



A Cloud Point Extraction to Comparative Determination of Mercury (II) in Various Water Samples by the Spectrophotometric Method

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ABSTRACT

Cloud point extraction (CPE) was used for the preconcentration of Hg (II) by spectrophotometric method. In this complex, Triton-X-114, Cetylpyridinium chloride (CPC) and NaCl were applied as the non ionic surfactant, sensitizing agent and electrolyte respectively. The lower limit of detection (LOD) acquired under the optimum conditions was $1.10 \mu\text{g L}^{-1}$. The relative standard deviations (RSDs) for ten replicate determinations at 250 and $750 \mu\text{g L}^{-1}$ were 1.98 and 2.21% respectively. A linear calibration curve in the range of 5-1100 $\mu\text{g L}^{-1}$ with a correlation coefficient of 0.9989 ($n = 20$) was acquired. The least square method was $A = 2.01 \times 10^{-3} C_{\text{Hg}} + 1.34 \times 10^{-2}$, where A is the absorbance and C_{Hg} shows the concentration of Hg (II) in $\mu\text{g L}^{-1}$. In the present work, we have used CPE to spectrophotometric determination of mercury (II) in water samples from the rivers located in industrial and nonindustrial areas and also spring water and tap water as the purified and unpurified water samples respectively.

Key words: Mercury (II), LitholRubine BK, Cloud point extraction, CPC, Triton X-114.

INTRODUCTION

The pollution of natural waters by heavy metals is a great concern nowadays due to their potentially toxic effects on living organisms. Urbanization, industrial development, and heavy traffic lead to contamination of water bodies by heavy metals.¹

Mercury has been considered as a human health hazard because it may cause kidney toxicity, neurological damage, paralysis, chromosome breakage, and birth defects.² The monitoring of mercury (Hg) in natural waters is very important due to its high toxicity and very high bioaccumulation factor (up to 10^6) in the food chain.³

Mercury is most often present in the inorganic form Hg^{2+} throughout the Earth's crust. Fish and shellfish are often exposed to toxic substances such as mercury because the aquatic environment is highly susceptible to contamination by industrial discharge.⁴ Chronic exposure to mercury causes toxic effects even at trace concentrations because it can cause irreversible neurological damage.⁵

Because of the importance of this issue, a lot of researchers have done studies regarding measuring of Mercury by various methods.⁶⁻¹²

Cloud-point extraction is based on the property that a solute present in aqueous solution of non-ionic surfactant is distributed between two phase¹³.

Aqueous solutions of non-ionic surfactants become turbid when they are heated above the temperature known as the cloud point. The solution is then separated into two isotropic phases, i.e. a surfactant-rich phase and a bulk aqueous phase. The hydrophobic solutes and metal ions, after the formation of sparingly water soluble complex, can be enriched into the surfactant-rich phase.¹⁴

The cloud point extraction (CPE) technique has also been applied as a procedure for determination and removal of dyes and pigments as well as analyzing metals.¹⁵⁻¹⁶

In the present work, we have used CPE to spectrophotometric determination of mercury (II) in water samples from the rivers located in industrial and nonindustrial areas and also spring water and tap water as the purified and unpurified water samples respectively.

EXPERIMENTAL

Apparatus

Absorption spectra and absorbance measurements were made by a Shimadzu UV-1800, UV-Vis spectrophotometer using 1 cm quartz cells (1.0 mL). A Metrohm digital pH meter (model 691) with a combined glass electrode was applied to measure pH values. A Hettich universal 320 centrifuge was used to hasten the phase separation.

Standard solutions and reagents

The non-ionic surfactant Triton X-114 (4%, v/v) was achieved from Sigma and was used without further purification. Stock solutions of Hg(II) and Hg(I) at concentration of 1000 mg L^{-1} were prepared by dissolving appropriate amounts of their nitrate salts in deionized water. Working standard solutions were prepared by appropriate dilution of the stock solution. A $1.0 \times 10^{-4} \text{ mol L}^{-1}$ solution LitholRubine BK was obtained by dissolving 0.0042 gr of this reagent in bidistilled water from the commercially available product (Sigma). A $0.0 \times 01 \text{ mol/L}$ of Cetylpyridinium chloride (CPC) solution was attained by dissolving 0.034 gr of CPC (Sigma) in water and diluting to 100 mL in a volumetric flask. Stock solution of NaCl (1.0×10^{-1}) was prepared by dissolving 0.584 g NaCl in distilled water and diluting to 100 mL in a flask. A citrate buffer pH 2.5 was prepared by dissolving 2.10 gr of citric acid (Merck) in 100 mL of water and adding 1.0 mol/L NaOH (Merck) to adjust the pH to 2.5 using a pH meter.

