

Separation and Spectrophotometric Determination of Iron (III) and Mercury (II) via Cloud Point Extraction with New Azo-Derivative

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ABSTRACT

A new coupled cloud point extraction (CPE) was developed as prompt, easy and economical preconcentration technique for spectrophotometric determination of tiny amounts of Fe³⁺ and Hg²⁺ in real samples. A modern thiazolylazo ligand [methyl phenyl thiazolyl azo]-3-methyl-4-methoxy-2-naphthol (MPTAN) was done for the CPE method in the preconcentration of Fe³⁺ and Hg²⁺ as an earlier step to its characterization by UV-VIS spectrophotometry. The analytical manner includes the formation of under study metals complex with new ligand and quantitatively extracted to the Cloud point layer (CPL) of TritonX-100 after heating. The concentration of MPTAN, metals, pH, thermodynamic data and volume of surfactant was optimized. The investigation of stoichiometry has the ratio of metal to ligand of 1:1. Under finest settings and conditions, the calibration curve was found to be linear in the concentration range of two ions (0.05-10) ppm and the limit of detection for Fe³⁺ and Hg²⁺ are (0.016 and 0.041) ppm respectively. The suggested CPE has an excellent methodology for characterization of trace metal ions in surrounding samples with a complex matrix as in soils, water, vegetable, meats, and fruits.

Keywords: cloud point extraction, preconcentration, thiazolylazo ligand

INTRODUCTION

Trace determination of biometals is one of the greatest issues of chemical analysis. Cloud point extraction has many advantages using a small amount of surfactant without using an organic solvent to limit environmental pollution. The small volume of CPL allows a design extraction plans and holds lower toxicity than those using organic solvents. Also, it attaches the green chemistry ideas. There are many applications for sensitive cloud point extraction methods, especially for separation of a micro amount of metal ions such as Mg(II), Zn(II) and others. Feasibly used CPL method is an indirect method of extraction that involves aqueous and surfactant phases. After heating these two phases separated by aggregation micelles, CPL can be in high density and small volume [1-4]. Special work has been conducted about separation and spectrophotometric characterization of iron in nutrient and water samples by CPE method as an innovative complexing agent forming a compound with pH of 4.5, that isolated in non-ionic X-114 Triton surfactant [5]. Trace components can be extracted to CPL layer ordinarily after the realization of a hydrophobic compound with a favorable chelating agent [6]. CPE has productively used for extraction and preconcentration Vitamins B1 and B2 [7] Dyes such as Malachite green, Crystal violet, Rhodamine B [8], Azo Dyes [9] and many trace elements from various samples [10,11]. CPE can be coupled with onium system to determine Fe³⁺ and Hg²⁺ in real samples [12]. There are several studies for determination of a lower amount of iron by using different organic reagents in the minor amount of the surfactant-rich phase [13-20]. Mercury is a heavy hazardous poisoning metal that can arise from exposing to water-soluble forms of mercury as in mercuric chloride or methylmercury by breathing mercury vapor, or by taking in any form of mercury [21-23]. CPE

methodology is feasibly used for Hg^{2+} determination in different matrices, coupled with spectrophotometric technique and different surfactants as in (TritonX-100 and Triton X-114) and organic reagents as in (DDTP, 4-(2-pyridylazo) resorcinol, and ThioMichler's Ketone). These studies include numerous investigational parameters as in pH, the concentration of chelating agent and surfactant [24-27]. The development of a new analytical method employing ultrasound assisted-cloud point extraction (UA-CPE) for the extraction of CH_3Hg^+ and Hg^{2+} species from fish samples has been achieved in [28]. The UA-CPE method has shown to be a suitable method. The results were in a good agreement (with Student's *t*-test at 95% confidence limit) with the certified values, and the relative standard deviation was lower than 3.2%. The limits of detection were 0.27 and 1.20 $\mu\text{g L}^{-1}$ for Hg^{2+} from aqueous calibration solutions and matrix-matched calibration solutions were spiked before digestion, respectively, while it was 2.43 $\mu\text{g L}^{-1}$ for CH_3Hg^+ from matrix-matched calibration solutions. A significant matrix effect was not observed from comparison of slopes of both calibration curves to represent the sample matrix. In [29], a new cloud point extraction procedure has been optimized for the selective determination of trace amounts of total iron in some environmental samples without using organic reagents. The determination of mercury via sensor in real aqueous along with real samples has been also reported as in [30, 31].

