Incorporation of Onium System with Cloud Point Extraction and Determination of Iron(III) and Mercury(II) in Different Samples

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ABSTRACT

By joined two sensitive methods which in onium method and Cloud point extraction method CPE for separation preconcentration and extraction Fe^{3+} and Hg^{2+} by using (BAEE) from acidic hydrochloric aqueous solution in the presence TritonX-100. Spectrophotometric studies shows wave length for maximum absorbance to onium species of Fe(III) was λ_{max}=362nm and for Hg(II) λ_{max}=293nm. Optimum condition studies was 1M HCl for both ions, 100µg of each metal ions ,using 1×10^{-4} M of (BAEE), as well as the method need heating for 85^0C to Fe^{3+} and 95^0C for Hg^{2+} ion and heating time 15min. for Fe^{3+} and 20min. for Hg^{2+} ion. so that need existance 0.5mL of TritonX-100 for both metal ion, the research involved many other studies. Thermodynamic data of Fe^{3+} and Hg^{2+} was ΔH_{ex}=0.195, 0.0592 kJ mol^{-1}, ΔG_{ex}= -66.480, -77.981 kJmol^{-1}, ΔS_{ex}=186.245, 212.065 Jmol^{-1}K^{-1}, respectively, application and spectrophotometric determination of Fe^{3+} ion and Hg^{2+} ion in different samples.

Keyword: Cloud point extraction, onium system, Nα-Benzoyl-L-arginine ethyl ester hydrochloride (BAEE), mercury, iron.

INTRODUCTION

Iron is known as one of the essential nutritional elements for many living organisms due to its role in most of metabolic processes, including oxygen and electron transport, and DNA synthesis. exposure to excess iron can cause several diseases or disorders such as endocrine problems, arthritis, diabetes and liver disease[1,2]. Mercury is a toxic element found throughout the environment. Its mobile nature allows it to diffuse through the air, soils and ultimately into water systems[3] Trace determination of heavy metals is one of the most important issues of chemical analysis[4] In 1978, Watanab introduced cloud point extraction (CPE) as a new extraction method for determination of Zn with l-(2-Pyridylazo)-2-Naphthol ligand[5]. Since then CPE was applied widely for determination of various analytes[6,7], mainly for the extraction of metal ions[8,11]. The most important feature of CPE is application of a surfactant, mostly

non-ionic as the extractant phase[12] which means that CPE avoids the consumption of large amounts of expensive, toxic and flammable organic solvents[13]. Use crown ether DB18C6 and from acidic HCl media extracted Fe^{3+} ion by application CPL after change Fe^{3+} into $FeCl_4^-$ TritonX-100 was necessary to obtained higher extraction efficiency Thermodynamic data was ΔH_{ex}=0.159 kJ mol^{-1}, ΔG_{ex}=-62.43 kJ mol^{-1}, ΔS_{ex}=174.83 J mol^{-1}K^{-1}, there are another empirical application for this study in real samples[14]. Used CPE methodology for determination Hg^{2+} in different tissues of grilled chickens with application clod vapors atomic absorption and organic agent (DDTP) so Triton X-114[15]. By application of CPE method coupled with spectrophotometric technique for extraction and determination of Hg^{2+} in different samples of fish, new thiazolylazo reagent was synthesized 7-(6-Bromo2-benzothiazolylazo)-8-Hydroxyquinoline and Triton X-114 at specific pH=5, DOL=7.4 ng mL^{-1} [16] .Sensitive application method of solvent extraction used onium system for extraction Zn^{2+} from acidic aqueous solution of HCl as

oxonium species by using methyl stearate Stearate as sensitive extract ant dissolved in chloroform the study show extracted species giving maximum absorbance at wave length λ_{max}=275nm, Sandell's sensitivity= 0.00832 µg.cm^{-2} [18].

EXPERIMENTAL

Materials and solutions

For spectroscopic studies and absorbance measurements used double beam spectrophotometer (*Biochrom Libra 560*) (UK)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).