Procedure

In a standard CPE process, an aliquot of the solution containing of Hg(II) , (in the range of $5-1100 \mu\text{g L}^{-1}$), 2.75 mL of LitholRubine BK ($1.0 \times 10^{-4} \text{ mol L}^{-1}$), 1.5 mL of 4% (v/v) of Triton X-114, 0.5 mL of $1 \times 10^{-3} \text{ mol L}^{-1}$ of CPC, 1.5 mL of 0.1 mol L^{-1} of NaCl and 1.5 mL of citrate buffer (pH = 2.5) was transferred into a 15 mL tube, and equilibrated at 40°C in a thermostat bath for 10 min. The separation into two phases was accelerated by centrifuging at 3500 rpm for 10 min. After the separating two phases, the mixture was cooled in an ice bath to enhance the viscosity of the surfactant-rich phase for 8 min, and the upper aqueous phase was decanted. The surfactant-rich phase of this procedure was dissolved and diluted to 0.8 mL with the methanol and transferred into a quartz cell. The absorbance of the solution was assessed at 440 nm. A blank solution was also submitted to the same procedure and estimated in parallel to the samples.

Preparation of samples

The Appropriate amounts of water samples including river water located in two industrial (karoon river, ahvaz city) and non industrial (zohreh river, Gachsaran city) area, spring water and tap water were filtered through a $0.25 \mu\text{m}$ micropore membrane prior to use.

RESULTS AND DISCUSSION

In this work, spectrophotometric determination was coupled with the CPE preconcentration. Lithol Rubine BK dye was applied as a chelating agent for the determination of a mercury. Surfactants can interact with dye and/or the metal-dye complex as an individual molecule or aggregates. The addition of sensitizing agent improves the selectivity and sensitivity of the metal determinations. We used CPC as the sensitizing agent. Electrolyte increases the efficient extraction. After testing 3 kinds of electrolyte (KCl, NaCl, KI), NaCl showed the most impact on the absorbance and extraction efficiency.

The maximum wavelength of absorption for the resultant sample was at 440 nm. To have the maximum absorbance, it is necessary to optimize various conditions which can affect the extraction. Hence, the effects of various operating conditions have been investigated and the optimum concentrations have been established for CPE.

Effect of pH

The complex formation of metal-chelate and its chemical stability are two significant factors for cloud point extraction. The pH, which plays a singular role on formation of the complex and stability of the complex, proved to be a main factor for cloud point extraction efficiency. Fig. 1 shows the effect of pH on the mercury extraction. It was studied in the pH range of 1-6. Since, at pH 2.5 there was the highest absorbance, therefore pH 2.5 was selected for next experiments.

Effect of Lithol Rubine BK dye concentration

Lithol Rubine BK is a reddish synthetic azo dye. It has the appearance of a red powder. It is slightly soluble in hot water, insoluble in cold water, and insoluble in ethanol. It can be used as a ligand. The extraction efficiency as a function of the Lithol Rubine BK concentration was investigated. For this work, various quantities of Lithol Rubine BK were subjected to the CPE process. The extraction efficiency was the highest when 1.83×10^{-5} mol L⁻¹ Lithol Rubine BK was applied, it showed the highest

Table 1: Determination of Arsenic in different water samples and recovery tests.

Sample	added ($\mu\text{g L}^{-1}$) Found ^a				
	Hg(II) ($\mu\text{g L}^{-1}$)	Recovery (%)	RSD (%)	Total Hg ($\mu\text{g L}^{-1}$)	RSD (%)
River water ^b	-	9.14 ± 0.14-1.31	13.21 ± 0.18	4.20	
	50	58.20 ± 0.159	8.463.05	63.11 ± 0.25	2.71
	100	110.20 ± .090	100.911.73	114.71 ± 0.15	1.53
River water ^c	-	5.13 ± 0.32-2.61	7.19 ± 0.29	1.21	
	50	54.32 ± 0.1798.531.20	57.11 ± 0.352.59		
	100	103.21 ± 0.2898.174.13	104.73 ± 0.39	2.89	
Tap water ^d	-	ND ^f	1.624.19 ± 0.31	3.31	
	50	48.21 ± 0.21	96.432.85	53.21 ± 0.25	1.77
	100	103.11 ± 0.151	03.111.71	104.51 ± 0.24	2.56
Springwater ^e	-	5.01 ± 0.12-2.93	7.27 ± 0.18	1.11	
	50	57.10 ± 0.161	03.802.07	56.83 ± 0.11	2.91
	100	102.13 ± 0.31	97.261.71	106.12 ± 0.35	2.12

^a $\bar{x} \pm ts\sqrt{n}$ at 95% confidence (n = 5).

