

Micelle Mediated Preconcentration of Mercury in pH Controlled Mode for Trace Analysis

Jafari Atrabi, Rasoul; Shokoufi, Nader; Kargosha, Kazem*⁺

Chemistry and Chemical Engineering Research Center of Iran,

P.O. Box 14335-186 Tehran, I.R. IRAN

ABSTRACT: A micelle-mediated phase separation method for preconcentration of ultra-trace quantities of mercury as a prior step to its determination by UV-Vis spectrophotometry has been developed. The method is based on Hg(II)-dithizone complex formation in alkaline aqueous solution, and extraction of this Hg(II)-dithizone secondary complex into the surfactant-rich phase of the non-ionic surfactant octylphenoxypolyethoxyethanol (Triton X-114). This cloud point method of extraction was carried out at 54 °C and the surfactant-rich phase containing analyte was dissolved in 250 μ L of ethanol with pH 8. The obtained solution was introduced into a micro quartz cell and the analyte was determined by UV-Vis spectrophotometry. Complexation and cloud point extraction of the mercury in alkaline solution markedly facilitate the phase-separation process, lower the temperature of the cloud point, enhances the complex to background absorption ratio and eliminates the interference of Cu^{2+} , Al^{3+} and Fe^{3+} . Under the optimal extraction and reaction conditions, detection limits, relative standard deviations and linear calibration graphs were, 0.9 ng/mL, lower than 2% and 3.0–250.0 ng/mL respectively. This detection limit is 15 times lower than one obtained by using the same method but at acidic media. The method was applied to the determination of Mercury in soft water and physiology serum samples.

KEYWORDS: Cloud point extraction; UV-Vis spectrophotometry; Mercury; Triton X-114; Preconcentration.

INTRODUCTION

Although mercury is not an abundant chemical element in nature, it has become widespread as a result of many industrial and agricultural applications [1-3]. Elementary mercury finds extensive use industrially in lamps, batteries, thermometers, and as amalgams, and especially in the electrolytic manufacturing of chlorine and sodium hydroxide. Mercury compounds have been used as catalysts, fungicides, herbicides, disinfectants, pigments and for other purposes. Thus, monitoring

the environment in view of mercury pollution is very important. Generally, the concentration of Hg(II) in the environmental samples is very low unless exposed in some industrial area. The development of analytical methods for the determination of extremely low concentration of Hg(II) is still a challenge. Consequently, considerable effort and progress have been made to develop the techniques in which the determination of Hg(II) in the contaminated samples can be carried out

* To whom correspondence should be addressed.

+ E-mail: k.kargosha@ccerci.ac.ir

1021-9986/16/2/79

9/\$2.90

rapidly without any complicated processing steps [4,5]. Different analytical techniques have been used for mercury determination at low concentration including Cold Vapor Atomic Absorption Spectrometry (CV-AAS) [6-8] Cold Vapor Atomic Fluorescence Spectrometry (CV-AFS) [9], flow Injection-Inductively Coupled Plasma Optical Emission Spectrometry (FI-ICP-OES) [10], Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [11]. Although the use of these analytical instruments allow great enhancement in aspect of analysis, in some cases these do not have enough sensitivity for the determination of ultra trace mercury in environmental samples. In these cases, efficient separation and preconcentration procedures are required prior to determination. Several separation and preconcentration procedures including preconcentration on gold amalgamator [12], liquid-liquid extraction [13], cloud point extraction [14] and solid phase extraction [15] have been reported.

The analytical potential of the cloud-point phenomenon mediated phase separations, Cloud-Point Extraction (CPE), has been demonstrated [16]. CPE is an impressive alternative to conventional solvent extraction because it produces high extraction efficiencies and uses inexpensive, non-toxic reagents. A very interesting feature is that cloud point partition constants of metal chelates depend on the nature of metal ions [17], with consequent potential increase of selectivity. The cloud point methodology has been used for the extraction and preconcentration of metal ions after the formation of complexes [18].

In Cloud-Point Extraction (CPE), separation procedure is based on the peculiar properties of aqueous solution non-ionic surfactant, has been proposed as an alternative to the use of traditional organic solvents. In aqueous solution, and at low concentrations, surfactant molecules are found in monomer form. The concentration above which surfactant molecules are dynamically associated (~ 50–150 of monomer) to form molecular aggregates (micelles) are called Critical Micellar Concentration (CMC). Depending on the nature of surfactant and solvent, the aggregates may form micelles, reverse micelles, micro emulsion, vesicles, monolayers and bilayers [19].