For preparing all the solutions needing in experiment used high purity materials received from commercial sources without further purification and used Doubly distilled water with set of suitable glassware, stock solution 1mg/mL of Fe^{3+} ion

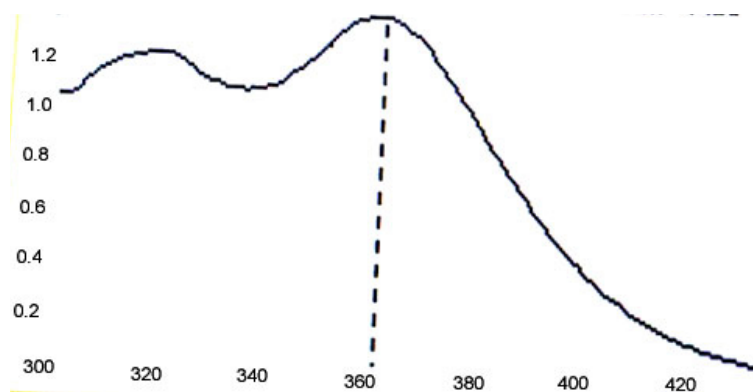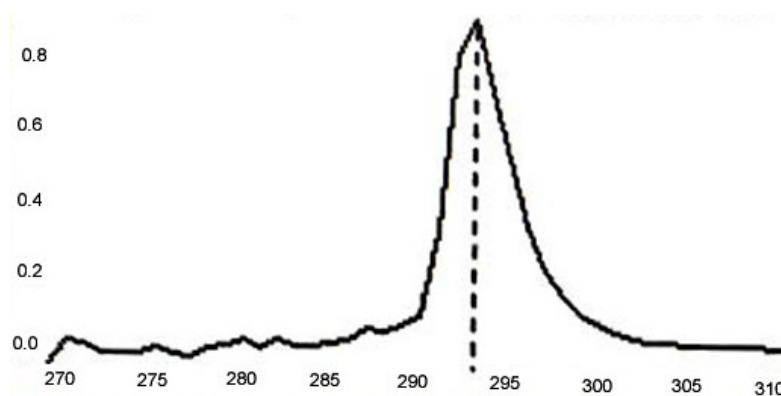Fig. 1: UV-VIS. absorption spectrum for onium species of Fe^{3+}.

Fig. 2: UV-VIS. absorption spectrum for onium species of Hg^{2+}.

prepared by dissolving 0.2880 gm in of $FeCl_3$ in 100 mL and for Hg^{2+} ion dissolved 0.1353 gm of $HgCl_2$ in 100 mL of distilled water other working solutions preparing by dilution method with distilled water in suitable volumetric flask, so 1×10^{-2} M of $N\alpha$-Benzoyl-L-arginine ethyl ester hydrochloride (BAEE) was prepared by dissolving (0.08571gm) in (25mL) distilled water. Other working solutions were prepared by dilution method with distilled water.

Comprehensive method

10 mL aqueous solution contain 100 µg of metal ion under study Fe^{3+} and Hg^{2+} with optimum concentration HCl and 1×10^{-4} M (BAEE), in the presence 0.5 mL of non-ionic surfactant Triton X-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 λ_{max}=362nm for Fe^{3+} and λ_{max}=293nm 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 Dithiazone spectrophotometric method[18] to determine remainder quantity of metal ions in aqueous solution after extraction and subtraction this quantity from original quantity 100µg to determine the transferred quantity to CPL to formation onium species extracted then calculated distribution ratio (D).

$$D = [M^{n+}]_{CPL} / [M^{n+}]_{aq} \qquad ...(1)$$

Whereas $M^{+n} = Fe^{3+}$ & Hg^{2+}

RESULTS AND DISCUSSION

Spectrophotometry

10 mL aqueous solution contain 100 µg of Fe^{3+}or Hg^{2+} with 1M HCl and 1×10^{-4} M (BAEE), 0.5mL 1% Triton X-100. Heating the solution in electrostatic water bath for suitable temperature and time until formation cloud point layer CPL with
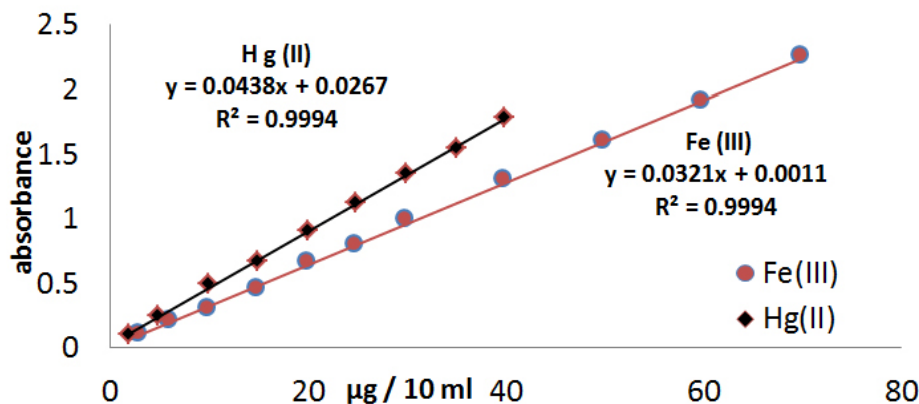

