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Determination of Trace Mercury by Cloud Point Extraction Preconcentration Coupled with Spectrophotometry

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Abstract: A new micell-mediated phase separation method for preconcentration of ultra-trace quantities of mercury as a prior step to its determination spectrophotometry has been developed. The method is based on the Cloud Point Extraction (CPE) of mercury with Triton X-100 in the absence of chelating agent. Mercury react with sodium diethyldithiocarbamate (DDTC) in a surfactant solution yielding a hydrophobic complex, which then is entrapped in surfactant micelles. Separation of the two phases was accomplished by centrifugation for 10 min at 4000 rpm. Under the optimum conditions i.e., pH 9.0, cloud point temperature 45°C, [DDTC] = 1.6×10^{-5} mol L⁻¹, [Triton X-114] = 0.032%. Analytical graphs were rectilinear in the concentration range of 4-240 µg L⁻¹ and relative standard deviation for five replicate determinations of Mercury at 8 (µg L⁻¹) concentration level, were 1.9%, respectively (n = 5, c = 8 µg L⁻¹).

Key words: Cloud point extraction, mercury determination, spectrophotometry, Triton X-100

INTRODUCTION

The development of separation/preconcentration procedures prior to trace element determinations has been explored in considerable depth in recent decades (Carabias-Martinez *et al.*, 2000). These steps might be important because the analytical methods do not present enough sensitivity or the selectivity could be affected due to the presence of concomitants (Coelho *et al.*, 2005). Among the techniques used are liquid-liquid extraction, ion exchange, co-precipitation, sorption and micellar systems (Carabias-Martinez *et al.*, 2000; Cave *et al.*, 1999). The latter systems have been exploited in different fields of analytical chemistry, mainly those focusing on separation and preconcentration based on cloud point procedures (Manzoori and Bavili-Tabrizi, 2002a).

The cloud point is the temperature above which aqueous solutions of non-ionic surfactants become turbid (Coelho and Arrudat, 2005). This temperature is named cloud point. Above the cloud point, the solution separates into two phases: the surfactant-rich phase with very small volume and the bulk aqueous solution, containing surfactant monomers (Chena *et al.*, 2005; Manzoori and Bavili-Tabrizi, 2002a). The use of micellar systems as an alternative to other techniques of separation offers several advantages including low cost, safety and high capacity to concentrate a wide variety of analytes of widely varying nature with high recoveries

and very high concentration factors (Shemirani *et al.*, 2005; Manzoori and Bavili Tabrizi, 2002b; Pramauro and Pelezetti, 1996). The cloud point extraction has been used to pre-concentrate trace metals based on the formation of chelates in the surfactant aggregate. The cloud point extraction has also been used to separate and pre-concentrate organic compounds.

In the present research we report the results obtained in a study of the cloud point preconcentration of Mercury, after the formation of a complex with sodium diethyldithiocarbamate (Na-DDTC) and later analysis by spectrophotometry using p-octylpolyethyleneglycolphenyether (TritonX-100) as surfactant.

MATERIALS AND METHODS

Apparatus and software: The present study was conducted in the Laboratory of University (2006-2007). We used a double beam UV-vis spectrophotometer BIO-TEK-KONTRON (UVIKON 922) equipped with a quartz cell for recording absorbance spectra.

The pH values were measured using a Horriba pH-meter, Equipped with a glass-combination electrode.

A thermostated water bath maintained at the desired temperatures was used for cloud point temperature experiments and The phase separation was assisted with a centrifuge.

Reagents: The non-ionic surfactant Triton X-100 was obtained E.Merck and was used without further purification. A 10% (v/v) solution of Triton X-100 was prepared from Merck product.

Stock standard solution of Mercury at a concentration of 1000 ppm was prepared from pure Mercury chloride (II). Working standard solutions were obtained by appropriate dilution of the stock standard solutions.

0.01 mol L⁻¹ sodium diethyldithiocarbamate (Na-DDTC) solution was prepared from the Merck product by dissolving 0.56 g of (Na-DDTC) in 250 mL of water.

A buffer solution at pH 9.0 was prepared from the Merck by mixing appropriate volumes of 0.2 mol L⁻¹ boric acid, 0.05 mol L⁻¹ citric acid and 0.1 mol L⁻¹ sodium carbonate solution.