^bkaroon, Ahvaz (industrial area)

^cpol-e- Zohreh (nonindustrial area)

^dAs a purified water sample

^eAs a unpurified water sample

^f Not Detection

absorbance and concentrations greater than $1.83 \times 10^{-5} \text{ mol L}^{-1}$ have no effect on the extraction of the mercury. Thus we chose it as the optimum concentration of the chelating agent. The results are shown in Fig. 2.

Effect of non ionic surfactants concentration

Three nonionic surfactants containing Triton X-114, Ponpe 7.5 and Triton X-45 to extract the hydrophobic Hg-complex into the surfactant rich phase were studied in the range of 0.13–1.06% (v/v). The highest extraction efficiency was acquired in presence of Triton X-114. Thus, Triton X-114 was selected for further studies. The effect of Triton X-

114 concentration, was studied in the range of 0.13–1.06% (v/v) and the highest absorbance was in 0.4%. It is shown in Fig. 3. Therefore it was chosen as the optimum concentration.

Effect of sensitizing agent concentration

At the first step, the two cationic surfactants containing CPC and CTAB as the sensitizing agent were investigated in the various amounts. The most extraction efficiency was attained in the presence of CPC. Thus CPC was specified as the sensitizing agent. The effect of CPC was investigated in the various quantities. It is shown in Fig. 4. The highest extraction efficiency was at $3.33 \times 10^{-5} \text{ mol L}^{-1}$. Hence,

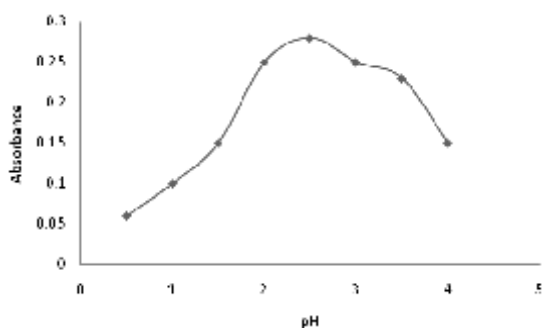


Fig. 1: The concentration effect of pH on CPE

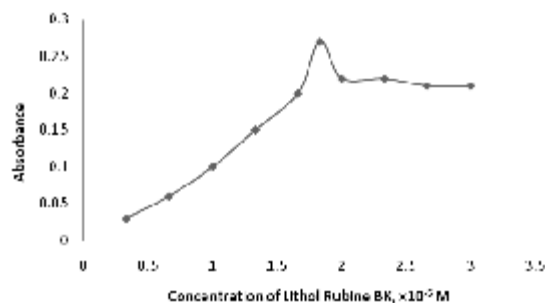


Fig. 2: The concentration effect of LitholRubine BK on CPE

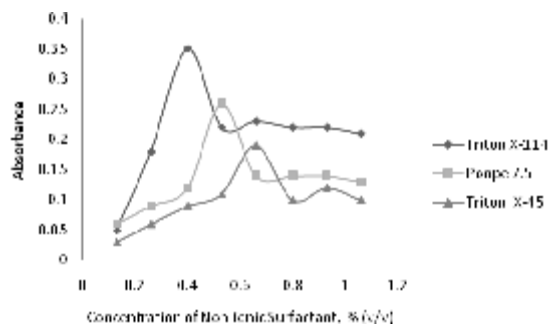


Fig. 3: The concentration effect of non ionic surfactant on CPE

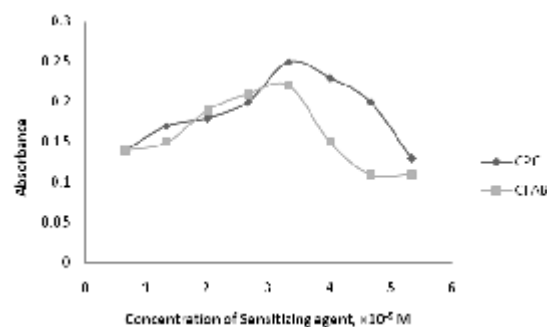


Fig. 4: The concentration effect of sensitizing agent on CPE

the $3.33 \times 10^{-5} \text{ mol L}^{-1}$ CPC solution was selected as the optimal sensitizing agent concentration.

