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Surfactant-sensitized spectrophotometric determination of Hg(II) in water samples using 2-(2-thiazolylazo)-p-cresol as ligand and cetylpyridinium chloride as cationic surfactant

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A new, reliable, surfactant-sensitized method is described for the spectrophotometric determination of total and dissolved inorganic mercury at trace levels. The method is based on the ternary complex formation of Hg(II) with 2-(2-thiazolylazo)-p-cresol and a cationic surfactant, cetylpyridinium chloride, at pH 9.5. The detection and quantification limits of the method with surfactant were 6 and 19 $\mu\text{g L}^{-1}$, while those of the method without surfactant were 22 and 67 $\mu\text{g L}^{-1}$, respectively. The method obeys Beer's law at up to approximately 10 mg L^{-1} Hg(II) in an aqueous surfactant medium. The relative errors and relative standard deviations of the method were 2.2% and 3.2%, while those of the direct method were 11% and 4.4% (1.0 mg L^{-1} , n = 10), respectively. The accuracy and reliability were examined by the recoveries of spiked solutions at 3 and 5 mg L^{-1} for the determination of mercury in tap water, drinking water, dental unit wastewater, and artificially prepared model water samples. It was found that the results were very good and comparable for both the present method and the modified dithizone method, which was used as an independent reference method. Speciation studies for binary mixtures containing Hg(I) plus Hg(II) ions at known concentration ratios were also conducted.

Key Words: Surfactant media, spectrophotometry, 2-(2-thiazolylazo)-p-cresol, Hg(I), Hg(II), speciation, environmental water samples

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Introduction

Mercury is a serious environmental pollutant with toxic effects in all living organisms.¹ Its effect on the immune system is potentially harmful, possibly contributing to diseases such as leukemia.² Mercury and its compounds could be present as trace contaminants as a consequence of natural or anthropogenic activities in various environmental samples.³ It is usually present in natural waters at trace levels.⁴ The lakes, rivers and coastal waters in the vicinity of industries that utilize mercury in production are important indicators of environmental pollution. The development of analytical methods for the determination of mercury is still a challenge.⁵ A serious problem encountered in the determination of mercury is that target species are usually present in low concentrations.

The main species of mercury in natural waters to be identified and determined are inorganic mercury (Hg^{2+}) and methyl mercury (CH_3Hg^+). Recent reports estimate total mercury concentration in natural waters to range from 0.2 to 100 ng L^{-1} , while methyl mercury levels are much lower (approximately 0.05 ng L^{-1}).⁶

Numerous analytical and sophisticated techniques such as inductively coupled plasma mass spectrometry (ICP-MS)^{7,8} inductively coupled plasma atomic emission spectrometry (ICP-AES),^{9,10} cold vapor atomic absorption spectrometry (CV-AAS),¹¹⁻¹³ neutron activation analysis (NAA),¹⁴ X-ray fluorescence spectrometry (XRF),¹⁵ atomic fluorescence spectrometry (AFS)^{16,17} and spectrophotometry¹⁸⁻²¹ have been used to determine Hg(II) at trace levels. Each of the above techniques has its own merits, but each also shares some of the common problems of poor reproducibility and limited sample adaptability. ICP-AES and ICP-MS are useful for trace determination without any preconcentration. However, the necessary instruments are costly and expensive to maintain. Moreover, these suffer from some inherent interference.^{7,10} CV-AAS is a suitable and widely used technique for the accurate determination of mercury due to its simplicity although it has a limited linear range and spectral interference from volatile species.^{12,22} Therefore, it is not directly applicable to environmental or biological samples in view of low analyte contents and the required preconcentration steps to enhance sensitivity. Amalgamation onto a gold trap²³ and sorption on resins¹³ have been used for this purpose. Although a number of photometric reagents, such as 1-(2-pyridylazo)-2-naphthol, 4-(2-pyridylazo) resorcinol, crystal violet, triphenyl tetrazolium chloride, triphenylphosphine oxide, and diphenylcarbazone have been used for spectrophotometric determination of Hg(II), dithizone, which forms a water-insoluble complex, is among the most commonly used reagents^{18-21,23} The complex is extracted in either CCl_4 or CHCl_3 prior to photometric determination.²⁴ Such organic solvents are known to be carcinogens.²⁵ Moreover, the extraction and preconcentration steps are tedious and time-consuming and sometimes an incomplete extraction may appear to give significant improvement in the sensitivity while yielding erroneous results. In the absence of a suitable specific method, there is an ever-increasing need for the development of newer methods for the trace determination of mercury in environmental samples.¹⁰

Hg(II) is a very soft Lewis acid that forms stable complexes, preferentially with soft Lewis bases such as sulfur ligands. It should be remembered that the major natural form of mercury is sulfides.^{26,27} Pyridylazo and thiazolylazo reagents have been used for spectrophotometric determinations because of their good selectivity and sensitivity, although for conventional spectrophotometric analysis in aqueous solutions, the low solubility of these azo-compounds and their complexes is a significant drawback. This drawback can be overcome by adding organic solvents or surfactants. Pyridylazo dyes, such as 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol derived from

m-aminophenol, are characterized by high molar extinction and are considered as highly sensitive chromogenic reagents for the photometric determination of several metal ions.^{28–32} The solubilization properties of micellar systems provide additional advantages over existing analytical methods using extraction with toxic organic solvents for determination in aqueous media and for their significant increase in sensitivity and selectivity.^{32,33} The action of thiazolylazo dyes as ligands is the basis for their masking properties used in analytical procedures. 2-(2-Thiazolylazo)-p-cresol (TAC) has been employed as a masking agent to minimize the interference of Ni and Cu in the determination of Bi in high Ni and Cu by hydride generation atomic absorption spectrometry (HG-AAS).³⁴

Recently, enhanced sensitivity in spectrophotometry was achieved by utilizing the ability of certain surfactants to sensitize the binary complexes of the metal ion with chromogenic ligands^{35,36} Sensitizations are a result of the replacement of acidic protons of the liganded dye molecule by surfactant³⁷ or adsorption of the metalreagent complex on the micelles of the surfactant³⁸ Cationic, anionic and nonionic surfactants are often used to sensitize the metallochromic indicators. In this context, updated surfactant-sensitized reactions have recently been developed in spectrophotometry.^{39–43}

The present study was hence planned to suggest a very simple and reasonably good method for the determination of mercury ions at low concentrations, using the reported reagent, TAC as a binary complex and sensitizing the reagent with cetylpyridinium chloride (CPC) as a ternary complex using a spectrophotometer which is still frequently used because of its low cost and simplicity.

