



Preconcentration of Mercury in Water Samples by Cloud Point Extraction and its Determination by Electrothermal Atomic Absorption Spectrometry

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A pre-concentration and determination methodology for mercury at trace levels in water samples was developed. Cloud point extraction was successfully employed for pre-concentration of mercury prior to electrothermal atomic absorption spectrometry (ETAAS) using Triton-X-100 as surfactant. In this study the effect of different modifiers on mercury determination were also investigated. Under the optimum conditions, the limit of detection (LOD) was $1.2 \mu\text{g L}^{-1}$. RSD for 10 replicate determinations of $10 \mu\text{g L}^{-1}$ Hg was 4.7 %. The calibration graph was linear in the range of $10\text{-}100 \mu\text{g L}^{-1}$ with a correlation coefficient of 0.997. The method was successfully applied to determine mercury in sea water samples.

Key Words: Cloud point extraction, Electrothermal atomic absorption spectrometry, Triton-X-100, Mercury.

INTRODUCTION

It is well known that mercury is one of the most toxic heavy metals because of its accumulative and persistent character in the environment and living organisms. Although mercury is not an abundant chemical element in nature, it has become dangerously widespread as a result of many industrial and agricultural applications¹⁻⁴. Therefore, the determination of mercury is very important in environmental and toxicological studies. One of the routes of incorporation of mercury into the human body is by drinking water¹⁻⁵. Hence, its determination in water samples has become very important. Due to the usually low concentration of Hg found in biological samples, a pre-concentration step is often required prior to its determination. One interesting alternative to conventional pre-concentration techniques is the use of cloud point extraction (CPE) as a new and green potential alternative method of pre-concentration to conventional liquid-liquid extraction⁶. Compared with traditional liquid-liquid extraction, cloud point extraction is advantageous due to the fact that it uses a very small amount of relatively non-flammable and non-volatile surfactants during the extraction procedure^{7,8}. Cloud point extraction is based on the phase separation exhibited by aqueous solutions of non-ionic surfactants, which becomes turbid and is separated in two phases when the temperature is increased above the cloud point temperature⁶. One phase consists of almost totally the surfactant and the other phase

contains a small portion of surfactant equal to the critical micellar concentration. Analytes complexed with chelating reagents with hydrophobic properties are isolated from the bulk aqueous solution and entrapped into the surfactant's micelles in the surfactant rich phase (in very small volume). During the course, the analytes in aqueous phase are preconcentrated⁸. The analytes in the surfactant rich phase can be determined by an adequate measuring technique and the sensitivity of detection can be enhanced greatly. As a benign of liquid-liquid extraction method, cloud point extraction (CPE) has been employed in analytical chemistry to separate and preconcentrate both organic compounds and metal ions in recent years⁹⁻¹⁶.

EXPERIMENTAL

A stock mercury standard (1000mg L^{-1}) was prepared from mercury(II) chloride (Merck, Darmstadt, Germany) in nitric acid (Merck, Darmstadt, Germany) and made to 1000 mL with ultrapure water. Triton-X-100 (Merk, Germany) and sodium diethyldithiocarbamate ($\text{NaDDTC}\cdot 3\text{H}_2\text{O}$) (Merck, Germany) were used without further purification. Different modifier such as 0.1 % (w/v), Pd, Rh, Ru, W, V, Zr, ascorbic acid in water were tested to stabilize and enhance the atomic absorption signal for Hg.

An AA670 atomic-absorption spectrometer, equipped with a graphite furnace was used in this study. An Hg hollow cathode lamp was employed as the radiation source at 253.7 nm.

The spectral band pass was 0.7 nm. Argon of 99.99 % purity was used as both protective and purge gas. The integrated absorbance mode was used throughout the experiment. A 20 μL micro syringe (Hamilton) was employed to introduce the extraction solution of the organic phase (4 μL) and to inject it into the electrothermal atomic absorption spectrometry (ETAAS) after extraction.

Procedure: An aliquot of the solution containing an appropriate amount of Hg(II) ($1\text{--}100\ \mu\text{g L}^{-1}$) was transferred to a 10 mL graduated centrifuge tube. After adding 0.1 mL sodium diethyldithiocarbamate ($10^{-4}\ \text{M}$) and Triton X-100 (0.6 % w/v), the pH was adjusted at 6.6. The sample was shaken and left to stand in a thermostatically controlled water bath for 10 min at $90\ ^\circ\text{C}$ before centrifugation. Separation of two phases was achieved by centrifugation for 5 min at 3500 rpm. The mixture was cooled in an ice bath to increase the viscosity of the surfactant-rich phase, and the aqueous phase was easily decanted by simply inverting the tube. The micellar extract of this procedure was diluted to 1 mL with ethanol and used for determination of its mercury content by electrothermal atomic absorption spectrometry.