Effect of salt concentration

It is well known that, addition of electrolytes (salting-out effect) has a pronounced effect on the phase separation of analyte and decreases cloud

point (CP) temperature of surfactant, resulting in a more efficient extraction.¹⁷ Thus, the effect of NaCl, KCl and KI was studied in the range of $0.33 \times 10^{-2} \text{ mol L}^{-1}$ to $1.66 \times 10^{-2} \text{ mol L}^{-1}$. The absorbance of solution increased on increasing electrolyte concentration, but the best extraction efficiency was for NaCl. Hence it was selected for this work.

The various amounts of 0.1 mol L^{-1} of NaCl solution was tested. The absorbance of the solution reached a maximum value at concentration of 0.01 mol L^{-1} of NaCl and remained constant. 0.01 mol L^{-1} NaCl was selected as the optimal concentration.

Effect of equilibration temperature and time

To obtain simple phase separation and efficient preconcentration, it is essential to optimize the equilibration temperature and incubation time. It is favorable to use the shortest incubation time and the lowest possible equilibration temperature. The impact of the equilibration temperature was investigated by various temperatures from 20 to 60°C . The results demonstrated which the maximum absorbance was obtained for 40°C . The dependence of extraction efficiency upon incubation time was studied over the time period of 5–25 min. An incubation time of 10 min was adequate for the highest absorbance. A centrifuge time of 10 min was chosen as optimal at 3500 rpm.

Analytical performance

The analytical curve was linear in the concentration range of $5\text{--}1100 \mu\text{g L}^{-1}$. The calibration equation resultant by the least square method is $A = 2.01 \times 10^{-3} C_{\text{Hg}} + 1.34 \times 10^{-2}$ for $5\text{--}1100 \mu\text{g L}^{-1}$ of Hg^{2+} with a correlation coefficient of 0.9989 ($n = 20$). A shows the absorbance and C_{Hg} demonstrates the Hg^{2+} concentration ($\mu\text{g L}^{-1}$). Limit of detection (LOD) was found to be $1.10 \mu\text{g L}^{-1}$ as the concentration that gave signal equal to three times the standard deviation of the blank solution. The observed relative standard deviation (RSD) value for 10 replicate analyses at 250 and $750 \mu\text{g L}^{-1}$ were 1.98 and 2.21% respectively.

Interference studies

In order to investigate the selectivity of the method, aliquot of aqueous solutions containing $250 \mu\text{g L}^{-1}$ Hg (II) and various amounts of other ions was taken and the proposed procedure was followed. Mercury recovery was studied in the presence of other species with tolerance limits (error $< 5\%$). Tolerance limits are as follows: Cu^{2+} (50 folds), SO_3^{2-} , Sn^{2+} , Al^{3+} (100 folds), SCN^{2-} , Ni^{2+} , SO_4^{2-} (250 folds), Sr^{2+} , Ag^+ , HCO_3^- , Br^- , HPO_4^{2-} (500 folds), Na^+ , Pb^{2+} , NO_3^- , Ca^{2+} , Sb^{3+} (800 folds), F^- , K^+ , NH_4^+ , Cl^- , H_3BO_3 . Fe^{2+} (1000 folds).

Application

The presented procedure was applied for determination of Hg(II) in water samples. The results are demonstrated in Table 1. Practically, this work offers the results for a contrast among quantities of mercury in the industrial and nonindustrial water samples and also tap (purified) and spring (unpurified) water. Total mercury in water samples was determined as Hg (II) after oxidizing Hg (I) to Hg (II) in the water samples. A few drops of 1.0 mol L^{-1} H_2SO_4 and 1.5 mL of 1% (w/v) KMnO_4 solution were added to 25 mL of water samples to oxidize Hg (I) ions. Then, the solution was heated in water bath for 15 min. After that it was cooled to room temperature, 3 drops of 1% (w/v) NaN_3 solution was added to the final solution. The solution was neutralized with diluted NH_4OH and transferred into a 50 mL volumetric flask. The concentration of Hg (I) was determined by calculating the difference between total Hg and Hg (II). The percentage recovery was always higher than 96% confirming the accuracy.

CONCLUSION

The proposed method requires inexpensive instrumentation and is safe, sensitive, accurate, selective and rapid that can be applied to the determination of mercury in real samples. In addition, a non-ionic surfactant of Triton-X-114 used in the CPE makes the micellar extraction procedure simple, greener and economical and thus toxic solvent extraction has been avoided. The limit of detection of the proposed method seems to be satisfactory in comparison with some other preconcentration techniques, benign organic solvent is employed; therefore, the chemical waste is limited only to a small quantity of surfactant, Triton X-114, which is commercially available at low cost.

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