An aqueous solution of non-ionic surfactant changes from single isotropic phase to two isotropic phases when the temperature of the solution exceeds the Cloud Point Temperature (CPT). This change of phase is reversible

and on cooling, again it reverts to a single isotropic phase. Actual mechanism of phase separation above CPT is not known. But, several authors proposed some mechanism using the phase separation phenomenon [20]. Nilsson *et al.* suggested that the dielectric constant of water decreases with increase in temperature, which reduces the interaction between the hydrophilic portion of surfactant and water [21]. Thus above the CPT, dehydration process occurs in the external layer of micelles of non-ionic surfactant. Also it has been proposed that the phase separation could be due to the increase in micellar size (increasing aggregation number) with temperature.

Organic micellar media are very useful in analytical applications, including the improved analyte sensitivity in UV-Vis spectrophotometric methods [22-25]. Especially, the surfactants have been used to improve UV-Visible spectrophotometric determination of trace metal ions with complexing agents. Generally, the metal-chelate complexes formed in the surfactant media are more stable than those formed in the absence of surfactant [26]. The combination of CPE with spectrophotometric detection of metals, was first reported by *Watanabe* and co-workers, who studied the extraction of Ni with 1-(2-thiazolylazo)-2-naphthol in Triton X-100 micellar solution [27]. However, Cloud Point Extraction and Pre-concentration (CPE/P) procedure was then applied for determination of several metals using spectrophotometric detection [27-30].

Dithizone (diphenylthiocarbazone) has been used as complexing agent in cloud point extracting and preconcentration of trace amounts of mercury. This mercury complex has been formed in acidic aqueous solutions of non-ionic surfactant. After phase separation based on CPE, the mercury in the surfactant rich phase has been determined using spectrophotometric detection [14]. The main difficulty with the use of dithizone in CPE at neutral or acidic pH is low complex to background absorption ratio, which is mainly due to the presence of uncomplexed dithizone and formation of Hg(II)-dithizone primary complex (ML).

In the present work, cloud point extraction and preconcentration of Hg(II)-dithizone complex are carried out in alkaline solution. Under these conditions, Hg(II)-dithizone secondary complex (M_2L_2) is formed [31], and the complex to background (blank solution) absorption ratio increased significantly. Consequently detection limit

improved by a factor of more than 15 compare to the reported one [14].

EXPERIMENTAL SECTION

Reagents and chemicals

All chemicals used were of analytical grade reagent. The non-ionic surfactant Triton X-114 was obtained from Acros, USA. The rest of reagents were purchased from Merck, Germany. The stock solution of Mercury at concentration of 1000 $\mu\text{g/mL}$ was prepared from HgCl_2 . Working standard solutions were obtained by appropriate dilution of the stock solution. A solution of 10^{-3} mol/L dithizone was prepared in pure ethanol. The 5% (w/v) NaOH solution was prepared by dissolving appropriate amount of the NaOH in high pure water. The glassware and vessels were kept in 10% nitric acid for at least 24 h and subsequently washed four times with double distilled water prior to use.

Apparatus

A Perkin Elmer (USA) model Lambda 2 spectrophotometer with 1 mL quartz cell (Hellma, Germany) was used for the determination of Hg(II)-dithizone complex at 539 nm. By using height adjustable cell holder, the height of cell exposed to the radiation was adjusted so that we could use a minimum volume as 250 μL of the preconcentrated sample. A centrifuge was used to accelerate the phase separation process (Sigma, Germany). A thermostated bath model RCT-B (IKA, Germany) maintained at the desired temperature was used for the cloud point temperature experiments. All pH controlled made with a digital pH meter model 780 (Metrohm, Switzerland).

Procedure

Aliquots of 10.0 mL of the sample or standard solutions containing the Mercury (3.0-250 ng/mL), Triton X-114 (0.1% (w/v)), dithizone (3×10^{-6} mol/L) and NaOH (0.5% (w/v)), were kept in a thermostated bath at 54 $^{\circ}\text{C}$ for 6 min. Separation of the aqueous and surfactant-rich phases was accomplished by centrifugation for 5 min at 3500 rpm.. The supernatant aqueous phase was then separated completely. To decrease the viscosity of the surfactant rich phase and facilitate sample handling, 250 μL of ethanol with pH 8 was added and resultant solution was introduced into the quartz cell.

The absorbance was measured at the wavelength of maximum absorbance of the complex (539 nm).

RESULTS AND DISCUSSION

Hg(II)-dithizone complexation and extraction

Based on experiments carried out in this lab., it was revealed that there are some difficulties, with the use of dithizone in complexation and CPE of the mercury at neutral or acidic media. These drawbacks are high background absorption, high CPE temperature and unpractical complete separation of the surfactant rich phase from aqueous solution. To overcome these drawbacks, NaOH solution (5% w/v) was added to the sample solutions prior to complexation and CPE and determination of the mercury was carried out at alkaline media. The added NaOH could also act as salting-out agent which decreases the temperature of the cloud point [32,33]. But the main effect was found to be the enhancement of the complex to background absorption ratio (see Figs. 1 and 2).