Fig. 3: calibration curve for determination metal ions in aqueous solutions.
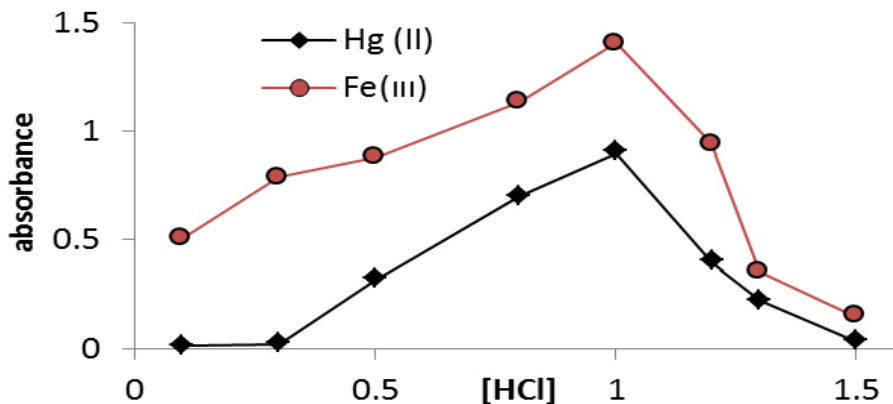

Fig. 4: effect of HCl concentration on formation and stability of onium species

smaller volume then volume, then separated CPL from aqueous solution and dissolved CPL in 5mL ethanol and talking absorption spectrum in (UV-Vis) region against blank prepared in the same manner without metal ions. The results were as in Figures 1 and 2.

The spectrum show wave length for the maximum the absorbance of onium species of Fe^{3+} ion was λ_{max}= 362 nm but onium species of Hg^{2+} ion was λ_{max}= 293 nm.

Variation of hydrochloric acid concentration

Two set 10mL aqueous solutions contain 100µg of Fe^{3+} or Hg^{2+} with different concentration

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

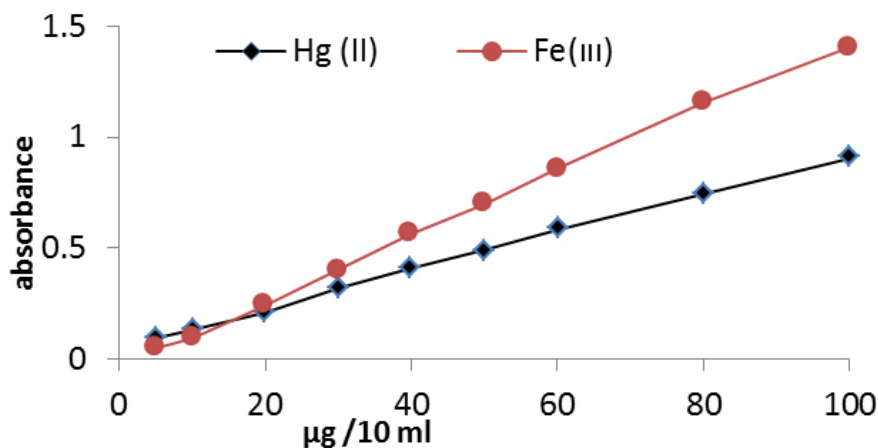| Electrolyte salts	Fe^{3+}		Hg^{2+}	
	Abs. 362 nm	D	Abs. 293 nm	D
LiCl	1.832	114.45	1.725	218.5
NaCl	1.716	106.31	1.631	183.3
KCl	1.638	99	1.51	165.7
NH_4Cl	1.601	91.51	1.48	151.4
$MgCl_2$	1.813	109.52	1.646	192.8
$CaCl_2$	1.616	94.53	1.575	171.21