Experimental

Reagents, solutions and instrumentation

Ultrapure water with a resistivity of $18.2 \text{ M}\Omega \text{ cm}^{-1}$ was prepared during trace analysis with a Milli-Q water purification system. Before use, all containers (glassware and PTFE bottles) were treated for at least 1 week, first with 1:4 HNO_3 and then with 1:4 HCl , and then they were abundantly rinsed with water. When not in use, the vessels were kept in 1:4 HCl . A stock solution of mercury, $3.1 \times 10^{-3} \text{ M}$, was prepared from Hg(II) nitrate (Merck). The surfactant solutions were $3.5 \times 10^{-3} \text{ M}$ sodium dodecyl sulfate (SDS), $2.9 \times 10^{-3} \text{ M}$ hexadecyltrimethyl ammonium bromide (HDTAB), $2.9 \times 10^{-3} \text{ M}$ CPC, $2.0 \times 10^{-3} \text{ M}$ polyoxyethylene mono-octylphenyl ether (Triton X-114), and $1.7 \times 10^{-3} \text{ M}$ polyoxyethylene octyl phenyl ether (Triton X-100). The TAC working solution, $5.0 \times 10^{-3} \text{ M}$, was prepared by dissolving 0.1031 g of the reagent (Sigma-Aldrich) in 30 mL of ethanol (Merck) and completing the volume with water to 100 mL. A $\text{NH}_3/\text{NH}_4\text{NO}_3$ buffer solution of pH 9.5 was prepared by mixing 350 mL of 1 M NH_4NO_3 and 650 mL of 1 M NH_3 in a calibrated 1-L flask. The H_2SO_4 solution, 1 M, was prepared by diluting 13.6 mL of concentrated H_2SO_4 to 250 mL with water. A sodium azide solution, 0.39 M, was prepared by dissolving 2.53 g of solid NaN_3 in water and diluting the mixture to 100 mL. A KMnO_4 solution, 0.064 M, was prepared by dissolving 1.01 g of KMnO_4 in water followed by dilution to 100 mL. A dithizone solution was prepared by diluting 0.5 mL of 0.38 M stock solution to 1 L with isoamyl alcohol.

During the present study, a UV-Vis spectrophotometer (Agilent 8453) was used for all spectrophotometric measurements. The pH measurements were conducted with a pH meter (Sartorius Basic) with an accuracy of

± 0.1 pH unit. Standard pH buffer solutions of 7.0 and 10.0 were used for calibration of the pH meter. In order to check the temperature of the reaction media, an external temperature-controlled water bath (BM302, Nüve) was used. A stopwatch was used to monitor the reaction time.

General procedure

A known aliquot of solution containing Hg(II) ions in the concentration range of $0.5\text{--}20\text{ mg L}^{-1}$, 2 mL of 250 mg L^{-1} TAC solution, 1 mL of 150 mg L^{-1} CPC solution and 1 mL of $\text{NH}_3/\text{NH}_4\text{NO}_3$ buffer solution was transferred to a 10-mL volumetric flask. The mixture was completed to 10 mL with water. The absorbance measurements were taken at 548 and 530 nm with and without CPC against water, respectively.

Micellar enhanced spectrophotometric comparative method

In a 10-mL volumetric flask 0.11 mL of a slightly acidic solution containing $0.5100\text{ }\mu\text{g}$ of Hg(II) was mixed with 5 mL of 0.6 M SDS and 1 mL of 1 M H_2SO_4 , followed by the addition of a molar excess, from 20-fold to 100fold of dithizone solution (preferably 1 mL, $1.95 \times 10^{-4}\text{ M}$). The mixture was diluted to the mark with water. Absorbance was measured against a reagent blank prepared in a manner similar to this mixture (without mercury) at 490 nm. The Hg(II) content of the unknown sample was determined using a calibration graph under optimized conditions.

Speciation analysis of Hg(I) and Hg(II) in mixtures

The appropriate portions of the Hg(I) and Hg(II) mixture (at ratios of 1:1, 1:5, 1:10, and 1:15) were taken in 25-mL flasks. For oxidation from Hg(I) to Hg(II) ions, a few drops of 1% (w/v) KMnO_4 solution and 1-2 mL of 1 M H_2SO_4 were added to this mixture. Water (5 mL) was added to the mixture, which was heated gradually in a shaking bath by steam for 10-15 min and then cooled to room temperature. Next, 3-4 drops of a freshly prepared solution of NaN_3 (2.5% (w/v)) were added, and the mixture was slowly heated with the addition of 2-3 mL of water. When necessary, in order to remove excess NaN_3 the heating was continued for 5 min and then the mixture was cooled to room temperature. Reaction mixtures were quantitatively transferred to calibrated 10-mL flasks for analysis by the comparative method, and 5 mL of 0.6 M SDS was added to them. Subsequently, 1 mL of 1 M H_2SO_4 and 1 mL of $1.95 \times 10^{-4}\text{ M}$ dithizone reagent solution were added, and 2 mL of 250 mg L^{-1} TAC, 1 mL of 150 mg L^{-1} CPC and 1 mL of $\text{NH}_3/\text{NH}_4\text{NO}_3$ buffer were also added to the mixtures for analysis with the proposed method. The calibrated flasks were filled with water to the mark. The absorbances were measured against the reagent blank or water at 490 and 548 nm for the modified method and the general method, respectively. Total mercury content was calculated by means of calibration graphs. When necessary, the standard addition method was applied to the analysis of water samples in order to suppress the matrix effect and control the accuracy of the method. This value gave the measure of Hg(II) originally available in the mixture. These values were subtracted from the value of total mercury to determine the amount of Hg(I) present in the mixtures.

Analysis of real samples

The tap water, drinking water, and dental wastewater samples were directly filtered through a filter with a pore size of $0.45 \mu\text{m}$ before use. Wastewater supplied from the dental clinic at the Faculty of Dentistry of Cumhuriyet University, Sivas, Turkey, was collected during 1 working day and completely oxidized with KMnO_4 in a H_2SO_4 medium, and the pH of the obtained homogeneous solution was adjusted to approximately 7.0 with diluted NH_3 solution. Samples of 2-5 mL were added to 10-mL volumetric flasks, and then the mercury content was comparatively determined according to the general procedure and the modified dithizone procedure. The standard Hg(II) solutions were independently added to the calibrated flasks so that the Hg(II) concentration in the final volume was 1, 3 and 5 mg L^{-1} . The mixtures were completed to 10 mL with water. The absorbance measurements ($n = 5$) were taken against the reagent blank and water at 490 and 548 nm. Additionally, in order to test the applicability of the developed method a model saline water sample with high salt content was artificially prepared in the laboratory and used in analysis for validation. While the water sample was prepared, the major ions most abundant in the composition of natural seawater at lower levels than their real concentrations were considered as the reference; the sample was prepared as a mixture composed of $1000 \text{ mg L}^{-1} \text{ Cl}$, $550 \text{ mg L}^{-1} \text{ Na}^+$, $250 \text{ mg L}^{-1} \text{ K}^+$, $25 \text{ mg L}^{-1} \text{ HCO}_3^-$, $75 \text{ mg L}^{-1} \text{ Mg}^{2+}$, $20 \text{ mg L}^{-1} \text{ Ca}^{2+}$, $15 \text{ mg L}^{-1} \text{ Sr}^{2+}$, $5 \text{ mg L}^{-1} \text{ SO}_4^{2-}$, $4 \text{ mg L}^{-1} \text{ Br}$, $5 \mu\text{g L}^{-1} \text{ F}^-$, and $1.5 \mu\text{g L}^{-1} \text{ H}_3\text{BO}_3$ and it was analyzed using the proposed method. Because the mercury level in water is below the detection limit of the method, the standard Hg(II) solutions were spiked in the samples so that the Hg(II) concentration in the final volume was 1, 3 and 5 mg L^{-1} . The mixtures were then completed to 10 mL with water. The absorbance measurements ($n = 5$) were made against reagent blank and water at 490 and 548 nm.