The absorption of the alkaline blank solution is mainly due to the presence of the uncomplexed dithizone. The enhancement of the absorption ratio is mostly because of the secondary Hg(II)-dithizone (M_2L_2) formation [31]. This enhancement was evaluated by carrying out the complex formation and CPE processes at presence and absence of the NaOH. As we can see in Figs. 1 and 2, the Hg(II)-dithizone complex to background absorption ratio at 539 nm is enhanced by a factor of five times with adding NaOH. The absorption spectra of the complex formation and extraction from the alkaline and neutral solutions are shown in Fig. 3. As also Fig. 3 reveals, the presence of the NaOH causes complex absorption enhancement.

Optimization of the complexation and separation

The CPE can be used for the preconcentration of metal ions after the formation of sparingly water-soluble complexes. The CPE efficiency depends on the hydrophobicity of the ligand and the complex formed the apparent equilibrium constants in the micellar medium, the kinetics of the complex formation, and the transference between the phases. In this work, dithizone was used as the chelating agent. Fig. 4 shows the effect of dithizone concentration on the CPE of Hg (II)-dithizone complex. The concentration of dithizone was tested ranged

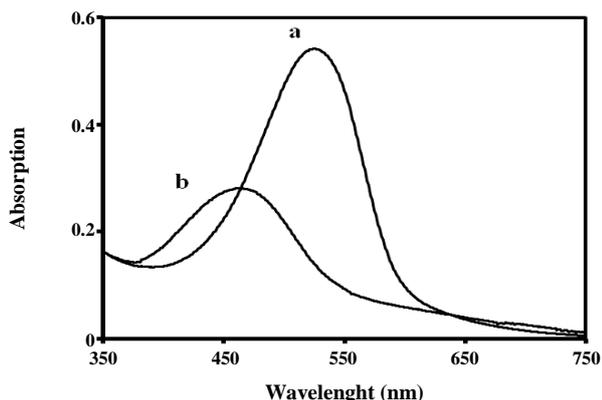


Fig. 1: Absorption spectra of (a) Hg(II)-dithizone complex, (b) blank, in alkaline pH. Conditions: 0.1% (w/v) Triton X-114, 0.5 % (w/v) NaOH, 3×10^{-6} M dithizone, 100 ng mL^{-1} Hg.

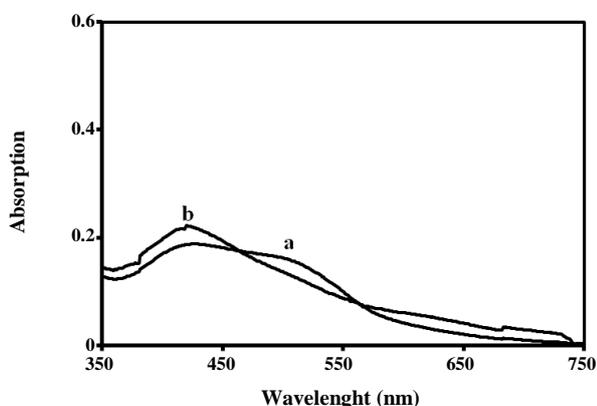


Fig. 2: Absorption spectra of (a) Hg(II)-dithizone complex, (b) blank, in neutral pH. Conditions: 0.1% (w/v) Triton X-114, 3×10^{-6} M dithizone, 100 ng mL^{-1} Hg.

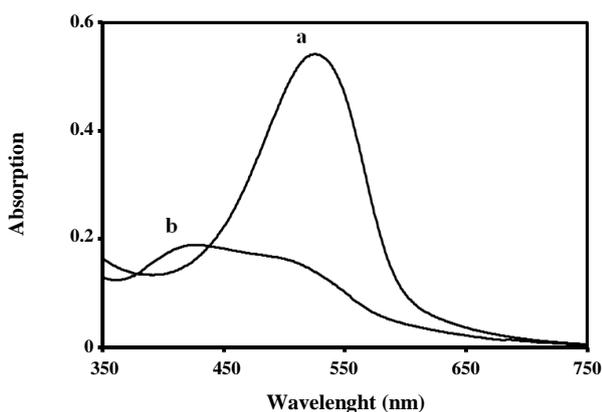


Fig. 3: Absorption spectra of Hg(II)-dithizone complex (a) at presence of 0.5 % (w/v) NaOH and (b) at absence of NaOH. Conditions: 0.1% (w/v) Triton X-114, 3×10^{-6} M dithizone, 100 ng/mL Hg(II).

from 0.49 to $4.95 \mu\text{M}$. As it is seen for Hg (II) complex, the signal increases up to a known concentration of dithizone, reaching a plateau, which is considered as complete extraction. Therefore, a dithizone concentration of 3×10^{-6} M was employed for further experiments.

