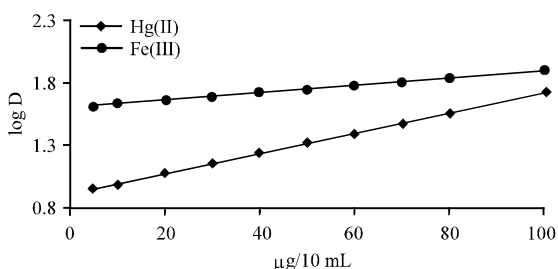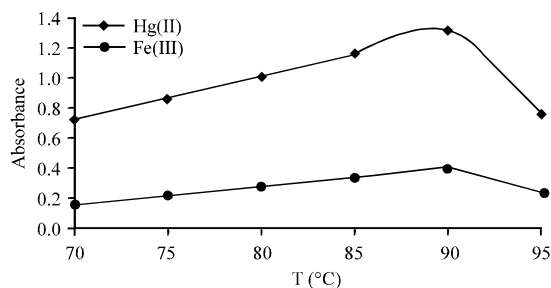

Fig. 9: D = f [metal ions]

Fig. 10: Effect temperature on CPL formation and ion pair complex extracted

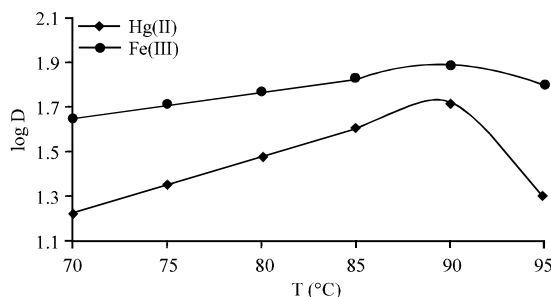
Fig. 11: Effect temperature on extraction efficiency and D-value

Table 1: Thermodynamic data of extraction

Metal ions	Δh_{ex} (kJ mol^{-1})	Δg_{ex} (kJ mol^{-1})	ΔS_{ex} J (mol^{-1}K^{-1})
Fe^{3+}	0.0266	-65.604	180.800
Hg^{2+}	0.0547	-68.082	187.980

concentration in aqueous solution and this straight line relation continue to 100 µg metal ion in limit aqueous solutions then deviation in the presence more, this explain effect of metal ion concentration as thermodynamic parameter on equilibrium of formation ion pair association and extracted and that is mean the increasing of metal ion concentration effect to increase the rate of forward direction of equilibrium relation and increase ion pair association complex extracted until 100 µg more than that effect to decline extraction efficiency because effect to increase the rate of backward direction of equilibrium that is mean relation increase dissociation of complex according to mass action law.

Effect of temperature: According to comprehensive method extracted 100 µg of Fe^{3+} and Hg^{2+} from 10 mL aqueous solution at optimum conditions in different temperature at constant time of heating the results were as in Fig. 10 and 11.

The results appear increase in ion pair association complex concentration extracted and extraction efficiency with rising temperature to optimum value 90°C, then calculated extraction constant K_{ex} at rising temperature by following the relation Eq. 2:

$$K_{ex} = \frac{D}{[M^{n+}][BAEE]} \quad (10)$$

Diagram log K_{ex} against 1/T K as in Fig. 11. From the slope value in Fig. 11 and the relations below calculated thermodynamic data as in Table 1:

$$Slope = -\frac{\Delta H_{ex}}{2.303 R} \quad (11)$$

$$\Delta G_{ex} = -RT LN K_{ex} \quad (12)$$

$$\Delta G_{ex} = \Delta H_{ex} - T\Delta S_{ex} \quad (13)$$

The small values of ΔH_{ex} reflect the closely neared together ion pair association complex. So that, the large value of Δs_{ex} appears the method was entropic in region.