Table 1: Thermodynamic data of extraction

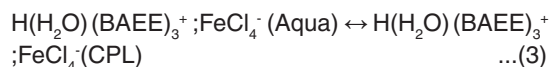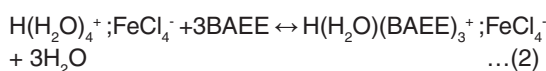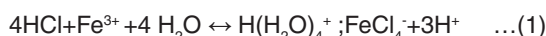| Metal ions	ΔH_{ex} kJ mol^{-1}	ΔG_{ex} kJ mol^{-1}	ΔS_{ex} J mol^{-1}K^{-1}
Fe^{3+}	0.195	-66.48	186.254
Hg^{2+}	0.0592	-77.981	212.065
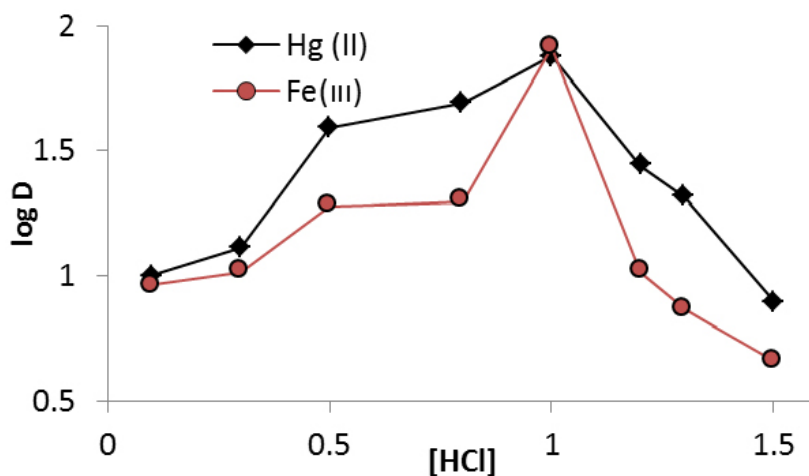
Fig. 5: effect of HCl concentration on extraction efficient and D value

Fig. 6: effect of metal ions concentration on formation and stability of onium species extracted

HCl and 1×10^{-4} M (BAEE), 0.5mL 1% Triton X-100. Heating the solution to suitable temperature and time until formation CPL, then separated CPL from aqueous solution and complete the procedure according to comprehensive method. The results were as in Figures 4 and 5.

The results shows 1M HCl was the optimum molar concentration of HCl in aqueous solution for extraction onium species of Fe^{3+} and Hg^{2+} ions at this molar concentration reached to higher extraction efficiency appear higher absorbance and D values because at this molar concentration reached to favorable equilibrium of formation onium species so that partitioning into cloud point layer CPL

$$4HCl+Fe^{3+}+4\ H_2O \leftrightarrow H(H_2O)_4^+\ ;FeCl_4^-+3H^+ \quad …(1)$$

$$H(H_2O)_4^+\ ;FeCl_4^- +3BAEE \leftrightarrow H(H_2O)(BAEE)_3^+\ ;FeCl_4^- + 3H_2O \qquad …(2)$$

Table 3: Effect of interferences on extraction efficiencies

Interferences	Fe^{3+}		Hg^{2+}	
	Abs. 362 nm	D	Abs. 293 nm	D
Ni^{2+}	0.235	16.56	0.469	40.11
Co^{2+}	0.328	22.12	0.321	28.65
Cd^{2+}	0.807	57.44	0.646	60.34
Cu^{2+}	0.61	40.57	0.478	47.32
Zn^{2+}	0.689	43.83	0.701	80.51
Mn^{2+}	0.901	63.81	0.512	54.47

$$H(H_2O)(BAEE)_3^+\ ;FeCl_4^-\ (Aqua) \leftrightarrow H(H_2O)(BAEE)_3^+ ;FeCl_4^-(CPL) \qquad …(3)$$

Any concentration of HCl less than optimum value being not enough to reach favorable equilibria and giving decline in extraction efficiency so that any concentration of HCl in aqueous solution more than optimum value effect to decrease extraction efficiency because effect to increase the rate of backward direction of equilibrium.

Effect of metal ions concentration

Extracted Fe^{3+}or Hg^{2+} according to onium system as detailed in comprehensive method from 10 mL aqueous solutions contain rising quantity of metal ions with existence 1M HCl The results were as in Figures 6 and 7.

The results appear linear relation between extraction efficiency and metal ion concentration in aqueous solution to optimum value of metal ion concentration equal to 100 µg at constant of other constant conditions, that in mean increasing in onium species formation and partitioning to CPL with increasing metal ion concentration.
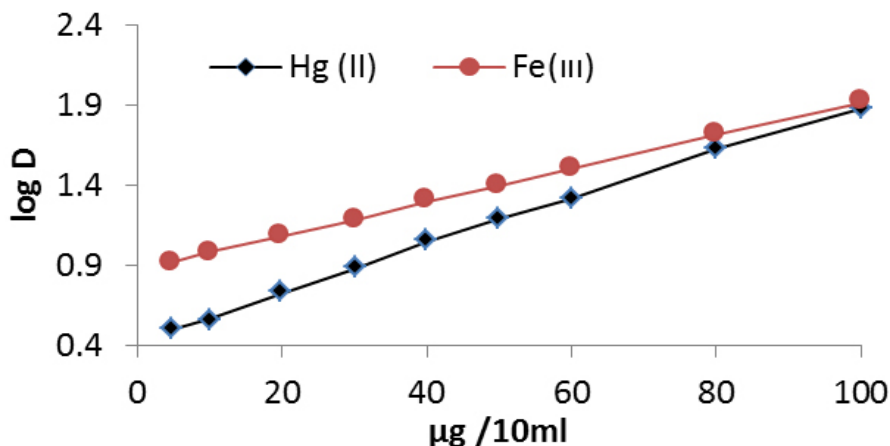
Rising BAEE concentration effect