Using NaOH for formation of alkaline solution result in Hg(II)-dithizone secondary complex that has higher absorption than Hg(II)-dithizone primary complex which forms in neutral solution. This effect was examined with addition of NaOH, ranged of 0.05–1% (w/v). As shown in Fig. 5, the maximum absorbance for Hg (II) was achieved in the 0.5 % (w/v) concentration of NaOH.

In this work, Triton x-114 is chosen as the nonionic surfactant because of its low cloud point temperature and high density, which facilitate phase separation by centrifugation. The variation in extraction recovery of Hg (II)-dithizone complex was evaluated within the concentration range of 0.025–0.5% (w/v) of the Triton x-114 (Fig. 6). The results revealed that a concentration of 0.1% (w/v) can be selected as optimum surfactant concentration.

To achieve easy phase separation and efficient preconcentration, time of the equilibration and CPE temperature are also necessary to be optimized. The effect of the CPE temperature was investigated from 35 to $83 \text{ }^\circ\text{C}$. It was found that the CPE efficiency increased with increase in temperature from 35 to $54 \text{ }^\circ\text{C}$, and reaches the maximum at $54 \text{ }^\circ\text{C}$ (Fig. 7). Over $54 \text{ }^\circ\text{C}$, the CPE efficiency decreased probably due to the stability problems for chelates and chelating agents. So, a CPE temperature of $54 \text{ }^\circ\text{C}$ was used.

Studies on the effect of the equilibration time from 3 to 15 min showed that the maximum extraction efficiency could be obtained in 6 min (Fig. 8). Further increase in the time resulted in a decrease of the efficiency probably due to the thermal instability of the formed complexes. For the rest experiments, an equilibration time of 6 min was used.

The surfactant-rich phase containing the mercury complex was separated from the aqueous solution by centrifugation. Handling and quantitative transferring of this surfactant-rich phase is unpractical due to the high viscosity of this phase. Ethanol was used as diluting agent. The pH of this diluting agent was found to affect the absorption signal. Ethanol solutions in pH range of 4 to 12 were tested (Fig. 9). The best results were obtained when Ethanol with pH of 8 was used.

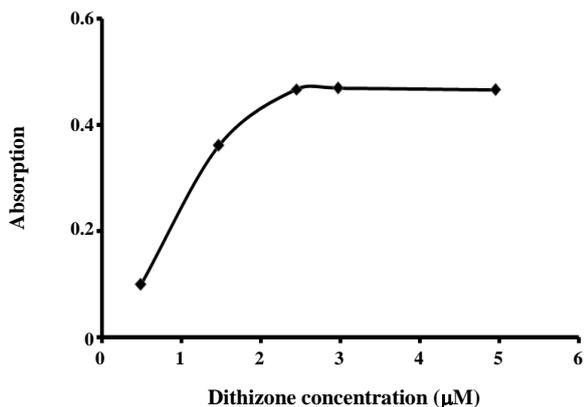


Fig. 4: Effect of the concentration of dithizone on the cloud point extraction of the Hg(II)-dithizone complex. Conditions: 0.1% (w/v) Triton X-114, 0.5 % (w/v) NaOH, CPE temperature 54 °C and 100 ng/mL Hg(II).

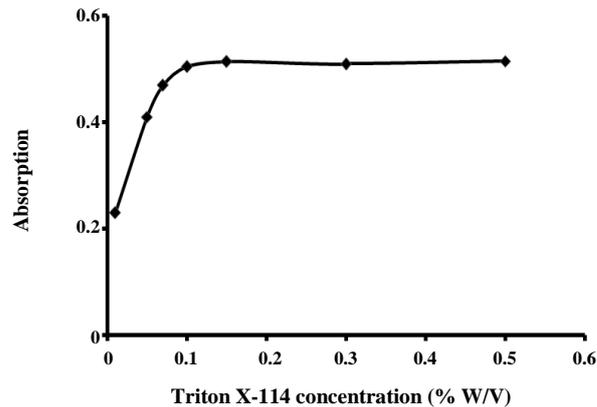


Fig. 6: Effect of the Triton X-114 concentration on the cloud point extraction of 100 ng mL⁻¹ Hg (II). Other conditions: 0.5 % (w/v) NaOH, 3×10⁻⁶ M dithizone, equilibration temperature 54.