Results and discussion

Figure 1 shows the absorption spectra of the ternary complex formed in the presence of CPC against water with increasing mercury concentrations at 3 different mercury levels. The mercury complex of TAC at pH 9.5 is insoluble or slightly soluble in water but easily dissolved in the presence of CPC, indicating that it will kinetically form a highly stable ion-associate complex in the pre-micellar region below its critical micelle concentration (CMC).

Surfactant selection

In order to improve sensitivity the effect of different surfactants on the complex formation reaction was investigated. Triton X-100 and Triton X-114 as nonionic surfactants, SDS as an anionic surfactant, and HDTAB and CPC as cationic surfactants were used. The surfactant concentration was changed within the range of 5-50 mg L^{-1} in a final volume of 10 mL. A concentration giving the maximum absorbance change was chosen as the optimal value. The optimal values were in the pre-micellar region due to the lower values of their CMCs. The best sensitivity with an absorbance change of $\Delta A = 0.169$ was obtained with a concentration of 15 mg L^{-1} in the presence of CPC. Therefore, CPC as a sensitivity enhancement agent was used for further studies. The results are given in Table 1.

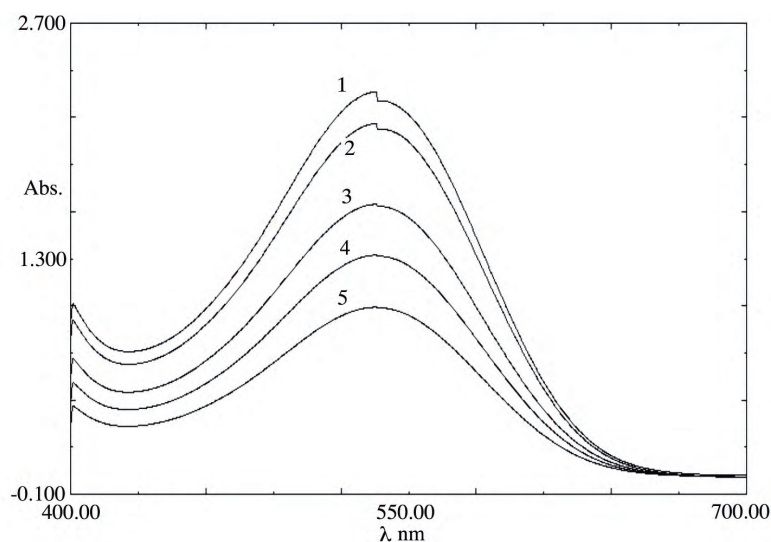


Figure 1. Absorption spectra of TAC with increasing Hg(II) concentrations in linear range in the presence of CPC at pH 9.5 against water under the optimized conditions: 1) 1.0 mL $\text{NH}_3/\text{NH}_4\text{NO}_3$ buffer + TAC; 2) 1.0 mL $\text{NH}_3/\text{NH}_4\text{NO}_3$ buffer + TAC + CPC; 3) 1.0 mL $\text{NH}_3/\text{NH}_4\text{NO}_3$ buffer + TAC + CPC + Hg(II), 2 mg L^{-1} ; 4) 1.0 mL $\text{NH}_3/\text{NH}_4\text{NO}_3$ buffer + TAC + CPC + Hg(II), 4 mg L^{-1} ; 5) 1.0 mL $\text{NH}_3/\text{NH}_4\text{NO}_3$ buffer + TAC + CPC + Hg(II), 6 mg L^{-1} .

Table 1. UV-Vis absorption properties of Hg(II)-TAC complex in different surfactant media under optimized conditions.

Surfactant	Nature of surfactant	Maximum absorption wavelength, λ_{max} (nm)	Wavelength shift, $\Delta\lambda_{\text{max}}$ (nm)	^a CMC (M)	^b Optimal value (M)	Absorbance change, ΔA	Absorbance	Molar absorption coefficient, ϵ_{max} ($\text{L mol}^{-1} \text{ cm}^{-1}$)
TAC	-	430	-	-	-	-	0.073	8.93×10^2
In water	-	530	-	-	-	-	1.237	1.34×10^4
SDS	Anionic	539	9	8.2×10^{-3}	1.04×10^{-4}	0.122	1.359	4.07×10^4
HDTAB	Cationic	541	11	9.2×10^{-4}	5.49×10^{-3}	0.143	1.380	4.35×10^4
CPC	Cationic	548	18	1.24×10^{-3}	4.41×10^{-5}	0.169	1.406	4.69×10^4
Triton X-100	Nonionic	539	9	3.0×10^{-4}	3.87×10^{-5}	0.110	1.347	4.20×10^4
Triton X-114	Nonionic	539	9	2.0×10^{-4}	4.65×10^{-5}	0.127	1.364	4.22×10^4

^aCritical micelle concentration

^bSurfactant concentration giving maximum absorbance change in the range of 5-50 mg L^{-1} in a final volume of 10 mL

Effect of pH

In the presence of CPC, the pH effect on the Hg(II)-TAC system was investigated by using buffer solutions ranging from 7 to 10.5 pH and monitoring the pH values with a pH meter (Figure 2).

The system showed maximum absorbance at pH 9.5. For this purpose, different buffers such as $\text{NaH}_2\text{PO}_4/\text{NaOH}$, $\text{NH}_3/\text{NH}_4\text{NO}_3$, borate, Britton-Robinson (BR) and $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ systems were used. The most suitable buffer was $\text{NH}_3/\text{NH}_4\text{NO}_3$ giving maximum sensitivity. The $\text{NH}_3/\text{NH}_4\text{NO}_3$ buffer solution was thus adopted to keep the pH constant at 9.5. The effect of the buffer volume in the presence of CPC was also studied in the range of 0.2-2.0 mL. It was observed that the absorbance of the ternary complex at 548 nm increased with increasing buffer volumes up to 1.0 mL and then gradually decreased. When the buffer

volume was 1.0 mL, the absorbance change showed a maximum and constant value. A buffer volume of 1.0 mL was thus decided to be suitable for further studies.