Since our survey through literature did not find any synthesis or using of [methylphenyl thiazolyl azo]-3-methyl-4-methoxy-2-naphthol (MPTAN) as a chelating agent for metal ions in CPE or other methods. This study explains the synchronous preconcentration of Fe^{3+} and Hg^{2+} , after the construction of ion-pair association complex with MPTAN and then analyzes the spectrophotometry employing TritonX-100 as a surfactant. This study presents the determination of iron and mercury separation through cloud point extraction as flexible and accurate technique that can be utilized for characterization of metal ions in meat, vegetable, soil, water, and fruit.

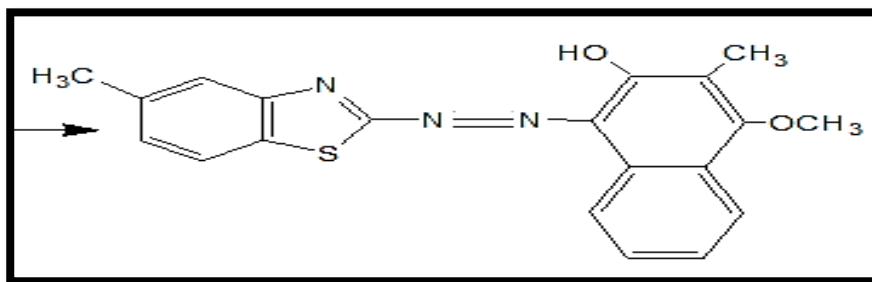
EXPERIMENTAL

Instrument

A double beam spectrophotometer Biochrom (80-7000-11) Libra S60 Cambridge CB40FJ model and 1.00cm quartz cell were used for spectroscopic studies with Shimadzu FTIR spectrophotometer 8400 series (Japan). Electrostatic water bath (WNB7-45) (England) has been used for CPT heating with all needed experiments balance (A& D company, Limited, Dool, CE, HR 200, Japan)($\pm 0.0001\text{g}$).

Reagents

Each solution has been formulated with deionized water. An analytical grade of acids, salts, bases and other materials employed in this paper has been gotten from Merck, Darmstadt, Germany. Stock solution of Fe^{3+} ion was prepared by dissolving 0.2880g of FeCl_3 in 100mL and for Hg^{2+} ion dissolved 0.1353g of HgCl_2 in 100 mL of purified water. Other employed solutions have been prepared by dilution technique with purified water in an appropriate volumetric flask. The MPTAN ligand as presented in **Scheme 1** was created in relation to [32] by reacting methyl phenyl thiazolyl amine with 3-methyl-4-methoxy-2-naphthol after controlling all conditions as reported in [32]. Consequently, $1 \times 10^{-2}\text{M}$ of MPTAN was prepared by dissolving 0.363g in 100mL distilled water containing Triton X-100.



Scheme 1. The structure of ligand new azo derivative [methyl phenyl thiazolyl azo]-3-methyl-4-methoxy-2-naphthol (MPTAN)

Comprehensive Method

10mL aqueous solutions containing 50 μg of metal ion under study Fe^{3+} or Hg^{2+} have been taken with optimal HCl concentration and $1 \times 10^{-4}\text{M}$ MPTAN in the presence of the optimal volume of surfactant with 1% TritonX-100. The solution has been heated in an electrostatic water bath for proper temperature up to the period of cloud point layer formation. At that point, it disjointed CPL from aqueous solution and liquefied CPL in 5mL ethanol. The absorption of an alcoholic solution was determined at $\lambda_{\text{max}}=485\text{nm}$ for Fe^{3+} and $\lambda_{\text{max}}=497\text{nm}$ for Hg^{2+} ion in

contradiction of blank arranged in the similar method without metal ions. Nevertheless, aqueous solution for Fe^{3+} ion has been handled along with thiocyanate method but Hg^{2+} ion has been handled according to Dithizone spectrophotometric process [33] to regulate the remainder amount of metal ions in aqueous solution along with extraction as in **Figure 1**. This quantity has been subtracted from the primary quantity of $50\mu\text{g}$ to evaluate the transferred quantity to CPL to extract ion-pair association complex. Then, distribution ratio (D) can be calculated according to Equation (1):

$$D = \frac{[M^{n+}]_{CPL}}{[M^{n+}]_{aq}} = \frac{\text{transferred quantity to cloud point layer}}{\text{remainder quantity in aqueous phase}} \quad (1)$$