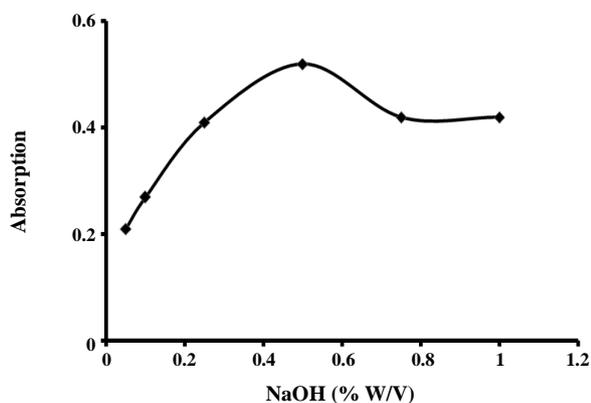


Fig. 5: Effect of the concentration of NaOH on the cloud point extraction of 100 ng mL⁻¹ Hg (II) . Other conditions: 0.1% (w/v) Triton X-114, 3×10⁻⁶ M dithizone, equilibration temperature 54 °C.

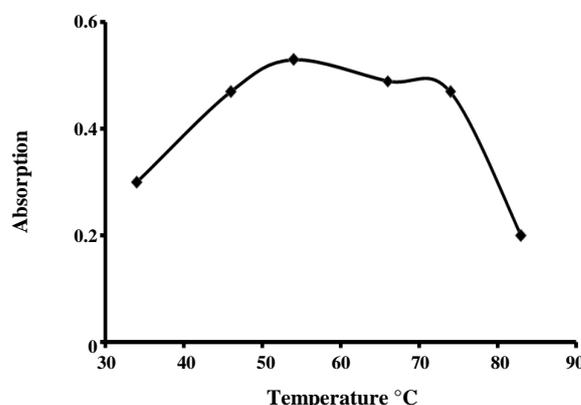


Fig. 7: Effect of the CPE temperature on the cloud point extraction of the Hg(II)-dithizone complex. Conditions: 0.1% (w/v) Triton X-114, 0.5 % (w/v) NaOH, 3×10⁻⁶ M dithizone, 100 ng/mL Hg (II).

Figures of merit

From measurements made under the optimum conditions described above, the calibration graph was linear in the range 3 to 250 ng/mL with a correlation coefficient of 0.9961. The calibration equation is $A = 4.7 \times 10^{-3}C + 8.7 \times 10^{-3}$, where A is the absorbance for Hg (II)-dithizone complex in the surfactant rich phase at 539 nm and C is the concentration of Hg (II) in the sample solution in ng/mL. The limit of detection, defined as $C_L = 3S_B/m$, was 0.9 ng/mL.

The reproducibility of the method was studied for five replicate determinations of Hg (II) in an aqueous sample

spiked with 100 µg/L of Hg (II). The Relative Standard Deviation (RSD) was lower than 2%. The enhancement factor, as the ratio of the slope of obtained calibration graphs with preconcentration to that without preconcentration, was 34.

Table 1 compares sample volume, solvent volume and enhancement factor of other determination methods of mercury with present method. It shows that in comparison with other more sensitive methods such as Hydride Generation Atomic Absorption Spectrometry (HG-AAS) and Cold Vapor Atomic Absorption Spectrometry (CV-AAS), the present method needs lower volume of sample and solvent.

Table 1: comparison of CPE-UV-Vis and other methods of mercury determination.

Determination technique	Sample volume (mL)	Solvent volume (mL)	EF ^a	Ref
CPE-HG-AAS	100	–	20	34
SPE-CV-AAS	3000	–	150	35
CPE-ICP-OES	10	0.5	18.7	36
CPE-UV-VIS	10	0.25	34	Present method

a) Enhancement factor. b) Linear dynamic range. c) Limit of detection.

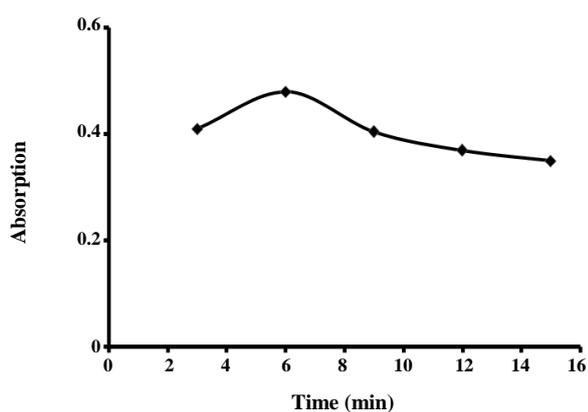


Fig. 8: Effect of equilibration time on the cloud point extraction of 100 ng/mL Hg (II). Other conditions: 0.1% (w/v) Triton X-114, 0.5 % (w/v) NaOH, 3×10^{-6} M dithizone, equilibration temperature 54 °C.