RESULTS AND DISCUSSION

60 μL of 0.1 % w/v palladium was used for pretreatment of the graphite tube at $1800\ ^\circ\text{C}$ and then analysis of Hg was performed. Following results were given in Table-1.

Injected portion	Volume of injection (μL)	absorbance
Blank	20	0.015
$1\ \text{mg L}^{-1}$ Hg	20	0.200

In order to investigate the effects of other modifiers Ir, Rh, Ru, W, V, Ni, Zr and ascorbic acid of 0.1 % w/v were used. The results are given in Table-2 and these modifiers show no effect on the absorbance of Hg and hence Pd was used as modifier throughout this study.

Modifier	% w/v	Temperature ($^\circ\text{C}$)	Absorption
Ir	0.1	1800	0.085
Rh	0.1	2000	0.009
Ru	0.1	2200	0.005
W	0.1	2000	–
V	0.1	1800	–
Zr	0.1	2200	0.005
Ascorbic acid	0.1	1300	0.028

Effect of palladium amounts for deposition onto the graphite tube: 60 μL of Pd with different concentrations (% w/v) were deposited onto the graphite tube and heated at $1800\ ^\circ\text{C}$ followed by determination of $1\ \text{mg L}^{-1}$ Hg at the optimized conditions. The results are given in Fig. 1 and 4 % Pd showed the highest sensitivity.

Optimization of volume of 4 % palladium: Different volumes of 4 % Pd were injected and deposited at $1800\ ^\circ\text{C}$

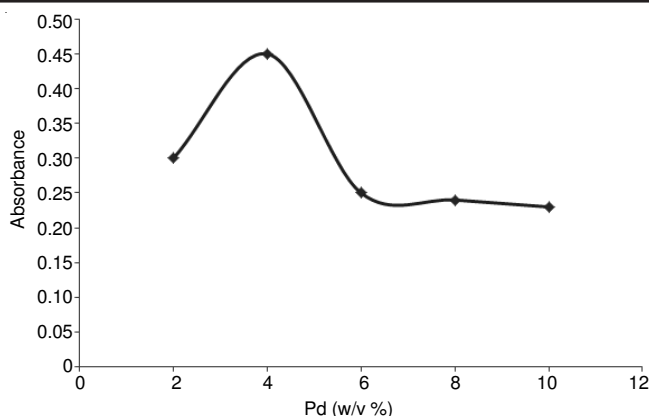


Fig. 1. Effect of % w/v Pd on Hg absorbance. Conditions: $1000\ \mu\text{g L}^{-1}$ Hg, deposited temperature $1800\ ^\circ\text{C}$

onto the graphite tube. The results are given in Fig. 2 and show that 120 μL would be sufficient as the optimum volume.

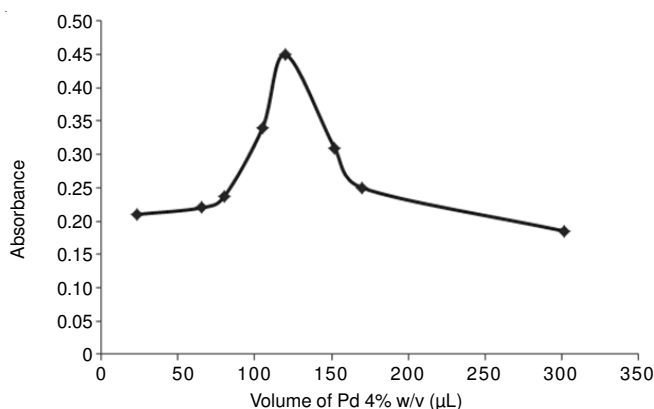


Fig. 2. Effect of volume of Pd on Hg absorbance. Conditions: $1000\ \mu\text{g L}^{-1}$ Hg, deposited temperature $1800\ ^\circ\text{C}$, 4 % w/v Pd

Graphite furnace temperature programs

Drying temperature: The drying temperature was varied over the range of $60\text{--}150\ ^\circ\text{C}$. The maximum absorbance for Hg was achieved at $80\ ^\circ\text{C}$, with a hold time of 10 s, which could remove the solvent completely.

Ashing temperature: In the ashing step, the temperatures between 100 and $600\ ^\circ\text{C}$ were studied at a constant atomization temperature of $1300\ ^\circ\text{C}$ with a hold time of 10 s. As shown in Fig. 3, a significant change in the mercury absorption was observed over this temperature range, thus the ashing temperature was set at $150\ ^\circ\text{C}$ to ensure maximum matrix removal without any signal loss.

Atomization temperature and time: A study of the atomization step was carried out in the range of $900\text{--}1800\ ^\circ\text{C}$. The optimum atomization temperature was selected to be $1300\ ^\circ\text{C}$ (Fig. 4). In addition, a hold time of 3 s was chosen for this step. At this temperature, no tailed peak was observed indicating no mercury absorption on the atomizer platform, so that it was completely eliminated after the atomization^{17,18}. In this study, the atomization time was also investigated in the range of 1-5 s. Optimized atomization time was selected as 3 s.