Procedure: For the cloud point extraction, aliquots of the cold solution containing the analyte, Triton X-100 and DDTC, buffered at a suitable pH, were kept for 10 min in the thermostatic bath at 45°C. Separation of the two phases was accomplished by centrifugation for 10 min at 4000 rpm. On cooling in an ice-bath, the surfactant-rich phase become viscous and was retained at the bottom of the tubes. the aqueous phases could be separated by inverting the tubes.

RESULTS AND DISCUSSION

Effect of pH on CPE: Cloud point extraction of mercury was performed in different pH buffer solutions. The separation of metal ions by the cloud point method involves prior formation of a complex with sufficient hydrophobicity to be extracted into the small volume of surfactant-rich phase, thus obtaining the desired preconcentration. Absorbance depends on the pH at which complex formation is carried out. Figure 1 shows the effect of pH on absorbance of mercury complexes. It can be seen that for mercury the absorbance increases with increase in pH up to 9, thereafter the absorbance decreases. Hence, pH 9.0 (boric acid +citric acid + sodium carbonate buffer) was chosen for the analyte. The pH range of 2-11 is optimized for CPE of Hg.

Effect of TritonX-100 concentration: The preconcentration efficiency was evaluated using Triton X-100 concentrations ranging from 0.016 to 0.072% (v/v). The highest absorbance (0.264 s) was obtained with 0.032% (v/v) Triton X-100. By decreasing the surfactant concentration to 0.016% (v/v) the signal was reduced (0.221 s). The signal also decreased to 0.153 s for a higher

Triton X-100 concentration (0.072% v/v). This result might be related to the presence of the high amount of surfactant, resulting in an increase in the volume of the surfactant-rich phase. In addition, the viscosity of the surfactant-rich phase increases, leading to poor sensitivity. At lower Triton X-100 concentrations (<0.016% v/v), the preconcentration efficiency of the complex was very low, probably due to assemblies that were inadequate to quantitatively entrap the hydrophobic complex. Although 0.032% (v/v) of Triton X-100 showed the highest absorbance, a surfactant concentration of 0.016% (v/v) was selected as a compromise between the results obtained (in terms of sensitivity) and the surfactant concentration (Fig. 2).

Effect of DDTC concentration: 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. In this study, DDTC was used as the chelating agent due to the highly hydrophobic nature of its metal complexes. The concentration of DDTC tested ranged from 0.4×10^{-5} - 3×10^{-5} mol L⁻¹.

The extraction efficiency is clearly higher when DDTC at 1.6×10^{-5} mol L⁻¹ is employed; this concentration was, therefore, selected for all procedures. Figure 3 also shows a considerable decrease in the absorbance signal with increasing DDTC concentration.

An amount of 1.6×10^{-5} mol L⁻¹ was chosen in order to achieve quantitative extraction and thereby the highest extraction efficiency.

Effects of equilibration temperature and time: It was desirable to employ the shortest equilibration time and the lowest possible equilibration temperature, which compromise completion of reaction and efficient separation of phases. It was found that a temperature of 45°C is adequate for Hg analysis. The dependence of absorbance upon equilibration time was studied within a range of 5-15 min.

An equilibration time of 15 min was chosen as the best to obtain quantitative extraction.

Effect of centrifugation time: In general, centrifugation time hardly ever affects micelle formation but accelerates phase separation in the same sense as in conventional separations of a precipitate from its original aqueous environment. Therefore, a centrifugation time of 10 min at 4000 rpm was selected as optimum, since complete separation occurred for this time and no appreciable improvements were observed for long time.