Extracted 100 µg of each metal ion under study in 10 mL aqueous solutions by rising concentration of BAEE at constant other condition according to comprehensive method, The results were as in Figures (8,9) (8 and 9):

The results shows linear relation and reflect increasing in onium species concentration formation

Fig. 7: D = f [metal ions]

and stability with increasing concentration of BAEE, that is mean BAEE is un thermodynamic parameter which in it increasing concentration effect to increase that rate of forward direction of formation onium species with increasing concentration of onium species formed.

Thermodynamic

Effect of temperature on extraction efficiency of onium species by joining onium system and CPE methods involved extraction 100 μg in 10 mL aqueous solutions of each ion in presence 1M HCl, $1×10^{-4}$M (BAEE), 0.5 mL 1% Triton X-100 at
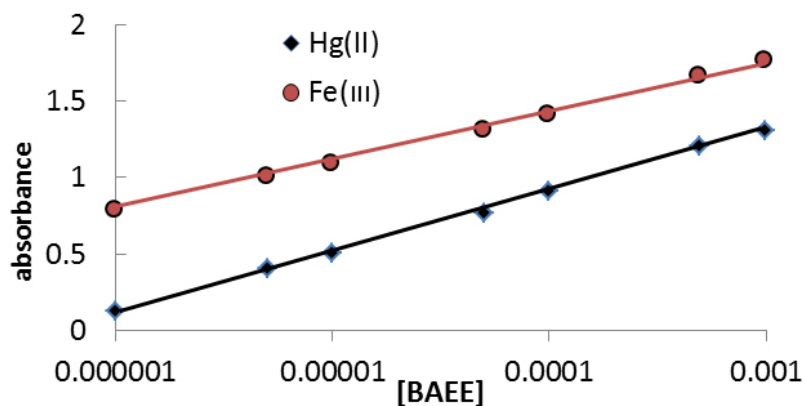

Fig. 8: Effect of BAEE concentration on formation and stability of onium species extracted.
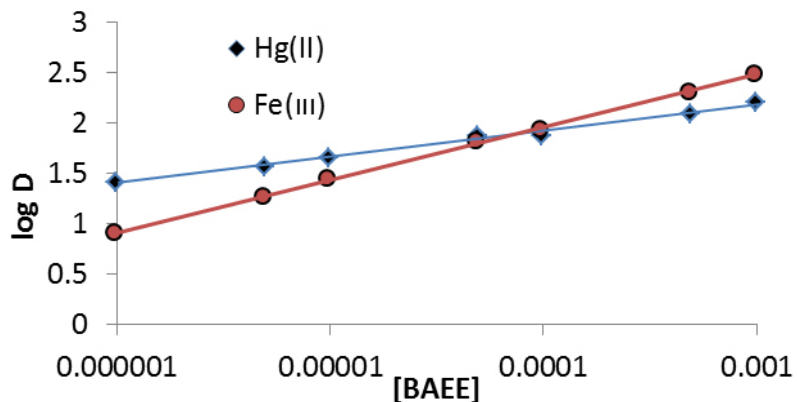

Fig. 9: Effect of BAEE concentration on extraction efficient and D value
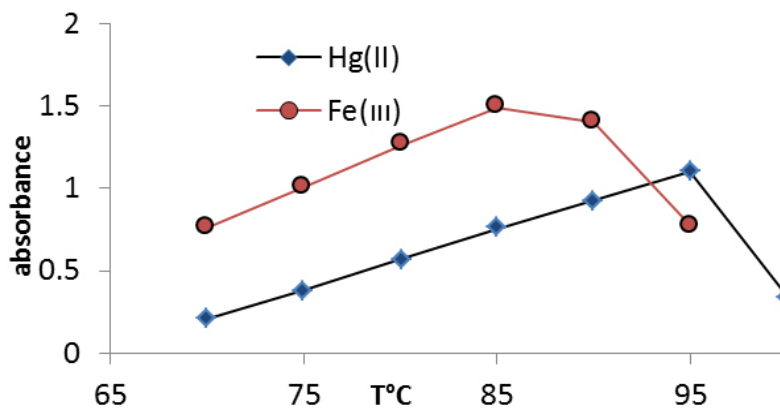

Fig. 10: effect temperature on formation CPL and extraction

rising temperature with 15 minutes of heating at each temperature according to comprehensive method. The results were as in Figures 10 and 11.