Rate of argon gas flow: Argon flow rates were used in the ranges of $0\text{--}1.6\ \text{L min}^{-1}$. The results show that by decreasing

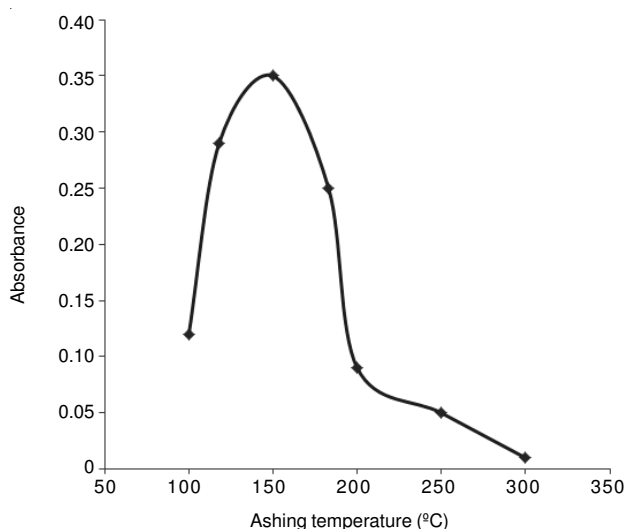


Fig. 3. Effect of ashing temperature on Hg absorbance. Conditions: $1000 \mu\text{g L}^{-1}$ Hg, 4 % w/v Pd, deposited temperature 1800°C

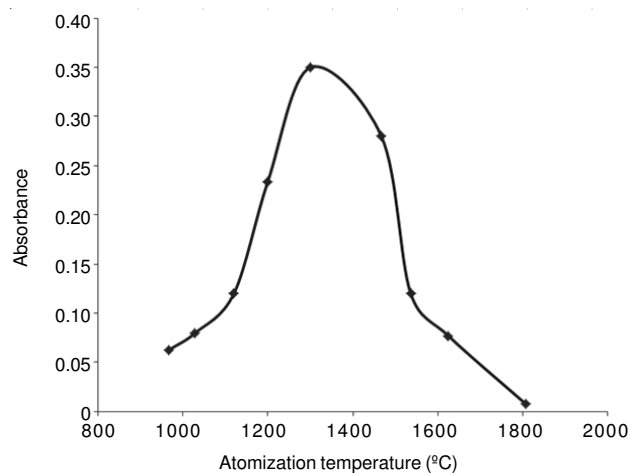


Fig. 4. Effect of the atomization temperature on Hg absorbance. Conditions: $1000 \mu\text{g L}^{-1}$ Hg, temperature time 3 s, 4 % w/v Pd, deposited temperature 1800°C

the flow, the atomic absorption signal will increase. In order to enhance the sensitivity of determination, gas stop mode was used during the atomization stage (Fig. 5).

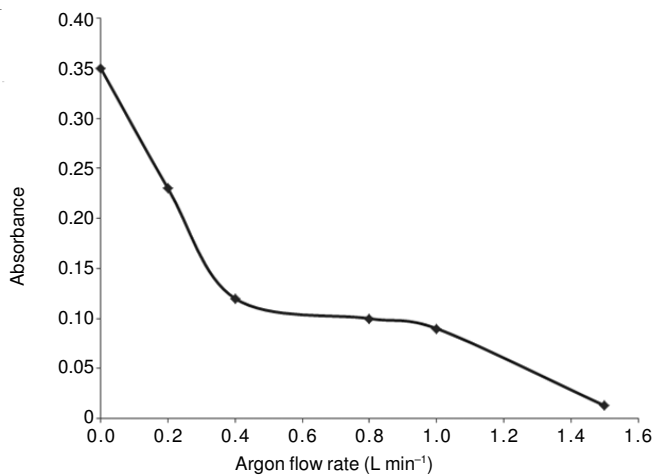


Fig. 5. Effect of argon flow rate on Hg absorbance. Conditions: $1000 \mu\text{g L}^{-1}$ Hg, 4 % w/v Pd, deposited temperature 1800°C

Effect of pH: pH plays an important role in metal-chelate formation and its chemical stability and hence the extraction yield depends on the pH at which complex formation is carried out¹⁹. Cloud point extraction of Hg was performed at different pH values in this study. The effect of pH in the range of 3-10 on the cloud point extraction of Hg was investigated. The results are shown in Fig. 6 and as shown that the maximum extraction of Hg was occurred at pH 6.6 and therefore, pH 6.6 was chosen as the optimum value for further experiments.