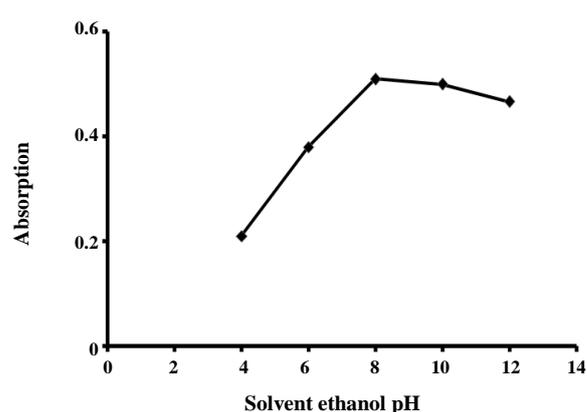


Fig. 9: Effect of the solvent ethanol pH on absorbance of 100 ng/mL Hg (II). Other conditions: 0.1% (w/v) Triton X-114, 0.5 % (w/v) NaOH, 3×10^{-6} M dithizone, equilibration temperature 54 °C.

Interferences

It is reported that Cu^{+2} , Al^{+3} and Fe^{+3} cause interference on the determination of mercury by complexation and CPE of analyte with dithizone at acidic pH [14]. In the present work, the effect of these interferent ions, as well as the common ions at the usual concentration found in natural water samples on the determination of 100 ng/mL by the same complexation and CPE method but at presence of NaOH (alkaline pH) was studied. An ion was considered as interferent, when it caused a variation in the absorbance of the sample greater than 5%. The tolerance limits are shown in Table 2. These results show that neither Cu^{+2} , Al^{+3} and Fe^{+3} nor other common ions found in natural water samples cause severe interference ion determination of mercury by proposed method.

Determination of Mercury in water samples

In order to validate the proposed methodology,

the developed procedure was applied for the determination of Hg in several spiked soft water and physiology serum samples. For this purpose, 10 mL of each of the sample was pre-concentrated and analysed following the proposed procedure. The results is shown in Table 3.

CONCLUSIONS

In the work presented here, an improved complexation and CPE method for separation and preconcentration of mercury in aqueous solutions is reported. Performing the complexation of the mercury with dithizone and CPE of this complex in alkaline media instead of acidic media (commonly used media) represented several advantages such as better limit of detection [14]. No severe interference, better signal to background ratio, lower CPE temperature and complete practical separation of the phases.

This improved method with spectrophotometric detection for mercury determination provides good accuracy,

Table 2: Tolerance limits of interfering ions.

Tested ion	Tolerance limit (mg/L)
Na ⁺	10
Cd ²⁺	3
Pb ²⁺	3
Zn ²⁺	5
Cr ³⁺	5
Ni ²⁺	2
Ca ²⁺	30
Mg ²⁺	10
K ⁺	>39
NH ⁴⁺	10
Cu ²⁺	<1
Fe ³⁺	5
Fe ²⁺	2
Al ³⁺	5
CO ₃ ²⁻	>30
SO ₄ ²⁻	>39.5
Cl ⁻	>53
F ⁻	2

Table 3: Determination of mercury in spiked samples.

Sample	Mercury concentration (ng/mL) ^a		Recovery (%)
	Taken	Found	
Soft water	-	ND ^b	-
	50	51±0.16	102.8
	100	102.4±0.19	102.4
Physiology serum	-	ND	-
	50	47.15±0.17	94.3
	100	93.36±0.18	93.36

a) Mean ± S.D (n = 3). b) ND: Not Detected.

recovery (98.21%) and precision (n=5, RSD=2%) and presents a detection limit of 0.9 ng/mL enhancement factor of 34. The proposed method compares to the reported method (CPE-FIA-LC) of complexation and CPE for mercury [14], is almost free of interferences and provides better detection limit (15 times).

Received : Oct. 8, 2015 ; Accepted : Nov. 23, 2015

REFERENCES

- [1] Seiler H., Sigel A., Sigel H., "Handbook on Metals in Clinical and Analytical Chemistry", Marcel Dekker, New York (1994).