The extraction method shows 85°C was optimum temperature for extraction Fe^{3+} ion but 95°C for extraction Hg^{2+} after calculated extraction constant K_{ex} for each ion by following the relation (2).

$$K_{ex} = \frac{D}{[M^{n+}][BAEE]} \qquad ...(2)$$

Diagram log K_{ex} against 1/T K as in fig Figure12.

From the slopes of straight lines in figure12 and relations (3-5) calculated thermodynamic data of extraction as in table(1).

$$slope = -\Delta H_{ex} / 2.303\ R \qquad ...(3)$$

$$\Delta G_{ex} = -RT\ Ln\ K_{ex} \qquad ...(4)$$

$$\Delta G_{ex} = \Delta H_{ex} - T\ \Delta S^{ex} \qquad ...(5)$$

At the optimum temperature reaching the thermodynamic equilibrium to formation CPL with favorable distribution to CPL to giving best extraction efficiency.

Effect of heating time.

According to comprehensive method extracted Fe^{3+} and Hg^{2+} from 10 mL aqueous solutions involved 100 µg of each metal ions and 1M HCl, 1×10^{-4}M (BAEE), 0.5 mL 1% Triton X-100. Heating at optimum temperature for rising time The
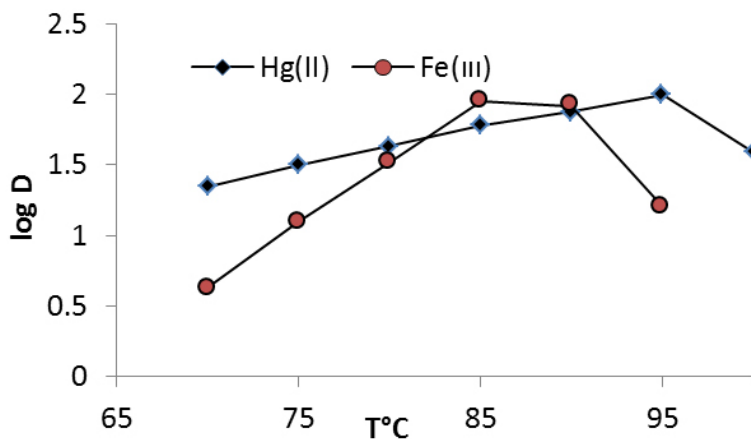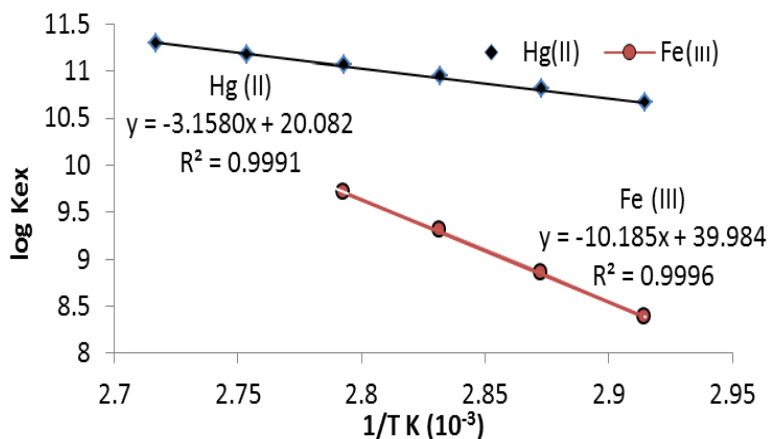

Fig. 11: D = f (T°C)

Fig. 12: effect of temperature on extraction constant.

time. The results were as in fig Figures 13 and 14.

The results shows (15 min) was the optimum heating time for extraction Fe^{3+} but for extraction Hg^{2+} ion needing (20 min) for heating.

Whereas the heating time represents kinetic side of extraction, at extraction at optimum value reach best equilibrium of CPL with higher density and small volume, as well as favorable dehydration at any heating time less than optimum not reached
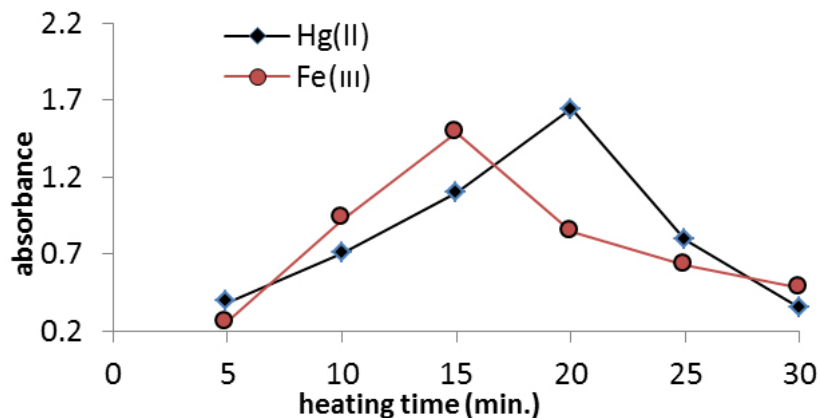