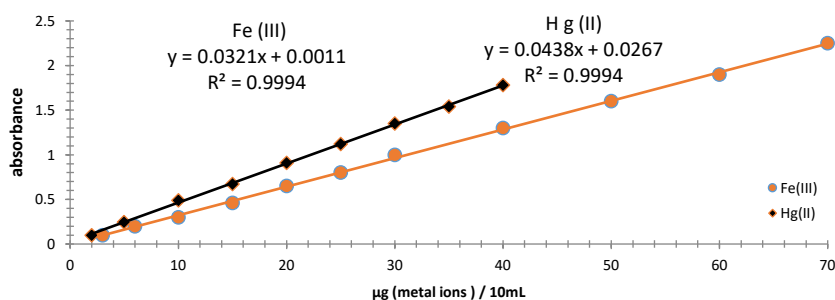


Figure 1. Calibration curve for determination Fe(III) and Hg(II) in aqueous solution

RESULTS AND DISCUSSION

Spectroscopy

For identification of new azo derivative reagent [methyl phenyl thiazolyl azo]-3-methyl-4-methoxy-2-naphthol, (MPTAN) UV-Vis and IR spectrums in **Figures 2** and **3** prove and put forward the true structure of new organic reagent with a wavelength of maximum absorbance equal to 475nm. IR spectrum shows a peak at a wave number of 3420 cm^{-1} belongs to stretching vibration -OH group but aromatic C-H appears at wave number more than 3000 cm^{-1} . Bending vibration for ether C-O giving a peak at 1262 and 1159 cm^{-1} , as well as the weak peaks at 1450 - 1350 cm^{-1} , belong to $\text{N}=\text{N}$, while at 1510 - 1100 cm^{-1} region belongs to all peaks for vibration of bridge azo group.

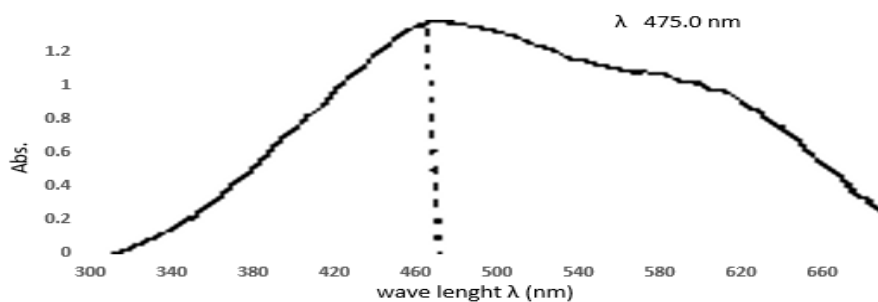


Figure 2. UV-VIS spectrum of new azo derivative (MPTAN)

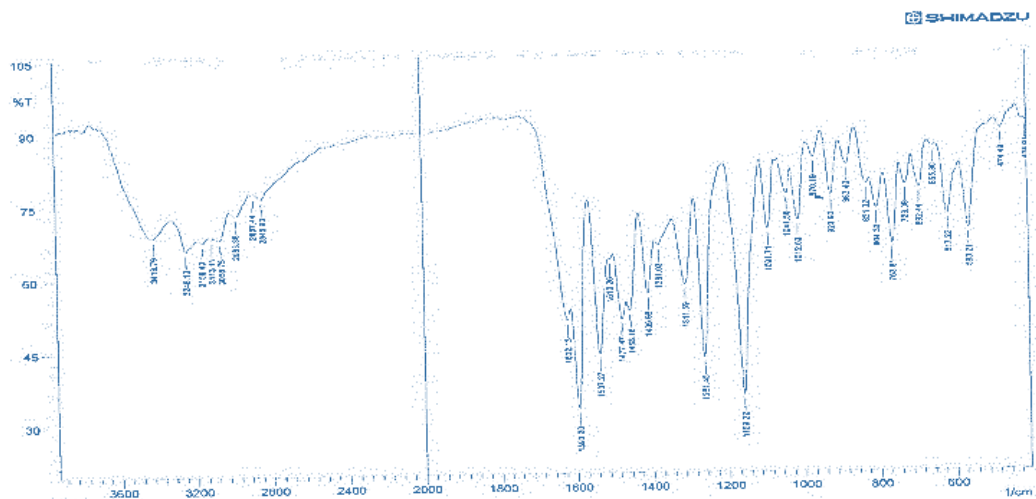


Figure 3. FT-IR spectrum for the new azo derivative (MPTAN)

The UV-VIS spectrophotometric investigations about extracted ion-pair association complexes of Fe^{3+} and Hg^{2+} are shown in Figures 4 and 5. The UV-VIS spectrum reveals that red shift in the bands and the complexes have less energy than reactants.