Effect of ligand concentration

While all other variables were held constant in the presence of CPC, the effect of TAC concentration in the range of 5-75 mg L⁻¹ was examined (Figure 3) and a maximum and constant absorbance at 50 mg L⁻¹ was obtained. In the range of 5-50 mg L⁻¹, absorbance increased with increasing ligand concentrations, reached a saturation limit at higher concentrations, and then became stable. For subsequent applications a ligand concentration of 50 mg L⁻¹ was considered to be the optimum concentration.

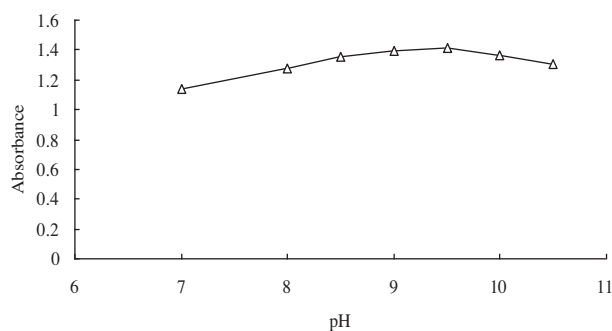


Figure 2. The effect of pH on absorbance of Hg(II)-TAC complex in the presence of CPC at 548 nm. Conditions: 10 mg L⁻¹ Hg(II), 50 mg L⁻¹ TAC and 15 mg L⁻¹ CPC in a final volume of 10 mL.

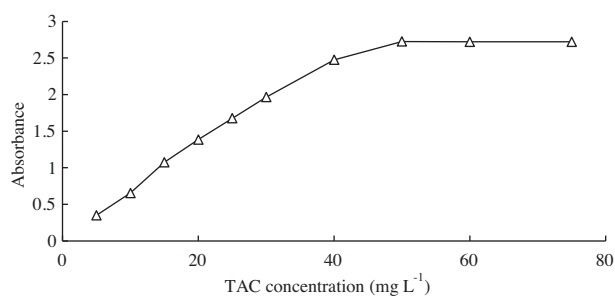


Figure 3. The effect of ligand concentration on absorbance of Hg(II)-TAC complex in the presence of CPC at 548 nm. Conditions: 10 mg L⁻¹ Hg(II) and 15 mg L⁻¹ CPC at pH 9.5 in a final volume of 10 mL.

Effect of CPC concentration

While all other variables were held constant in the determination of Hg(II), the effect of CPC concentration in the range of 2.5-25 mg L⁻¹ was examined (Figure 4), and a maximum absorbance at 15 mg L⁻¹ was obtained. At higher concentrations the absorbance gradually decreased. Therefore, a surfactant concentration of 15 mg L⁻¹ was chosen as the optimal value for further studies.

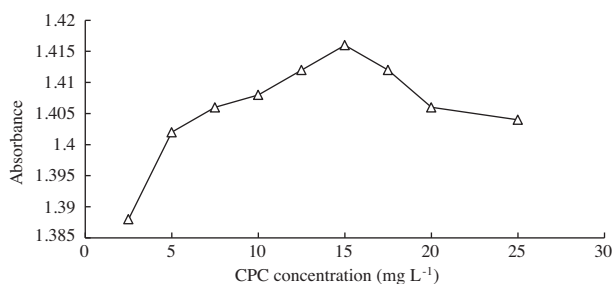


Figure 4. The effect of CPC concentration on absorbance of Hg(II)-TAC complex at 548 nm. Conditions: 10 mg L⁻¹ Hg(II) and 50 mg L⁻¹ TAC at pH 9.5 in a final volume of 10 mL.

Effect of ionic strength

Under optimized conditions the effect of ionic strength on complex formation was investigated in both aqueous and aqueous surfactant solutions. While all other variables were kept constant, standard NaNO₃ solutions ranging from 0.005 to 0.15 M were added to the reaction media, and absorbance measurements were taken against water at 530 and 548 nm, respectively. After the addition of 0.05 M NaNO₃ it was observed that a decrease in absorbance occurred in both media; however the decrease in absorbance without surfactant was sharper and increased more with the slope. This trend is a result of the surfactant's high resistance against the salt effect in terms of selectivity and the stability of the complex formed in surfactant medium is kinetically higher than that of complexes formed in aqueous medium.

Effect of temperature and time

In both aqueous surfactant and aqueous media the effect of the reaction temperature on the formation of the complex was examined in the range of 20-45 °C under optimal conditions. While all other variables were held constant, the temperature was gradually increased and absorbance measurements were taken against water. At temperatures above 35 °C it was observed that the decline in the absorbance of the solution without surfactant was higher and sharper. This can be explained by the fact that the stability constant of the ternary metal complex formed in surfactant media is larger than that of the binary metal complex formed in aqueous media as a measure of the stability of the metal complexes.

The effect of time on complex formation reaction was investigated in the range of 10-60 min under optimum conditions. A time interval of 5-10 min for each method was chosen as the appropriate time interval for the completion of complex formation. However, after a reaction time of 30 min, it was observed that absorbance decreased with a sharp slope in aqueous media. This may be because the binary Hg(II)-TAC complex with anionic character, which is formed in aqueous media, is degraded with time. It can also be explained by the fact that complex formation equilibrium proceeds in a backwards direction to give free Hg(II) ions with a decrease in absorbance especially at 530 nm.

Determination of composition of binary and ternary Hg(II)-TAC complex by Job's method

For the binary Hg(II)-TAC complex in the absence of CPC, the molar concentration ratio of Hg(II) to TAC was evaluated at isomolar concentrations using Job's method. The maximum absorbance was produced at a molar ratio of 1:2. In order to determine the composition of the ternary complex the mole fraction of the Hg(II)-TAC complex and CPC prepared in isomolar concentrations in a final volume of 10 mL was changed within the range of 0.1-1.0 and the obtained absorbance results were graphed. The maximum absorbance was produced at a molar ratio of 1:2:2. As a result, it was decided that the ternary complex had a molar ratio of 1:2:2 based on the formation of an ion-pair complex in aqueous surfactant media.

Complex formation constant and possible reaction mechanisms

For 4 different Hg(II) concentrations in the presence of a 10-fold excess of ligand the absorbance measurements were taken against water in aqueous and aqueous surfactant media at 530 and 548 nm, respectively. Based on dynamic equilibrium calculations in the range of the Lambert-Beer law, the complex formation constants were determined as $(2.8 \pm 0.4) \times 10^7$ and $(9.7 \pm 1.3) \times 10^7$ in aqueous and aqueous surfactant media at 530 and 548 nm, respectively. Whether or not the complex formation reactions spontaneously proceeded in aqueous and aqueous surfactant media was thermodynamically investigated by calculating the ΔG° , ΔH° and ΔS° values, on the condition that the following equations be considered with increases of 5 °C in the range of 20-40 °C.