Effect of heating time: According to comprehensive method extracted Fe^{3+} and Hg^{2+} from 10 mL aqueous solutions at optimum condition except different times of heating. The results were as in Fig. 12-14.
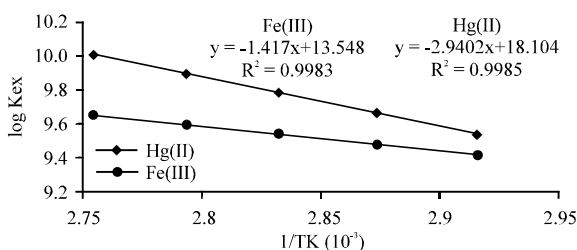
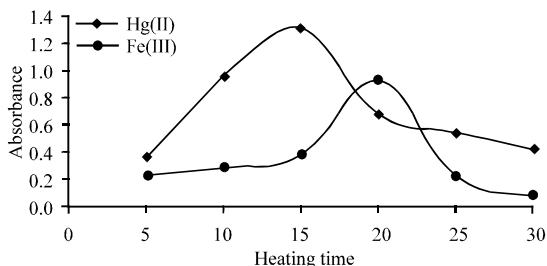Fig. 12: Effect temperature on extraction constant K_{ex}
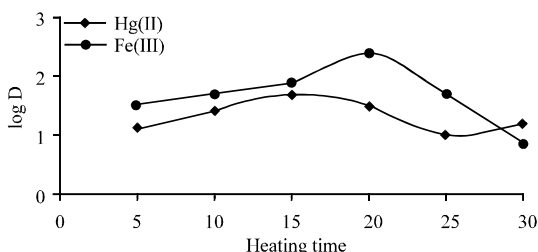

Fig. 13: Heating time effect on CPL formation

Fig. 14: Heating time effect on extraction efficiency and D values

The results appear optimum heating time was 20 min. for extraction Fe^{3+} ion and 15 min. for Hg^{2+} ion whereas the heating time represent the kinetic side of extraction method and at optimum heating time reached to the best kinetic energy of formation CPL and partitioning ion pair association complex to CPL.

Effect of surfactant volume: According to comprehensive method extracted Fe^{3+} or Hg^{2+} ions at optimum condition by using different volume of surfactant TritonX-100. The results were as in Fig. 15 and 16.

The results appear optimum surfactant volume was 0.5 mL TritonX-100 for extraction Fe^{3+} ion and 0.8 mL for extraction Hg^{2+} ion, at this volume of TritonX-100 formed best CPL because this volume allow to reaching critical micelles concentration CMC and at this state formed CPL with very suitable volume and density with higher dehydration to giving very good layer and phase to quantitative extraction ion pair association complex for
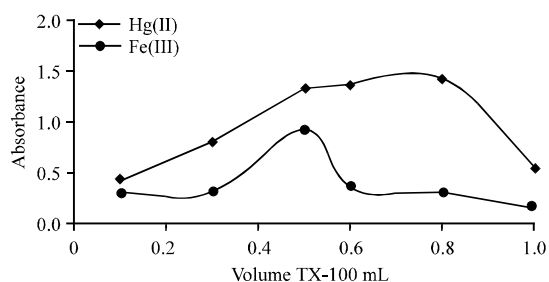

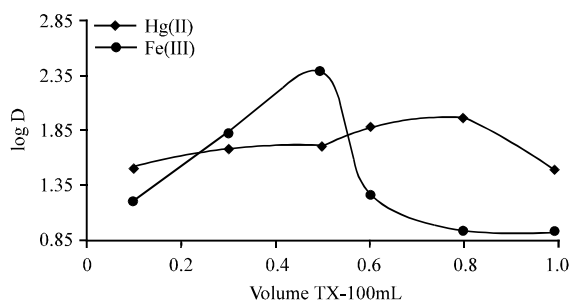Fig. 15: Effect of Triton X-100 volume on CPL ion pair association complex partition

Fig. 16: Effect of Triton X-100 volume on extraction efficiency and D-value

Fe^{3+} and Hg^{2+} ions, any volume less than optimum not allow to reached that, so, volume more than optimum effect to increase diffusion of micelles and decrease the favorable properties of CPL and decline in extraction efficiency.