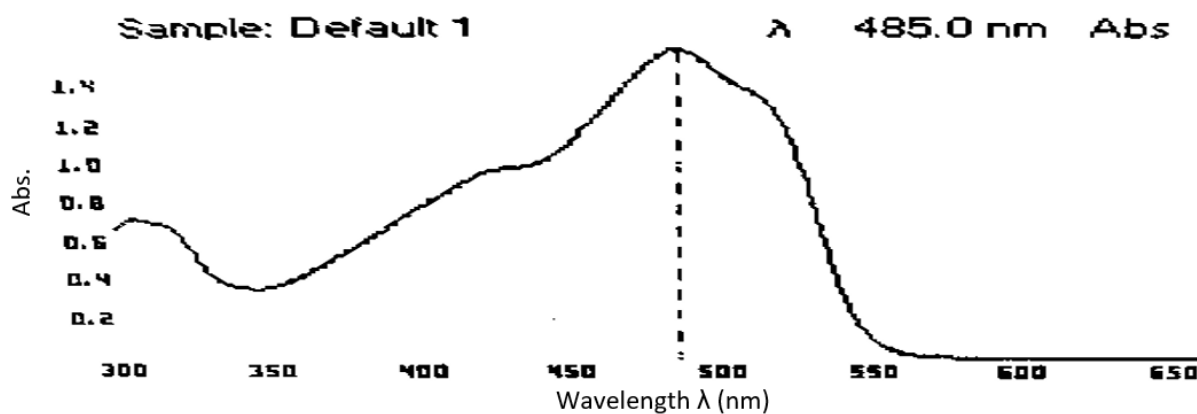


Figure 4. UV-VIS spectrum for ion-pair association complex of the Fe^{3+} ion

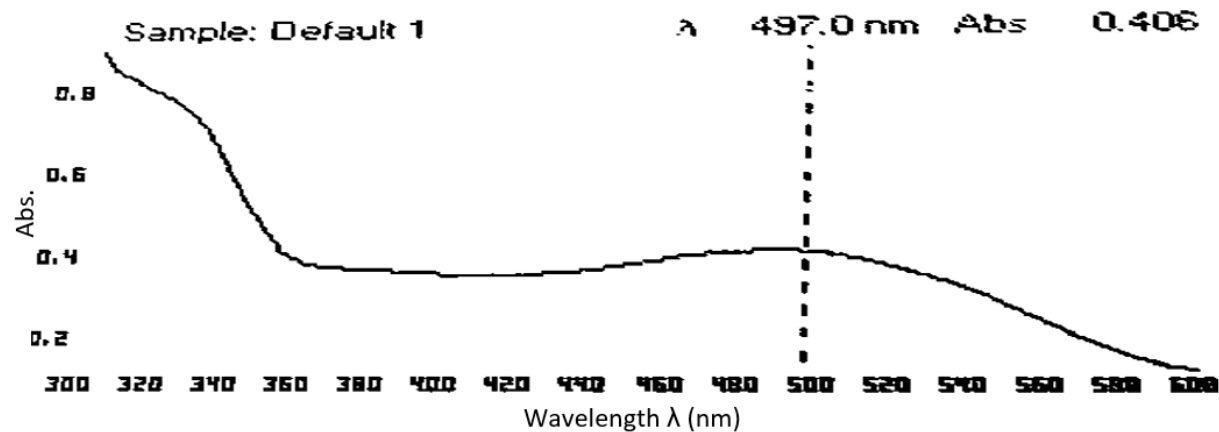


Figure 5. UV-VIS spectrum for ion-pair association complex of Hg^{2+} ion

Variation of pH

According to the comprehensive method, 50 μ g for each metal ion was extracted alone from 10mL aqueous solutions at different pH values in the existence of 1×10^{-4} M MPTAN and 0.5mL of 1% TritonX-100 after heating the solution in an electrostatic water bath at 90°C for 15 minutes. Up to realization of CPL, it was separated from the aqueous phase and liquefied in 5mL ethanol to complete the procedure. The results were shown in **Figures 6**. These results showed that optimum pH for extraction was $pH_{ex}=9$ for both ions. At this pH, the best rate was reached for thermodynamic formation ion-pair complex and partitioning to CPL. At pH less than the optimum value, the rate of complex formation was decreased but at more than optimal value, a side effect of OH⁻ ion has appeared in aqueous solutions with decreased extraction efficiency.