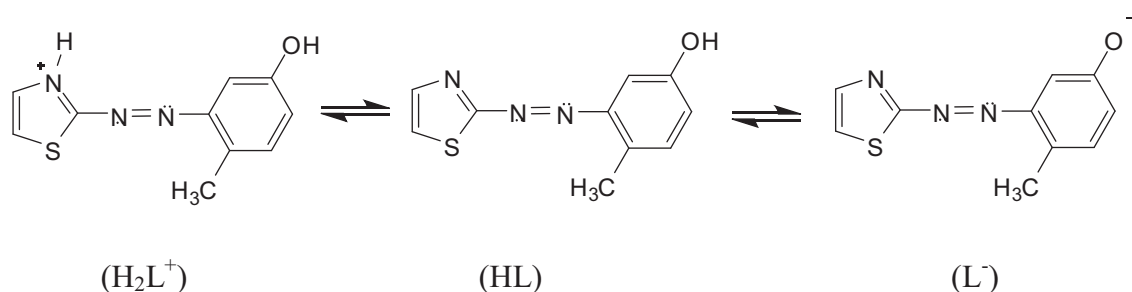
$$\Delta G^\circ = -RT \ln K_f \quad (1)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (2)$$

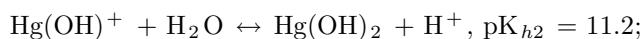
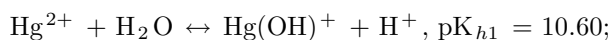
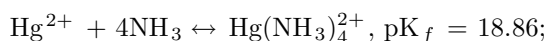
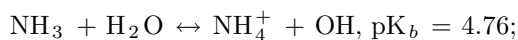
$$-RT \ln K_f = \Delta H^\circ - T\Delta S^\circ \quad (3)$$

$$\log K_f = -\frac{\Delta H^\circ}{2.303RT} + \frac{\Delta S^\circ}{2.303R} \quad (4)$$

With calculations based on the slope and intercept of the regression equations obtained from $\log K_f - 1/T$ curves with correlation coefficients of -0.9619 and -0.9585 , thermodynamic parameters ΔH° , ΔS° and ΔG° were $0.86 \text{ cal mol}^{-1}$, $33.63 \text{ cal mol}^{-1} \text{ K}^{-1}$ and $-10.90 \text{ kcal mol}^{-1}$ in aqueous surfactant solution, respectively and $1.62 \text{ cal mol}^{-1}$, $28.56 \text{ cal mol}^{-1} \text{ K}^{-1}$ and $-10.10 \text{ kcal mol}^{-1}$ in aqueous solution, respectively. In light of these data, due to a lower Gibbs free enthalpy, the complex formation reaction in the presence of CPC occurred spontaneously and more rapidly than in aqueous media. The pH-dependent ionization balances of TAC with acidity constants of $\text{pK}_{a1} = 0.5$ and $\text{pK}_{a2} = 8.0$ are shown below.



In $\text{NH}_3/\text{NH}_4\text{NO}_3$ buffer medium with pH 9.5, the possible acid-base, complexation, and hydrolysis equilibria are as follows:



where K_f is the result of the sum of the first 2 reactions. pK_f is equivalent to both $\log \beta_2$ and $\log K_{h1} K_{h2}$. If the pH is lower than 8.0, the mercury ions are in the forms of Hg^{2+} and $\text{Hg}(\text{OH})^+$, while in the case of $\text{pH} > 8.0$ the

mercury ions are in form of $\text{Hg}(\text{OH})_2$. If the pH is higher than 8.0, the ligand is in the anionic form of L. Because it is a soft Lewis acid, according to Pearson's classification soft-soft and hard-hard $\text{Hg}(\text{II})$ ions prefer to bond via hetero S-atoms or the soft alignment of the ligand.⁴⁴ Additionally, $\text{Hg}(\text{II})$ ions have the tendency to form more stable bonds by means of the $d^{10}\pi$ -interaction of its d^{10} -orbitals and π -orbitals of sulfur in backbonding. Due to configuration with d^{10} , the $\text{Hg}(\text{II})$ -TAC complex should be available in tetrahedral geometry. In all of these results, it is possible that $\text{Hg}(\text{II})$ ions form 1:2 anionic complexes with tetrahedral geometry with TAC at pH 9.5. This anionic tetrahedral complex with the cationic surfactant, CPC as an auxiliary ligand gives a more stable ternary complex in a ratio of 1:2:2 based on ion-paired complex formation with a hydrophobic character. As a result, it is possible that the $\text{Hg}(\text{II})$ ions are in the form of $\text{Hg}(\text{OH})_2\text{L}_2(\text{CPC})_2$ in the aqueous surfactant solution at 548 nm while they are in the form of $\text{Hg}(\text{OH})_2\text{L}_2^{2-}$ in the aqueous solution at 530 nm.

Calibration graph, detection limit and reproducibility

A series of standard solutions of $\text{Hg}(\text{II})$ (at least 12 samples covering the whole range of concentrations) were analyzed under optimal conditions to test the linearity of the calibration graph. The calibration graph was linear over the range of 0.029 mg L^{-1} with a correlation coefficient of 0.9998 at 548 nm while it was linear over the range 0.112 mg L^{-1} with a correlation coefficient of 0.9920 at 530 nm. The regression equations obtained in the presence and absence of CPC were as follows:

$$\text{Abs} = 0.016[\text{Hg}(\text{II}), \text{mg L}^{-1}] + 1.267 \quad (n = 12, r^2 = 0.9983 \text{ at } 548 \text{ nm});$$

$$\text{Abs} = 0.006[\text{Hg}(\text{II}), \text{mg L}^{-1}] + 1.186 \quad (n = 12, r^2 = 0.9920 \text{ at } 530 \text{ nm})$$

The limit of detection and limit of quantification of the method at 548 nm were 6 and $19 \mu\text{g L}^{-1}$, respectively, calculated by dividing 3.3 SD and 10 SD by the slope of the calibration curve, or 3.3 SD m^{-1} and 10 SD m^{-1} where SD is the standard deviation of 12 replicate measurements of 0.02 mg L^{-1} $\text{Hg}(\text{II})$ and m is the slope. A statistical study performed on 2 series of 5 samples containing 3 and 5 mg L^{-1} $\text{Hg}(\text{II})$ at 548 nm yielded relative errors (REs) and relative standard deviations (RSDs) of 2.2%-5.8% and 11.0%-5.1%, respectively while a statistical study performed on 2 series of 5 samples containing 4 and 6 mg L^{-1} of $\text{Hg}(\text{II})$ at 530 nm yielded REs and RSDs of 1.7%-2.0% and 3.1%-5.1%, respectively. The reproducibility of the method at 548 nm in terms of complex stability was studied by analyzing, within a 1-h time period in 1 day, 10 identical solutions of $\text{Hg}(\text{II})$ (10 mg L^{-1}). The 3 replicate measurements of each solution were taken; the intraday precision as RSD% was in the range of 2.3% to 3.7%. The figures of merit of the method for determination of mercury ions at trace levels are presented in Table 2a in detail.