- [2] Kothny E.L., "Trace Elements in the Environmental", American Chemical Society, Washington DC (1973).
- [3] Harrington C.F., The Speciation of Mercury and Organomercury Compounds by Using High Performance Liquid Chromatography, *Trends Anal. Chem.*, **19**: 167-179 (2000).
- [4] Liu Q., Direct Determination of Mercury in White Vinegar by Matrix Assisted Photochemical Vapor Generation Atomic Fluorescence Spectrometry Detection, *Spectrochim. Acta. B.*, **65**(7): 587-590 (2010).
- [5] Panichev N., Kalumba M.M., Mandiwana K.L., Solid Phase Extraction of Trace Amount of Mercury from Natural Waters on Silver and Gold Nanoparticles, *Anal. Chim. Acta.*, **813**: 56-62 (2014).
- [6] Payehghadr M., Shafiekhani H., Sabouri A.R., Attaran A.M., Rofouei M.K., Cold Vapor Atomic Absorption Determination of Hg in Crude Oil and Gasoline Samples after Solid Phase Extraction Using Modified Disks, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **33**(2): 1-10 (2014).
- [7] Romero V., Costas-Mora I., Lavilla I., Bendicho C., Cold Vapor-Solid Phase Microextraction Using Amalgamation in Different Pd-Based Substrates Combined with Direct Thermal Desorption in A Modified Absorption Cell for the Determination of Hg by Atomic Absorption Spectrometry, *Spectrochim. Acta. B.*, **66**(2): 156-162 (2011).
- [8] Bansal N., Vaughan J., Boulemant A., Leong T., Determination of Total Mercury in Bauxite and Bauxite Residue by Flow Injection Cold Vapour Atomic Absorption Spectrometry, *Microchem. J.*, **113**: 36-41 (2014).
- [9] Geng W., Nakajima T., Takanashi H., Ohki A., Determination of Mercury in Ash and Soil Samples by Oxygen Flask Combustion Method-Cold Vapor Atomic Fluorescence Spectrometry (CVAFS), *J. Hazard. Mater.*, **154**(1-3): 325-330 (2008).
- [10] Wuilloud J.C.A.D., Wuilloud R.G., Silva M.F., Olsina R.A., Martinez L.D., Sensitive Determination of Mercury in Tap Water by Cloud Point Extraction Pre-Concentration and Flow Injection-Cold Vapor-Inductively Coupled Plasma Optical Emission Spectrometry, *Spectrochim. Acta. B.*, **57**(2): 365-374 (2002).
- [11] Saint'Pierre T.D., Rocha R.C.C., Duyck C.B., Determination of Hg in Water Associate to Crude Oil Production by Electrothermal Vaporization Inductively Coupled Plasma Mass Spectrometry, *Microchem. J.*, **109**: 41-45 (2014).
- [12] Krishna M.V.B., Karunasagar D., Rao S.V., J. Arunachalam., Preconcentration and Speciation of Inorganic and Methyl Mercury in Waters Using Polyaniline and Gold Trap-CVAAS, *Talanta*, **68**(2): 329-335 (2005).
- [13] Hosseini M.S., Hashemi-Moghadam H., Sensitized Extraction Spectrophotometric Determination of Hg(II) with Dithizone After its Flotation as Ion-Associate Using Iodide and Ferroin, *Talanta*, **67**(3): 555-559 (2005).
- [14] Garrido M., Nezio M.S.D., Lista A.G., Palomeque M., Band B.S.F., Cloud-Point Extraction/Preconcentration On-Line Flow Injection Method for Mercury Determination, *Anal. Chim. Acta.*, **502**(2): 173-177 (2004)
- [15] Pourreza N., Ghanemi K., Determination of Mercury in Water and Fish Samples by Cold Vapor Atomic Absorption Spectrometry After Solid Phase Extraction on Agar Modified with 2-Mercaptobenzimidazole, *J. Hazard. Mater.*, **161**(2-3): 982-987 (2009).
- [16] Carabias-Martínez R., Rodríguez-Gonzalo E., Moreno-Cordero B., Pérez-Pavón J.L., García-Pinto C., Laespada E.F., Surfactant Cloud Point Extraction and Preconcentration of Organic Compounds Prior to Chromatography and Capillary Electrophoresis, *J. Chromatogr. A.*, **902**(1), 251-265 (2000).
- [17] Watanabe H., Saitoh T., Kamidate T., Haraguchi H., Distribution of Metal Celates between Aqueous and Surfactant Phases Separated from a Micellar Solution of a Nonionic Surfactant, *Microchim. Acta.*, **106**: 83-97 (1992).
- [18] Xiang G., Wen S., Jiang X., Liu X., He L., Determination of Trace Copper(II) in Food Samples by Flame Atomic Absorption Spectrometry After Cloud Point Extraction, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **30**(3): 101-107 (2011).
- [19] Myer D., "Surface, Interfaces and Colloids: Principles and Applications", VCH, New York (1991).