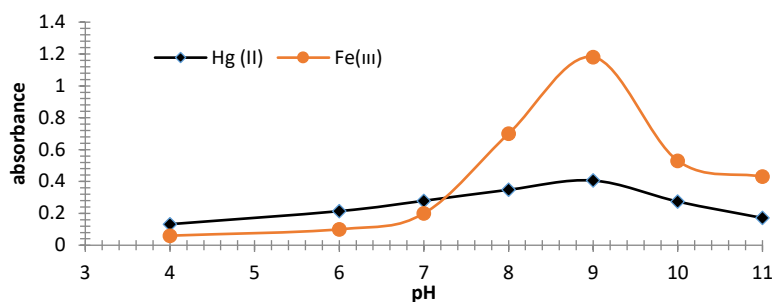


Figure 6. Effect of pH on formation and stability of ion-pair complex

Effect of Surfactant Volume

By following comprehensive method, 50 μ g of Fe³⁺ and Hg²⁺ was extracted each one alone in 10mL aqueous solutions at pH_{ex} of 9 in the existence of 1×10^{-4} M MPTAN with rising volume of a surfactant of 1% TritonX-100. The resultant absorbance curves were shown in **Figure 7**. The optimum surfactant volume giving higher extraction efficiency was 0.5mL for Fe³⁺ ion and 0.4mL for Hg²⁺ ion. This volume formed the best CPL for partitioning complexes and contributed to the formation of CMC state. Any volume less than optimal level was not suitable to form CMC and make the volume more than the finest volume effect to increase diffusion of micelles.

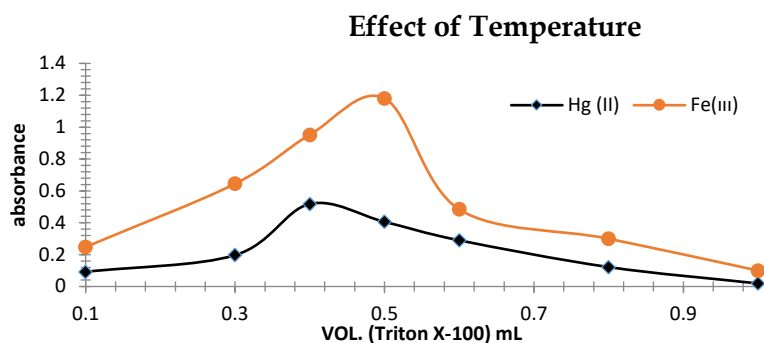


Figure 7. A consequence of surfactant volume on the efficiency of partitioning complex

Depending on the comprehensive method of extraction to determine rising temperature for Fe³⁺ and Hg²⁺, the absorbance results are shown in **Figure 8**. The finest temperature of two ions is 90°C that formed suitable CPL layer with more hydrophobic and smaller volume.

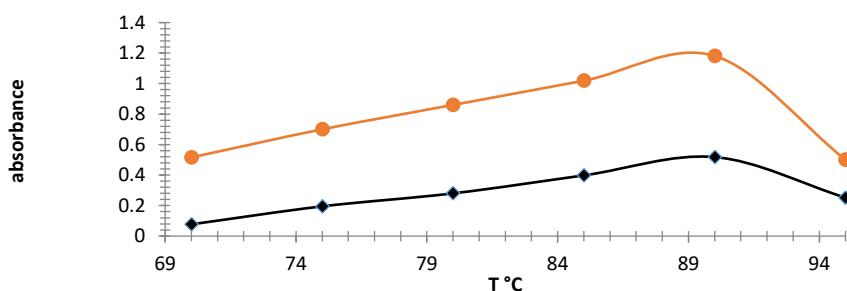


Figure 8. Consequence of temperature on the formation and quantitation partitioning of complexes