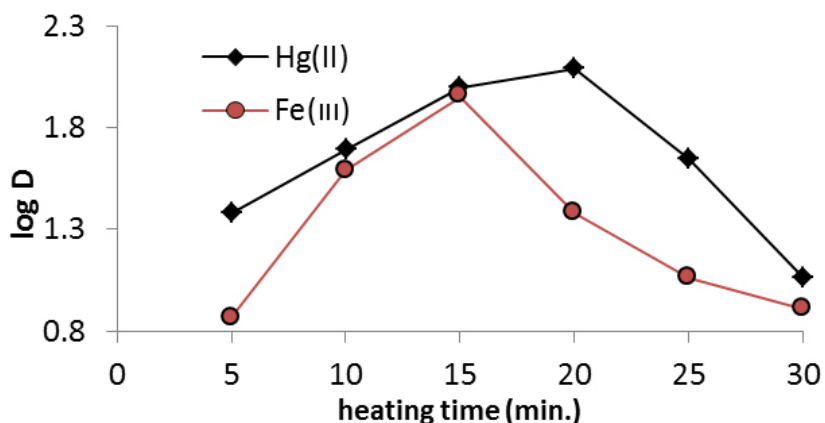**Fig. 13: heating time effect on CPL formation and onium species extracted**

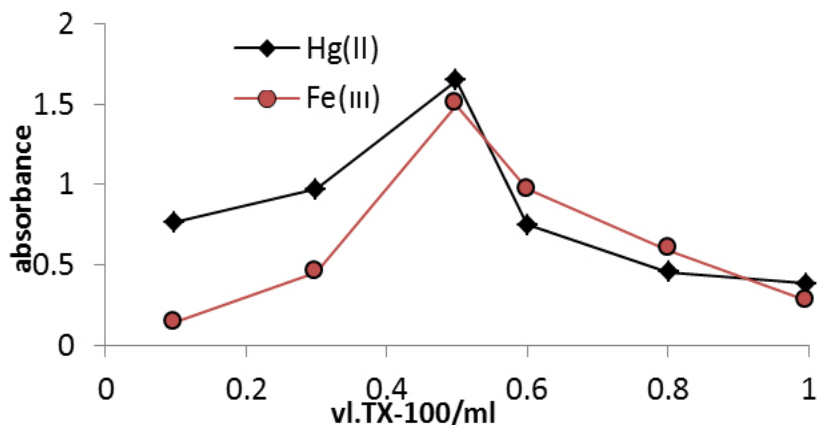**Fig. 14: heating time effect on extraction efficiency and D value.**

Fig. 15: effect of triton X-100 volume on onium species concentration extracted

to equilibrium so that at heating time more than optimum value increase the diffusion of micelles with decrease in dehydration so decrease in extraction efficiency.

Effect of surfactant volume

From 10mL aqueous solutions contain 100 µg of Fe^{3+}or Hg^{2+} ions at optimum condition in existence rising volume of surfactant Triton X-100 according to comprehensive method. The results were as in Figures (15),(16). (15 and 16):

The results shows 0.5 ml of TX-100 was the optimum surfactant volume for extraction both ion $Fe^{3+}$and Hg^{2+} this volume help to reached the state of critical micelles concentration CMC and produce best CPL enough to extracted higher quantity of onium species, volume less than optimum not allow to CMC, so that volume more than optimum value and by effect of electrostatic interaction between

micelles increase diffusion of micelles with decrease in CPL

Effect of electrolyte salts

Extracted metal ions according to comprehensive method at optimum condition and in presence 0.01mL of different electrolytes, the results were as in table(2).