The method's robustness was tested by making small incremental changes in TAC and CPC concentrations in a final volume of 10 mL, respectively, and equilibrium temperatures were also altered as a measure of the kinetic stability of the complex and selectivity under dynamic equilibrium conditions in an aqueous surfactant medium. To check the ruggedness, analysis was performed by 2 different analysts and on 2 different spectrophotometers by the same analyst. The robustness and the ruggedness were evaluated at 3 different mercury levels 1.0, 3.0 and 5.0 mg L^{-1} . The intermediate precision, expressed as RSD%, a measure of robustness and ruggedness was within the acceptable limits as shown in Table 2b.

Table 2a. Figures of merit of the method in the presence and absence of CPC.

	548 nm	530 nm
Calibration equation	$y = 0.016x + 1.267$	$y = 0.006x + 1.186$
Regression coefficient, r^2	0.9998	0.9920
Precision, SD* (0.02 and 0.07 mg L ⁻¹ , n = 12)	0.03 $\mu\text{g L}^{-1}$	0.04 $\mu\text{g L}^{-1}$
Detection limit, 3.3 SD m ⁻¹	6 $\mu\text{g L}^{-1}$	22 $\mu\text{g L}^{-1}$
Accuracy	2%	11%
Analytical sensitivity SD m ⁻¹	2 $\mu\text{g L}^{-1}$	7 $\mu\text{g L}^{-1}$
Quantification limit, 10 SD m ⁻¹	19 $\mu\text{g L}^{-1}$	67 $\mu\text{g L}^{-1}$
Sandell's sensitivity	0.067 $\mu\text{g cm}^{-2}$	0.234 $\mu\text{g cm}^{-2}$
ϵ_{max} , L mol ⁻¹ cm ⁻¹	4.7×10^4	1.3×10^4
Linear range	0.02-9 mg L ⁻¹	0.1-12 mg L ⁻¹

*Standard deviations (SDs) of 12 replicate measurements of Hg(II) as a measure of precision at levels of 0.02 and 0.07 mg L⁻¹ near the quantification limit at 548 and 530 nm, respectively

Table 2b. Robustness and ruggedness expressed as intermediate precision (RSD%).

Proposed surfactant-sensitized spectrophotometric method at 548 nm	Hg(II) taken, mg L ⁻¹	Method robustness			Method ruggedness	
		Parameter altered				
		TAC (250 mg L ⁻¹) mL ^a RSD% (n = 3)	CPC (150 mg L ⁻¹) mL ^b RSD% (n = 3)	Equilibrium temperature ^c RSD% (n = 3)	Interanalyst RSD% (n = 5)	Interinstrument RSD% (n = 5)
	1.0	3.5	3.6	4.4	3.8	3.5
	3.0	2.8	2.9	3.7	2.7	2.8
	5.0	2.2	2.2	2.8	2.1	2.1

^aTAC volumes used were 1.8, 2.0 and 2.2 mL.

^bCPC volumes used were 0.8, 1.0 and 1.2 mL.

^cEquilibrium temperatures of 20, 30 and 40 °C were employed in the developed surfactantsensitized method.

Interfering studies

In order to investigate the method's selectivity in the determination of mercury in the presence of CPC, model solutions containing both interfering ions at different and increasing concentration ratios and mercury ions at 0.5 mg L⁻¹ were prepared and analyzed by means of the present method under optimal conditions. The effect of each interfering species on the absorbance of the complex was separately investigated in the presence of CPC at 548 nm. The tolerance ratio was considered as the amount of interfering species causing a change of $\pm 5.0\%$ on the absorbance of the ternary complex at 548 nm. The tolerance limits of interfering species are given in Table 3a. Cu(II) and Bi(III) were found to interfere at concentrations higher than 2.5 mg L⁻¹. Their tolerance limits were increased by from 25-fold to 50-fold by using 0.1 and 0.2 mL of thiourea and Na₄P₂O₇ at equal-molar concentrations, respectively. Since the ions that are commonly present in water samples did not

significantly affect the recovery of mercury, the method was applied to study the recovery of mercury in tap water, drinking water, dental wastewater, and model saline water samples. The method had good selectivity even in the presence of bismuth and copper ions. This unique selectivity may be due to a high pH and the form of the stable complex of Hg(II) ions with TAC in the presence of CPC.

Table 3a. Tolerance limit of interfering ions in determination of 0.50 mg L⁻¹ Hg(II) ions using the method under optimized conditions.

Ions	Tolerance ratio, [interfering species]/[Hg(II)]
NH ₄ ⁺ , Na ⁺ and K ⁺	1500-2500
Mg ²⁺ , Ca ²⁺ , Sr ²⁺ and Al ³⁺	750-1250
Thiosulfate, thiourea, acetate, citrate and tartrate	350-650
H ₃ BO ₃ , H ₂ PO ₄ ⁻ , HCO ₃ ⁻ , CO ₃ ²⁻ , F ⁻ , Cl ⁻ , Br ⁻ , I ⁻ , and SO ₄ ²⁻	80-250
Borate and SCN	75-100
CN, C ₂ O ₄ ²⁻ , Co ²⁺ and Zn ²⁺	40-65
Mn ²⁺ , Ni ²⁺ , Hg ₂ ²⁺ and Fe ²⁺	25-50
Cd ²⁺ , Co ²⁺ , Fe ³⁺ , Pb ²⁺ and Cr ³⁺	10-30 (35-100)**
Cu ²⁺ and Bi ³⁺	5 (25-50)*

*Tolerance limits in the presence of 0.1 mL of 0.05 M thiourea and 0.2 mL of 0.05 M Na₄P₂O₇ as masking agents.

**Tolerance limits in the presence of 1.0 mL of 0.1 M sodium thiosulfate and 0.25 mL of 0.1 M citric acid.

Additionally, the spectral properties (absorption maxima and wavelengths) of metal ions such as Cd(II), Cu(II), Zn(II), Co(II), Ni(II), Fe(III), Fe(II), Cr(III) and Mn(II), which are commonly present in natural waters and form stable complexes with TAC at pH 8.5 including Hg(II) at isomolar concentrations were studied at fixed reagent concentrations as seen in Table 3b. Hg(II) ions had better absorbance than other metal ions with a NH₃/NH₄NO₃ buffer compared to borate, phosphate, carbonate and BR buffers in terms of sensitivity and selectivity in the presence of CPC. In the presence of the NH₃/NH₄NO₃ buffer the effect of the mentioned metal ions on the determination of mercury at 0.50 mg L⁻¹ and at different analyte-interfering ratios ranging from 1:1 to 1:100 at pH 8.5 was studied using the existing method. The results were represented as percentage changes causing a RE of ±5% in a net absorbance of 0.034 (corresponding to 0.5 mg L⁻¹) corrected against the reagent blank. Serious interference at ratios ranging from 1:5 to 1:80 was observed in the order of Cu(II) > Cd(II) > Zn(II), Cr(III) > Co(II), Mn(II) > Fe(III) > Fe(II), Ni(II). However, the selectivity was largely improved when a mixture of 1.0 mL of 0.1 M sodium thiosulfate and 0.25 mL of 0.1 M citric acid was used to suppress the matrix effect.