By application of mathematical thermodynamic relation below to calculate extraction constant K_{ex} at each temperature, the extraction consequences were depicted in **Figure 9**. The results explained that extraction method was endothermic with an optimum temperature of extraction (90°C) for both metal ions. The high value of entropy reflected the dependency of extraction method on entropy to form new stable system. It could be extracted quantitatively which was the ion-pair association complex for each metal ions.

$$K_{ex} = \frac{D}{[M^{n+}][MPTAN]} \quad (2)$$

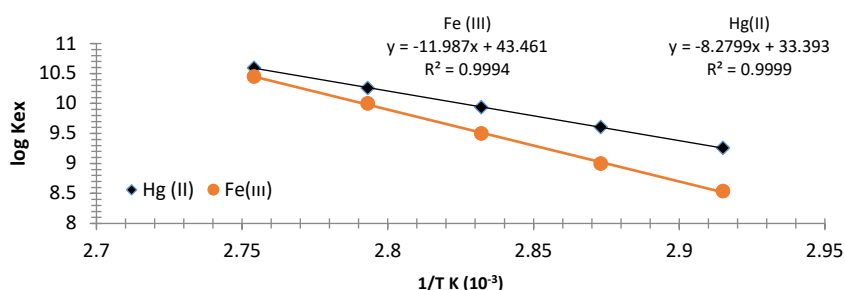


Figure 9. Variation extraction constant with temperature change

From the slope of straight relation above and relations below, calculated thermodynamic data of extraction results are shown in **Table 1**.

$$slope = -\frac{\Delta H_{ex}}{2.303 R} \quad (3)$$

$$\Delta G_{ex} = -RT \ln K_{ex} \quad (4)$$

$$\Delta G_{ex} = \Delta H_{ex} - T\Delta S_{ex} \quad (5)$$

Table 1. Thermodynamic details of extraction

Fe(III)			Hg(II)		
ΔH_{ex} KJ.mole ⁻¹	ΔG_{ex} KJ.mole ⁻¹	ΔS_{ex} J.mole ⁻¹ K ⁻¹	ΔH_{ex} KJ.mole ⁻¹	ΔG_{ex} KJ.mole ⁻¹	ΔS_{ex} J.mole ⁻¹ K ⁻¹
0.224	-71.056	169.366	0.1422	-72.051	198.880

Effect of Heating Time

50µg of each ion alone was extracted from 10mL aqueous solutions at the optimum condition and at different heating times. Accordingly, the absorbance consequences were shown in **Figure 10**. The results showed that the most probable heating time for both metal ions was 15 minutes. Giving best extraction efficiency at this time reached the cave of CMC in the formation of CPL with very good properties to give higher quantitatively partitioning of ion-pair complexes of metal ions under study. At less than optimum heating time, it was not able to reach to CMC state. However, at more than the optimum value, it increased the diffusion of micelles went far away from the optimum state and CMC formation.

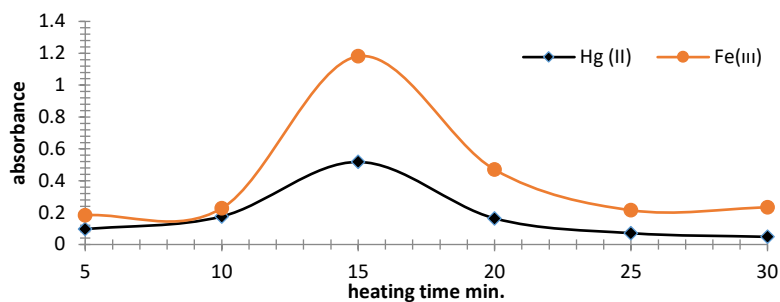


Figure 10. The consequence of heating time on formation CPL and partitioning of complexes

Stoichiometry

The most probable structure of ion-pair complex of both metal ions under study can be identified using two spectrophotometric methods which were slope ratio, slope analysis, mole ratio and continuous variation approaches. The results were explained in Figures 11 and 12. The results showed the metal to ligand ratio of 1:1 for all used methods.