Effect of electrolytes and Interferences: Extracted 100 μg of Fe^{3+} and Hg^{2+} from 10 mL aqueous solutions at optimum condition and in the existence of 0.01 M of different electrolytes or foreign ions, according to comprehensive method, the results were as in Table 2 and 3.

The results show enhancement in extraction efficiency Fe^{3+} and Hg^{2+} in the presence of electrolyte because the electrolyte effect to destroying the hydration shell of metal ion and increase formation anion chloro complex, so that, increase dehydration to formation CPL at CMC with very good proportion to increase the partitioning ion pair complex formed into CPL and increase extraction efficiency, this behavior reflected to metal ions radius of electrolyte smaller volume cation giving higher electrolyte effect then LiCl giving the higher extraction efficiency. The results appear there was an interferences for all these foreign metal cation in extraction method effect to decrease extraction efficiency of Fe^{3+} and Hg^{2+} ions and there is partially effect for each ion depending on the different behavior of each ion in extraction method

Table 2: Effect of electrolyte on extraction efficiency of Fe^{3+} or Hg^{2+} ions

Electrolyte salts	Fe^{3+}		Hg^{2+}	
	Abs. 477 nm	D	Abs. 476 nm	D
LiCl	0.615	122.50	1.721	110.55
NaCl	0.565	110.20	1.671	105.63
KCl	0.495	102.40	1.576	100.14
NH_4Cl	0.425	096.30	1.483	094.71
$MgCl_2$	0.587	115.70	1.691	107.55
$CaCl_2$	0.525	099.60	1.531	098.32

Table 3: Effect of interferences on extraction efficiencies

Interferences	Fe^{3+}		Hg^{2+}	
	Abs. 477 nm	D	Abs. 476 nm	D
Ni^{2+}	0.170	17.15	0.668	40.21
Co^{2+}	0.315	50.30	0.432	30.50
Cd^{2+}	0.221	32.80	0.659	38.22
Cu^{2+}	0.198	24.40	0.556	32.46
Zn^{2+}	0.199	25.30	0.616	36.75
Mn^{2+}	0.181	21.60	0.321	26.71
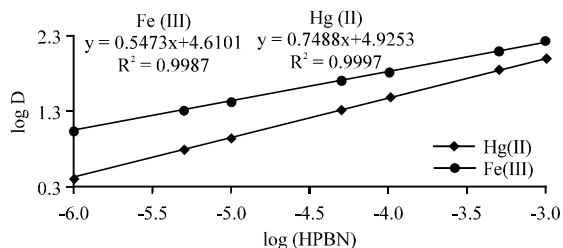
Fig. 17: Slope analysis for Fe^{3+} and Hg^{2+} ions

Fig. 18: Effect of HPBN concentration on the absorbance of ion pair complex extracted Slope ratio for Hg^{2+} = 2162.162/2162.162 = 1.000

Fig. 19: Effect of variation metal ion concentration on the absorbance of ion pair complex extracted Slope ratio for Fe^{3+} = 919.919/880.880 = 1.044

Fig. 20: a-c) Plot obserbance against ppm of metal

and interferences of these ion mean participation of each one of these ions to formation ion pair association complex and this participation effect to decline concentration of HCl and HPBN, less than optimum values necessary to extraction Fe^{3+} and Hg^{2+} ions.

Stoichiometry: For demonstrated the more probable structure of ion pair association complexes extracted to CPL following two spectrophotometric method, the first method was slope analysis involved extracted metal ions Fe^{3+} and Hg^{2+} according to comprehensive method at optimum condition, the results were as in Fig. 17.

So that, following the slope ratio as spectrophotometric method according to comprehensive method at optimum condition in variation metal concentration time and at different concentration of HPBN twice, the results were as in Fig. 18 and 19.