Applicability of the method to real samples

In order to test the analytical performance of the method, it was applied to measure the concentration of the ions in tap water, drinking water and artificially prepared model saline water samples. Because the Hg(II) contents of the samples was below the detection limit of the method except in dental wastewater, the reliability was checked by spiking experiments and independent analysis. To ensure that the method was valid and had

Table 3b. The spectral properties of TAC complexes of Hg(II) and other metal ions in the presence of different buffer systems at pH 8.5 and the percentage changes observed in the net absorbance difference of 0.034 corresponding to a mercury concentration of 0.50 mg L⁻¹ at different analyteinterfering ratios.

Buffer, pH 8.5	^a Absorbances at maximum absorption wavelengths, λ_{\max} (nm)										
	TAC	Hg(II)	Cd(II)	Cu(II)	Zn(II)	Co(II)	Ni(II)	Fe(III)	Fe(II)	Cr(III)	Mn(II)
NH ₃ /NH ₄ NO ₃	1.214, 530	1.248, 548	1.238, 543	1.242, 560	1.228, 598	1.216, 586	1.214, 605	1.212, 592	1.212, 580	1.221, 594	1.225, 570
NaH ₂ PO ₄ /NaOH	1.215, 532	1.228, 538	1.235, 543	1.238, 554	1.233, 590	1.221, 580	1.224, 594	1.224, 588	1.224, 574	1.232, 588	1.235, 563
NaHCO ₃ /Na ₂ CO ₃	1.184, 543	1.214, 560	1.228, 543	1.232, 570	1.242, 605	1.226, 592	1.236, 612	1.234, 602	1.235, 592	1.238, 603	1.230, 586
Borate	1.205, 525	1.232, 540	1.223, 543	1.225, 556	1.235, 592	1.235, 580	1.248, 595	1.243, 585	1.240, 572	1.230, 595	1.2224, 562
BR	1.208, 528	1.238, 543	1.216, 543	1.217, 558	1.227, 594	1.204, 582	1.254, 598	1.252, 588	1.232, 574	1.224, 597	1.214, 560
^b Percentage changes observed in net absorbance difference of 0.034 at different analyteinterfering ratios											
1:1	99.6	98.7	99.4	99.7	99.8	99.7	99.8	99.7	99.8	99.4	99.9
1:5	98.2	95.3 ^c	98.4	98.6	99.3	98.6	99.3	99.6	99.6	98.4	99.5
1:10	95.4 ^c	90.7	97.7	97.7	97.7	97.7	98.6	99.4	99.4	97.7	98.6
1:20	88.5	85.6	95.1 ^c	85.6	95.1 ^c	96.5	97.8	98.6	98.6	95.1 ^c	97.1
1:40	85.6	81.7	91.7	81.7	91.7	94.8 ^c	96.7	97.8	97.5	91.7	94.4 ^c
1:60	75.4	77.6	87.6	77.6	87.6	90.5	95.8	95.1 ^c	96.8	87.6	90.5
1:80	70.3	70.6	70.6	70.6	70.6	82.5	92.4 ^c	90.1	94.2 ^c	70.6	81.5
1:100	65.5	65.4	65.4	65.4	65.4	65.2	80.3	85.4	87.3	65.4	63.3
^d With a mixture of Na ₂ S ₂ O ₃ and citric acid	100.7	99.7	101.2	99.7	99.8	99.8	99.6	100.1	100.3	102.1	102.3

^a Absorbance values and characteristic wavelengths of the ligand and its metal complexes in the presence of CPC at pH 8.5.

^b Percentage changes observed in absorbance of Hg(II)-TAC complex for determination of 0.5 mg L⁻¹ Hg(II) in the presence of different metal ions at pH 8.5.

^c Tolerance limits of some metal ions interfering in determination of 0.5 mg L⁻¹ Hg(II) at NH₃/NH₄NO₃ buffer with pH 8.5.

^d Quantitative removal of interfering metal ions by using a mixture of Na₂S₂O₃-citric acid.

reasonable accuracy and precision, recoveries of the Hg(II) ions in the tap water, drinking water, artificially prepared model water, and dental wastewater samples were determined by both the proposed method and a comparative method, which was selected as a reference, and the results are shown in Table 4. It was found that the proposed method did not have significant difference compared to the modified dithizone method,⁴⁴ based on Student's t-test. The low RSDs represent the high reproducibility of these measurements. Therefore, the method could be applied to the determination of mg L^{-1} and even $\mu\text{g L}^{-1}$ levels of Hg(II) ions in real samples.

Table 4. The analysis results of natural water and wastewater samples under optimized conditions.

Samples	Added, mg L^{-1}	*Found by the proposed method, mg L^{-1}	Found by the modified dithizone method, mg L^{-1}	RE%	RSD%	Recovery%
Tap water	-	<LD**	-	-	-	-
	3	3.08	3.02	2.7	2.0	102.7
	5	5.10	4.95	2.0	2.2	102.0
Natural drinking water 1	-	<LD	-	-	-	-
	3	2.89	2.85	3.7	2.5	96.3
	5	5.14	5.09	2.8	2.2	102.8
Natural drinking water 2	-	<LD	-	-	-	-
	3	3.09	3.05	3.0	2.7	103.0
	5	4.92	4.88	1.6	3.1	98.4
Artificially prepared model saline water	-	<LD	-	-	-	-
	1	1.02	1.05	2.0	2.5	102.0
	3	3.09	3.04	3.0	2.7	103.0
***Dental wastewater	-	3.85	3.78	-	2.5 (2.4)	-
	1	4.87	4.81	2.0 (3.0)	2.4 (2.4)	102.0 (103.0)
	3	6.93	6.88	2.7 (3.3)	2.5 (2.5)	103.0 (103.3)

*Average value for 5 replicate measurements at 95% confidence level

**LD: Limit of detection.

***Results in parentheses indicate the total mercury values and their statistical parameters found by means of the modified dithizone method after oxidation with KMnO_4 in acidic medium

Speciation analysis in synthetically prepared binary mixtures

Suitable aliquots (1-2 mL) of Hg(I) and Hg(II) mixtures (preferably 1:1, 1:5, 1:10 and 1:15) were taken in a 25mL conical flask. Analysis of the mixtures was done according to the procedure described above in "Speciation analysis of Hg(I) and Hg(II) in mixtures" The total mercury content was calculated with the help of a calibration graph. An equal aliquot of the above Hg(I) and Hg(II) mixture was taken in a 10-mL volumetric flask; 5 mL of 0.6 M SDS was then added, followed by the addition of 1 mL of 1 M H_2SO_4 and 1 mL of 1.95×10^{-4} M reagent, and the volume was completed with water. The absorbance was measured against a reagent blank, as before. The mercury concentration was calculated in mg L^{-1} or $\mu\text{g L}^{-1}$ with the aid of a calibration graph. This gave a measurement of the Hg(II) originally present in the mixture. The value was subtracted from that of the total mercury to determine the Hg(I) present in the mixture.^{45,46} The results obtained compared favorably

with those obtained by the modified dithizone method. Extensive speciation results are given in Table 5.