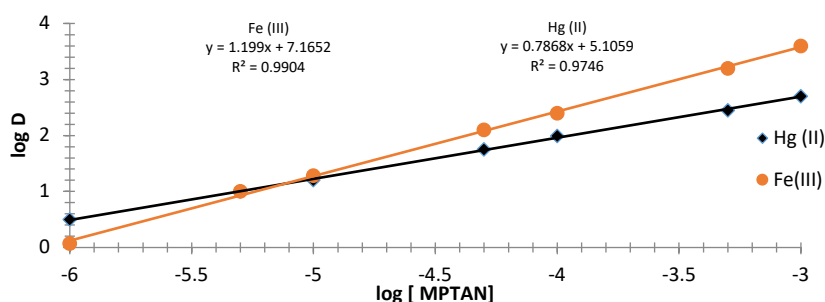


Figure 11. Results of slope analysis method $D=f[\text{MPTAN}]$

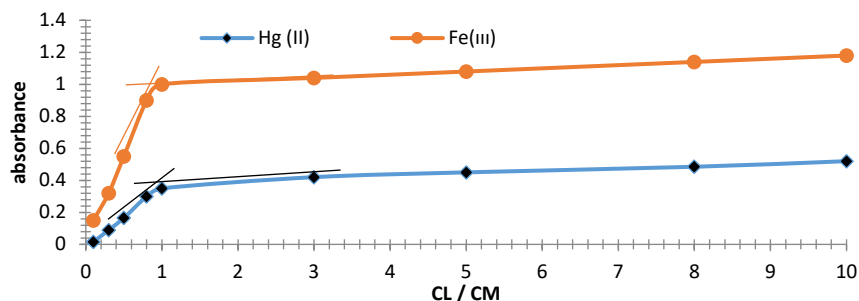
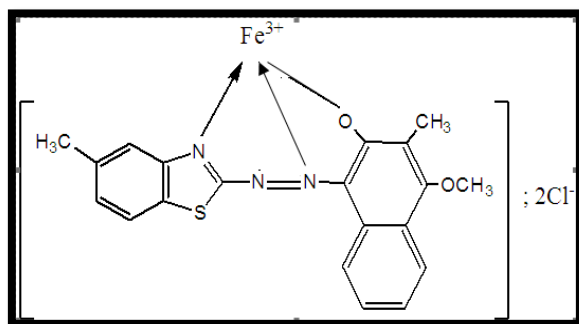
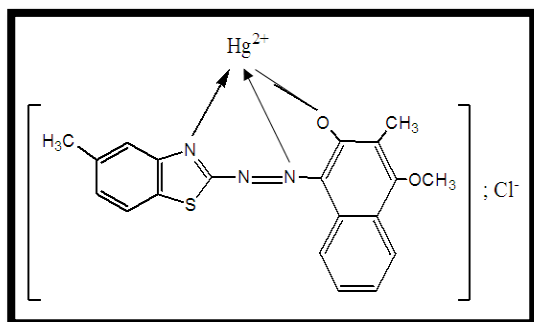


Figure 12. Results of mole ratio method

Accordingly, Schemes 2 and 3 show a more probable structure of ion-pair association complex extracted to CPL.



Scheme 2. More probable structure of Fe^{3+} ion pair extracted complex



Scheme 3. More probable structure of Hg^{2+} ion pair extracted complex

Effect of Electrolytes

50 μg of each metal ions alone has been extracted from 10mL aqueous solutions at the optimal situation in the presence 0.01M of some electrolyte salts according to an inclusive method. The results of electrolyte on extraction efficiency of Fe^{3+} or Hg^{2+} ions have been summarized in **Table 2**. These results show increased extraction efficiency by the presence of electrolyte salts in aqueous solutions and this increasing differs with different electrolyte salts dependent on nature and behavior of electrolyte in aqueous solutions which motivate water molecular withdrawing from hydration shell of metal ions and increases the chances of binding with MPTAN organic reagent to increase formation and stability of extracted ion-pair complex. The finest electrolyte salt was LiCl for the reason that it has a smaller ionic radius of a metal cation and more water molecular has been withdrawn from hydration shell of metal ions under study.

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

Electrolyte salts	Fe^{3+}		Hg^{2+}	
	Abs. 485 nm	D	Abs. 497 nm	D
LiCl	1.345	511.40	0.734	148.60
NaCl	1.243	448.40	0.669	131.40
KCl	1.284	386.50	0.610	115.50
NH_4Cl	1.203	296.61	0.545	108.30
MgCl_2	1.275	498.32	0.675	139.70
CaCl_2	1.198	355.80	0.565	112.81
without	1.181	249.00	0.518	99.00

Spectrophotometric Determination

By comprehensive application method at the optimum condition to determine Fe^{3+} and Hg^{2+} in different samples, a calibration curve for spectrophotometric determination was prepared to calculate analytical data for a calibration curve for a new sensitive method as illustrated in **Table 3**. The corresponding results in **Figure 13** consist of the linear relationship between concentration and absorbance. **Table 4** presents analytical results for the determination of analytes in different samples ($n=5$) by using this new method.