Applications: For spectrophotometric determination of Fe^{3+} and Hg^{2+} in different environmental and vital samples followed, the comprehensive method for extraction metal ion under study from 10 mL aqueous solutions contain different quantity of metal cation at
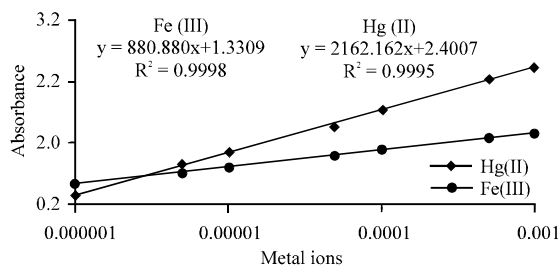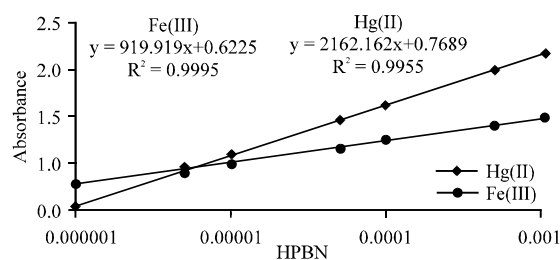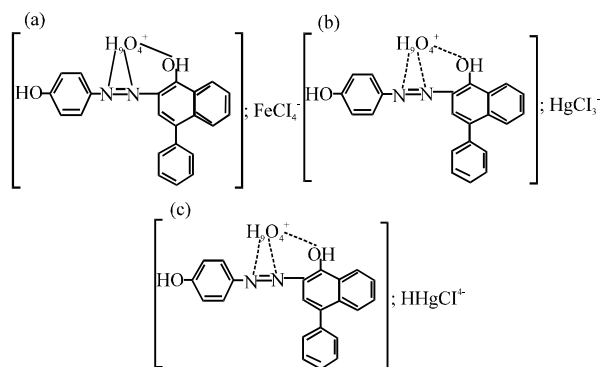
optimum conditions and after separated CPL from aqueous solutions and dissolved CPL in 5 mL ethanol and measure absorbance for ethanolic solutions against blank prepared in the same manner without metal ions, then plot absorbance against ppm of metal ion as in Fig. 20 and 21. Any sample after preparing treated according to comprehensive method at optimum condition after measure the absorbance and return to calibration curve for each metal ion determine metal ion in the sample. The results were as in Table 4.

Table 4: Fe^{3+} and Hg^{2+} content (ppm) in different samples

Samples	Fe^{3+}			Hg^{2+}		
	Thiocyanate method	Applied method*	RSD (%)	Dithizone method	Applied method*	RSD (%)
Agriculture 1	13.50	13.80	0.12	0.18	0.17	0.02
Agriculture 2	20.60	20.80	0.02	0.20	0.19	0.03
Cow meat	01.50	01.60	0.14	0.16	0.17	0.01
Chicken (breast)	07.20	07.10	0.12	0.16	0.16	0.05
Drainage fish	17.10	17.10	0.02	0.60	0.62	0.09
River water	01.00	01.10	0.01	0.48	0.48	0.01
Garden cress	06.30	06.28	0.13	0.40	0.41	0.14
Celery	05.00	04.90	0.15	0.10	0.11	0.12
Lettuce	06.80	06.50	0.11	0.15	0.16	0.14
Cucumber	05.00	04.94	0.01	0.08	0.05	0.17
Tomato	08.60	08.50	0.03	0.04	0.03	0.05

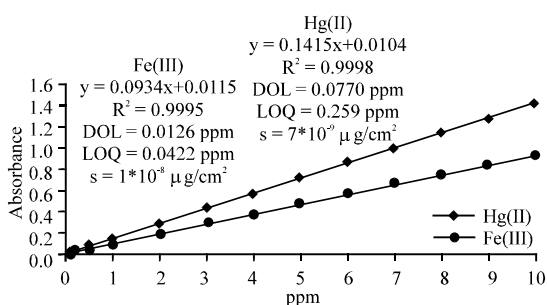*Values given represent the average of five analysis of each sample

Fig. 21: Calibration curve for spectrophotometric determination of Fe^{3+} and Hg^{2+} by joined method

CONCLUSION

As well as the research involved other studies such as electrolyte effect interferences effect, application for determination of Fe^{3+} ion and Hg^{2+} ion in biologic samples (Jawad *et al.*, 2017).

ACKNOWLEDGEMENTS

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