Table 5. Speciation results in binary mixtures containing Hg(I) and Hg(II) at known concentration ratios by the proposed method and the modified dithizone method after preoxidation under optimized conditions.

Mixture 1	With the proposed method						
	Ratio	Added Hg(II), mg L ⁻¹	Total Hg(I) plus Hg(II), mg L ⁻¹	*Found Hg(II), mg L ⁻¹	RE%	RSD%	Recovery%
**Hg(II)- to-Hg(I) ratio	1:1	0.5	1.02	0.52 ± 0.04	4.0	7.1	104.0
	1:5	2.50	3.08	2.58 ± 0.04	3.2	1.4	103.2
	1:10	5.00	5.63	5.13 ± 0.03	2.6	0.6	102.7
	1:15	7.50	8.12	7.60 ± 0.03	1.6	0.3	101.7
Mixture 2	With the modified dithizone method						
	Ratio	Added Hg(II), mg L ⁻¹	Total Hg(I) plus Hg(II), mg L ⁻¹	*Found Hg(II), mg L ⁻¹	RE%	RSD%	Recovery%
**Hg(II)- to-Hg(I) ratio	1:1	0.5	0.98	0.48 ± 0.04	4.0	7.3	96.0
	1:5	2.50	2.97	2.47 ± 0.04	1.2	1.4	98.8
	1:10	5.00	5.53	5.05 ± 0.04	0.6	0.5	100.7
	1:15	7.50	7.98	7.58 ± 0.02	0.3	0.3	99.7

*Average value and standard deviation of 3 replicate measurements at 95% confidence level

**Indicates increasing Hg(I) concentrations at a fixed Hg(II) concentration of 0.5 mg L⁻¹

The accuracy was verified by Student's-test with a value (1.59) less than the theoretical value (2.45, n = 8) at a confidence level of 95% for 1:1, 1:5, 1:10 and 1:15 Hg(II)-to-Hg(I) or Hg(I)-to-Hg(II) ratios in a linear range. The statistical F-test was also used to compare the precision of the method with that of the modified dithizone method. The F_{4,4}-test value at a 95% confidence level did not exceed the theoretical value (4.28, n = 8) with a value of 1.92 for the F-test indicating no significant difference between the performance of the proposed method and the reference method. Comparison of the proposed method and the modified dithizone method showed reasonable agreement.

A comparison of the proposed method with the existing methods in the literature is presented in Table 6. The surfactantsensitized procedure showed simplicity, adequate sensitivity, repeatability, reproducibility, a wide working range of 450fold a low limit of detection (up to 6 µg L⁻¹ in the linear range of 0.02-9 µg mL⁻¹) with comparatively little interference, and more sensitivity and accuracy than the other methods reported earlier.^{46,49,51,54,56} The proposed method can thus be successfully applied to the monitoring of trace amounts of total and inorganic mercury in different water samples such as tap water, lake water, river water, dental wastewater, and even sea water with a mixture of thiosulfate and citric acid in order to suppress the matrix effect.

Table 6. Comparison of some chelating agents for the spectrophotometric determination of mercury with and without surfactant.

Chelating agents	λ_{\max} (nm)	ϵ (10^4)	Linear calibration range (mg L ⁻¹)	Detection limit ($\mu\text{g L}^{-1}$)	Optimal conditions	Interference ions	References
H ₂ Dz	490	5.02	0.05-10	1	0.8-1.2 pH range, SDS micellar media		44
H ₂ Dz	485	7.1	0.1~2	1	pH 2.0~ 5.0, extraction CHCl ₃	Cu, Zn, Cd, Pb	45
CPDAAAB	540	22.2	0.08-0.8	20	Alkaline medium, pH 10.0	Co, Zn, Cd, Ni	46
DAA	514	22	0~0.8	2	pH 9.0, Triton X-100	Cd, Ag, Pb, Ni	47
BG	625	59.6	0.004~0.5	-	pH 5.0, flotation of Hg-I-BG with cyclohexane	Ni	48
CMPQ	512	8.0	0.08~2	40	pH 4.0~ 4.8, Triton X-100	Co, Cu, Pb, Zn, Ni	49
TPPS ₄	413	27.6	0~0.6	0.5	pH 8.0, heated in 100 °C water bath for 30 min	Mn, Cu, Ag, Pb, Fe, Co, Ni, Zn, Cd, Mg	50
PAR	500	6.8	0.1~2	10	pH 10.0	Cu, Ni, Co, Fe, Zn, Ag, Cr, V, W, Mo, Mn	51
NBS	430	-	1-10	0.2	Nitric acid medium	Cu, Zn, Cu	52
ABTR	545	12.1	0.01~3	0.02	pH 3.5, emulsifier-OP	CN ⁻ , SCN ⁻	53
2-MBT	Near 340	-	1.0×10^{-7} - 1.0×10^{-5} M	6.2	pH 10.0 borax buffer, CTAB, extraction with CHCl ₃ after 30 min	Cu, Bi	54
6-MP	315	26	2-4.8 $\mu\text{g L}^{-1}$	1	Detection after SPE with C18 disks, pH range of 5.0-8.0	Cu, Pb, Cd, Ag	55
8-HQ	395	0.65	0.5-4.0	30.8	pH 9.0, CPC micellar media	Co, Ni, Pb, Cd	56
TAC	548	4.69	0.02-9	6	pH 9.5 NH ₃ /NH ₄ NO ₃ buffer in presence of CPC	Partly Cu, Bi	Present study

Conclusion

The sensitization of TAC took place in the presence of CPC leading to the formation of a ternary complex with a bathochromic shift of 18 nm and increase in absorbance values at the shifted wavelength resulted in the formation of increased sensitivity and absorptivity at pH 9.5. The complex formed from the TAC and Hg(II) ions under study in the presence of CPC in the pre-micellar region is kinetically very stable with a RSD ranging from 2.8% to 4.4% in the range of 20-40 °C; it is more sensitive in the presence than in the absence of surfactant. An improvement of almost 3-fold in sensitivity was observed from the ratio of slopes of calibration curves obtained with and without surfactant. The method developed for the simultaneous determination of total and dissolved inorganic mercury at levels below mg L⁻¹ is inexpensive, involves the use of readily available reagents, allows for rapid determination with low operating costs and can be used with a simple laboratory pH meter and spectrophotometer.

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