The results appear enhancement in extraction efficiency in presence electrolyte in aqueous solutions because the electrolyte doing to destroying the hydration shell of metal ion Fe^{3+} and Hg^{2+} so that cause increase in dehydration of micelles that is mean increasing in onium species concentration formation and formation good $CPL_{,}$ also appear this effect differ from electrolyte to other according to behavior of electrolyte in aqueous solutions and LiCl giving the higher effect.
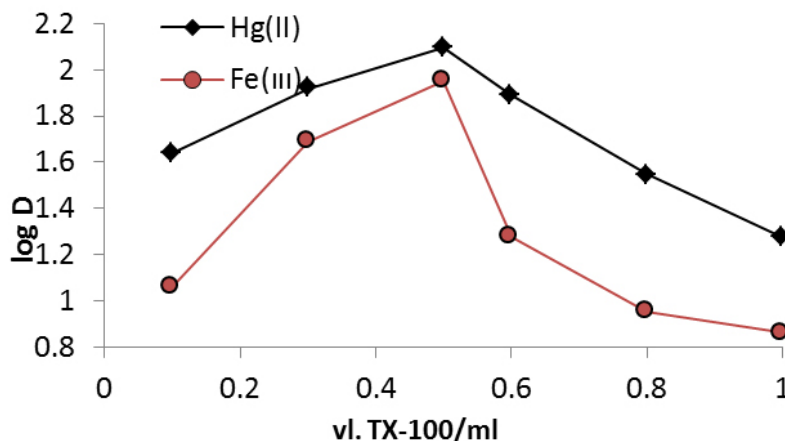

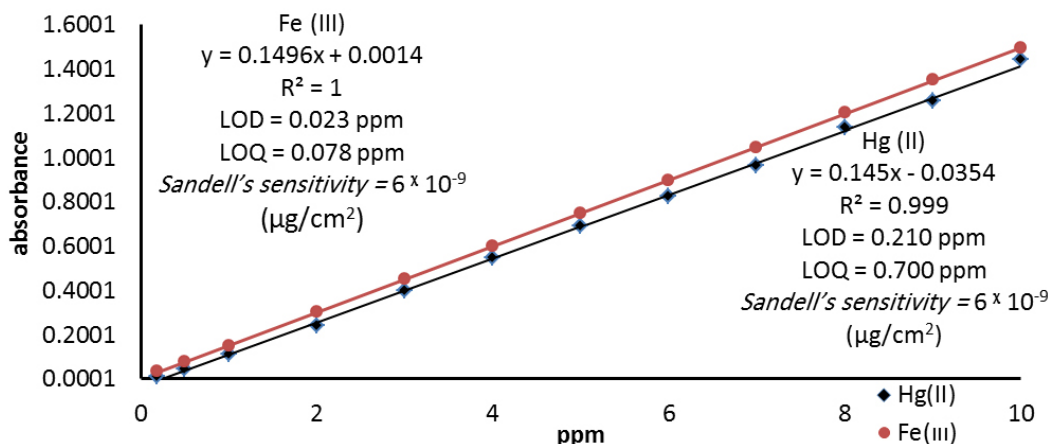**Fig. 16: effect of triton X-100 volume on extraction efficiency and D value**

Fig. 17: calculation curve for spectrophotometric determination of Fe^{3+} and Hg^{2+}

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

samples	Fe^{3+}			Hg^{2+}		
	Thiocyanate method[18]	Applied method*	RSD %	Dithiazone method[18]	Applied method*	RSD %
agriculture 1	13.5	13.2	0.12	0.18	0.17	0.02
agriculture 2	20.6	21	0.02	0.2	0.16	0.03
Cow meat (Beef)	1.5	1.6	0.14	0.16	0.2	0.01
chicken (breast)	7.2	7.4	0.12	0.16	0.21	0.05
Drainage fish	17.1	16.8	0.02	0.6	0.58	0.09
River water	1	0.9	0.01	0.48	0.51	0.01
garden cress	6.3	6.6	0.13	0.4	0.37	0.14
celery	5	5.2	0.15	0.1	0.09	0.12
lettuce	6.8	6.5	0.11	0.15	0.1	0.14
cucumber	5	5.4	0.01	0.08	0.1	0.17
Tomato	8.6	8.4	0.3	0.04	0.05	0.05

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

Interferences effect

From 10 mL aqueous solutions extracted 100 µg of Fe^{3+} or Hg^{2+} ions in presence 1M HCl, 1×10^{-4} M (BAEE), 0.5 mL 1% TritonX-100 and 0.01ml of some interferences at optimum condition according to comprehensive method. The results were as in Table(3).

The results appear all metal cation give partially interferences and effect to decrease extraction efficiency because all these metal ion participation in formation onium species and this participation effect to decline concentration of HCl, (BAEE), than optimum values needed to extraction Fe^{3+} and Hg^{2+} and this decline in concentration not allow to reached equilibrium of formation and extraction onium species, but by reason of different ability and behavior of these metal cation in aqueous solutions so different participation.

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 all 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 method without metal ions, then plot absorbance against ppm of metal ion as in Figure 17.

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) .

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