- [20] Nilsson P., Wennerstrom H., Lindman B., [Structure of Micellar Solutions of Nonionic Surfactants. Nuclear Magnetic Resonance Self-Diffusion and Proton Relaxation Studies of Poly\(Ethylene Oxide\) Alkyl Ethers](#), *J. Phys. Chem.*, **87**(8): 1377-1385 (1983).
- [21] Nilsson P., Wennerstrom H., Lindman B., [Nonionic Micelles Grow with Increasing Temperature](#), *J. Phys. Chem.*, **95**(15): 6053-6054 (1991)
- [22] Lee S.k., Choi H.S., [Spectrophotometric Determination of Cadmium and Copper with Ammonium Pyrrolidinedithiocarbamate in Nonionic Tween 80 Micellar Media](#), *Bull. Korean Chem. Soc.*, **22**(5): 463 (2001).
- [23] Park S.M., Choi H.S., [Sensitized Spectrophotometric Determination of Trace Hg\(II\) in Benzalkonium Chloride Media](#), *Anal. Chim. Acta.*, **459**(1): 75-81 (2002).
- [24] Y.S Choi., H.S Choi., [Sensitized Spectrophotometric Determination of Trace Cu\(II\) in Cationic Surfactant Media](#), *Bull. Korean Chem. Soc.*, **24**(2): 222-224 (2003).
- [25] Yun J., Choi H., [Micellar Colorimetric Determination of Iron, Cobalt, Nickel and Copper Using 1-Nitroso-2-Naphthol](#), *Talanta*, **52**(5), 893-902 (2000).
- [26] Garcia M.E.D., Sanz-Medel A., [Dye-Surfactant Interactions: A Review](#), *Talanta*, **33**(3): 255-264 (1986).
- [27] Miura J., Ishii H., Watanabe H., [Extraction and Separation of Nickel Chelate of 1-\(2-Thiazolylazo\)-2-Naphthol in Nonionic Surfactant Solution](#), *Bunseki Kagaku*, **25**(11): 808-809 (1976).
- [28] Silva M.F., Fernandez L.P., Olsina R.A., Stacchiola D., [Cloud Point Extraction, Preconcentration and Spectrophotometric Determination Erbium\(III\)-2-\(3,5-dichloro-2-Pyridylazo\) -5- Dimethylaminophenol](#), *Anal. Chim. Acta.*, **342** (2-3): 229-238 (1997).
- [29] Silva M.F., Fernandez L.P., Olsina R.A., [Monitoring the elimination of Gadolinium-Based Pharmaceuticals. Cloud Point Preconcentration and Spectrophotometric Determination of Gd\(III\)-2-\(3,5-Dichloro-2-pyridylazo\)-5-Dimethylaminophenol in Urine](#), *Analyst*, **123**(9): 1803-1807 (1998).
- [30] Sombra L., Luconi M., Silva M.F., Olsina R.A., Fernandez L.P., [Spectrophotometric Determination of Trace Aluminium Content in Parenteral Solutions by Combined Cloud Point Preconcentration-Flow Injection Analysis](#), *Analyst*, **126**(7): 1172-1176 (2001).
- [31] Cheng K.L., Ueno K., Lamura T., "CRC Handbook of Organic Analytical Reagents", CRC press, Boca raton, Florida, USA (1982).
- [32] Stalikas C.D., [Micelle-Mediated Extraction as a Tool for Separation and Preconcentration in Metal Analysis](#), *Trends Anal. Chem.*, **21**(5): 343-355 (2002).
- [33] Horvath W.J., Huie C.W., [Salting-Out Surfactant Extraction of Porphyrins and Metalloporphyrin from Aqueous Non-Ionic Surfactant Solutions](#), *Talanta*, **39**(5): 487-492 (1992).
- [34] Song J.Y., Hou M., Zhang L.X., [Determination of Meceruy at Trace Level in Natural Water Samples by Hydride Generation Atomic Absorption Spectrophotometry after Cloud Point Extraction Preconcentration](#), *Chinese. Chem. Lett.*, **17**: 1217-1220 (2006).
- [35] Shamsipur M., Shokrollahi A., Sharghi H., Eskandari M.M., [Solid Phase Extraction and Determination of Sub-ppb Levels of Hazardous Hg⁺² Ions](#), *J. Hazard. Mater. B.*, **117** (2-3): 129-133 (2005)
- [36] Li Y., Hu B., [Sequential Cloud Point Extraction for the Speciation of Mercury in Seafood by Inductively Coupled Plasma Optical Emission Spectrometry](#), *Spectrochim. Acta. B.*, **62**(10): 1153-1160 (2007).