Table 3. The analytical parameter of merit for CPE extraction of Fe and Hg

Parameter	Fe (III)	Hg (II)
λ_{max} (nm)	485	497
Regression equation with extraction	$Y = 0.2282x + 0.0435$	$Y = 0.1052x - 0.0018$
Determination coefficient (R^2)	0.9999	0.9999
Degree of freedom	14	12
RSD% ($n=5$) at 4 ppm	0.08136	0.07451
Molar absorptivity ($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$)	12742.688	21103.120
Sandell's sensitivity ($\mu\text{g}/\text{cm}^2$)	4×10^{-9}	9×10^{-9}
LOD (ppm)	0.016	0.041
LOQ (ppm)	0.054	0.136

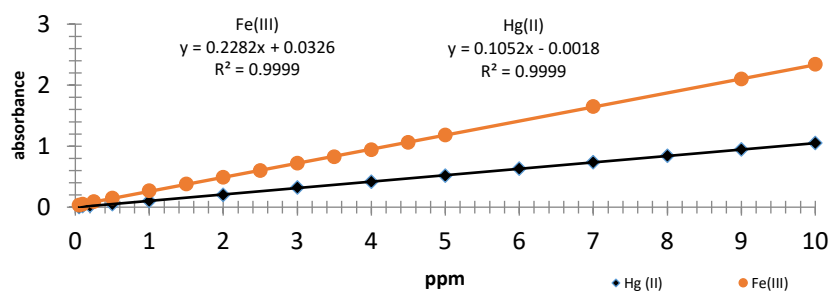


Figure 13. Calibration curve for spectrophotometric determination of Fe(III) and Hg(II) in different samples

Table 4. Fe³⁺ and Hg²⁺ content (ppm) in different samples

No. samples	Fe ³⁺			Hg ²⁺		
	Thiocyanate method ³³	Applied method [*]	RSD %	Dithizone method ³³	Applied method [*]	RSD %
1. Agriculture 1	13.50	13.20	0.05	0.18	0.20	0.11
2. Agriculture 2	20.60	20.56	0.32	0.20	0.20	0.51
3. Cow meat (Beef)	1.50	1.50	0.07	0.16	0.15	0.41
4. Chicken (breast)	7.20	7.19	0.14	0.16	0.19	0.02
5. Drainage fish	17.10	17.20	0.90	0.60	0.60	0.51
6. River water	1.00	0.80	0.03	0.48	0.46	0.08
7. Garden cress	6.30	6.41	0.31	0.40	0.41	0.02
8. Celery	5.00	4.99	0.21	0.10	0.12	0.03
9. Lettuce	6.80	6.79	0.01	0.15	0.15	0.02
10. Cucumber	5.00	5.20	0.06	0.08	0.08	0.04
11. Tomato	8.60	8.56	0.09	0.04	0.04	0.02

* Given values represent the average of five analyses of each sample

CONCLUSION

The speedy, reliable, economical and accurate method is applied in this work in presence of a new ligand MPTAN that has more selective Fe³⁺ and Hg²⁺. This method increases the extraction efficiency by the presence of electrolyte salts in aqueous solutions and this increasing differs with diverse electrolyte salts reliant on nature and performance of electrolyte in aqueous solutions that assists to withdraw water molecular from hydration shell of metal ions and increases the likelihoods of binding with MPTAN organic reagent to increase formation and stability of extracted ion-pair complex. The best electrolyte salt was LiCl since it has a smaller ionic radius of a metal cation. More water molecular has withdrawn from hydration shell of metal ions under study. TritonX-100 has been used as a non-ionic and green extractant solvent. The values of ΔH_{ex} of the resultant reaction were endothermic and the values of ΔG_{ex} showed that the reaction occurs spontaneously. Computerized genetic algorithms can be used in this study as future work to further optimize the desired analytical chemical outcomes using these algorithms with expected interesting performances.

ACKNOWLEDGEMENTS

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