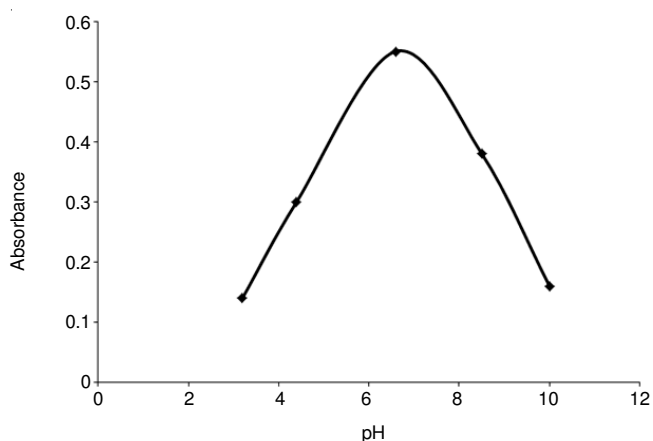


Fig. 6. Effect of pH on Hg absorbance, conditions: $10 \mu\text{g L}^{-1}$ Hg, 10^{-4} mol L^{-1} of DDTC, Triton-X-100 (0.6 % w/v) at 90°C for 10 min

Effect of Triton X-100 concentration: The concentration of Triton X-100 was also optimized keeping other parameters constant and the results are shown in Fig. 7. The integrated absorbance for Hg increased by increasing the Triton X-100 concentration up to 0.6 % (w/v) and decreased at higher values. A Triton X-100 concentration of 0.6 % (w/v) was then selected, as the optimum value.

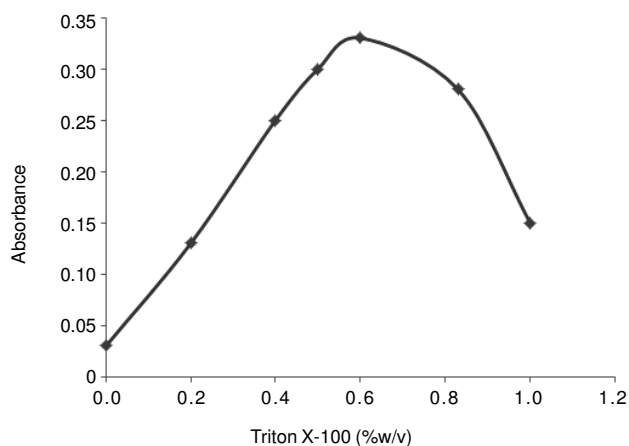


Fig. 7. Effect of Triton X-100 concentrations. $10 \mu\text{g L}^{-1}$ Hg, 10^{-4} mol L^{-1} of DDTC, Triton-X-100 at 90°C for 10 min

Interferences: Interfering species at 100 fold excess were added to the Hg solution and the extraction procedure followed. Table-3 shows the results.

Analytical figures of merit: The calibration curve was obtained by preconcentration of a suitable amount of Hg solution under the optimized experimental conditions, using

TABLE-3
EFFECT OF DIVERSE IONS ON THE
DETERMINATION OF 10 µg L⁻¹ OF Hg

Interference ions	Relative error (%)	Interference ions	Relative error (%)
Al ³⁺	-28.1	Sn ²⁺	1.5
La ³⁺	-33	Cr ²⁺	1.92
Zn ²⁺	0	Co ²⁺	-0.38
Mn ²⁺	-7.3	Fe ³⁺	1.15
Cd ²⁺	95	Mg ²⁺	-
Cu ²⁺	0	Cu ³⁺	-35

the proposed method. The calibration graph exhibited a good linearity over the range of 10-100 µg L⁻¹ Hg with a correlation coefficient of 0.997. The LOD based on 3Sb, often replicates of the blank measurement, was obtained to be 1.2 µg L⁻¹ (10 mL sample solution). The relative standard deviation (RSD) was 4.7 % (n = 10, C = 10 µg L⁻¹) and the enhancement factor (defined as the ratio of the slopes of the calibration curves with and without preconcentration) was 73.

Determination of mercury in sea water: The method was applied for mercury determination in sea water using standard addition method. In this method, Hg concentration in sea water was obtained 100 µg L⁻¹ (± 4) for 3 replicate, analysis of the sample.

Conclusion

Cloud point extraction (CPE) using Triton X-100 has shown to be an efficient, simple and versatile pre-concentration methodology to determine mercury by electrothermal atomic absorption spectrometry in water samples. Phase separation can be achieved at relatively low temperatures and the extraction percentages were high, resulting in high enhancement factors and low detection limits, enabling to determine mercury in water samples. Furthermore, the method is a promising method for Hg determination which joins the advantage of cloud point

extraction with the obvious advantage of electrothermal atomic absorption spectrometry method, *i.e.*, minimal reagent employment, feasibility and sensitivity.

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