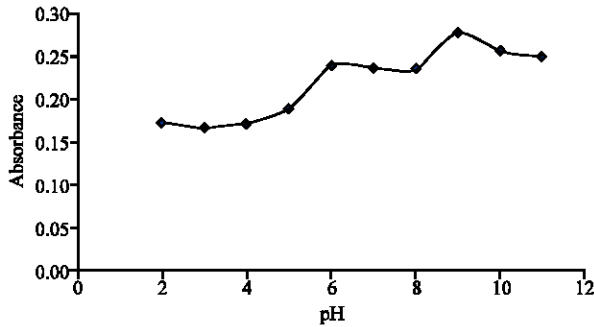


Fig. 1: Effect of pH on cloud point extraction of $0.24 \text{ mg L}^{-1} \text{ Hg}$; $1.6 \times 10^{-5} \text{ mol L}^{-1} \text{ DDTC}$; $0.032\% \text{ V/V Triton X-100}$

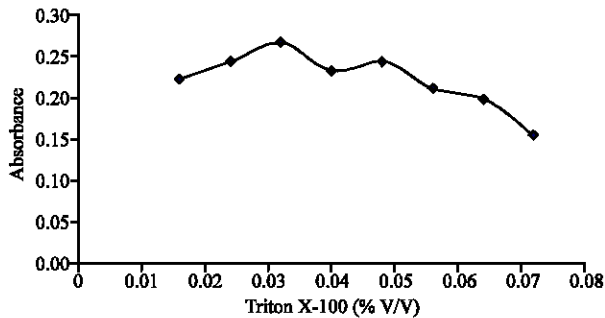


Fig. 2: Effect of Triton X-100 concentration on cloud point extraction of $0.24 \text{ mg L}^{-1} \text{ Hg}$; $1.6 \times 10^{-5} \text{ mol L}^{-1} \text{ DDTC}$; pH 9.0

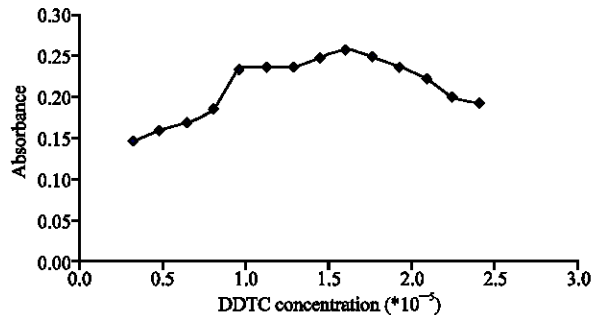


Fig. 3: Effect of DDTC concentration on cloud point extraction of $0.24 \text{ mg L}^{-1} \text{ Hg}$; $0.032\% \text{ V/V Triton X-100}$; pH 9.0

Calibration, precision and detection limits: Table 1 summarizes the analytical characteristics of the optimized method, including regression equation, linear range, limit limit of detection, defined as $CL = 3SB/m$ (where CL, SB and m are the limit of detection, standard deviation of the blank and slope of the calibration graph, respectively), was $0.53 \text{ } \mu\text{g L}^{-1}$.

Table 1: Analytical features of the proposed method

Regression equation (n = 6)	$A = 0.0012C + 0.0048$
Correlation coefficient	$R = 0.9993$
Linear range ($\mu\text{g L}^{-1}$)	4-240
Limit of detection ^a (3SB/m blank, ($\mu\text{g L}^{-1}$) (n = 5)	0.53
Limits of Quantification (LOQ)	1.38
Reproducibility ^b (RSD, %) (n = 5)	1.9

^a: Determined as three times the standard deviation of the blank signal.

^b: Values in parentheses are the Hg concentrations ($\mu\text{g L}^{-1}$) for which the RSD was obtained

Calibration graph was obtained by preconcentrating, aliquots of sample in presence of $0.032\% \text{ Triton X-100}$ in medium buffered at pH 9.0. A volume of the final solution was introduced into the spectrophotometer. In this case, the calibration graph using the preconcentration system for Mercury was linear with a correlation coefficient of 0.9993. Regression equation was $A = 0.0012X + 0.0048$. The Relative Standard Deviation (RSD) for 5 replicate determination of $8 \text{ } \mu\text{g L}^{-1} \text{ Hg}^{2+}$ is 1.9%.

CONCLUSIONS

The results obtained with the methods described above indicate that CPE methodology is a good alternative extraction technique for liquid samples and offers a series of highly interesting advantages from an analytical point of view, such as the possibility of extracting and preconcentrating the analytes in one step can be optimized by modifying the concentration of surfactant as well as the experimental conditions under which extraction and phase separation are carried out. Surfactants are less toxic and cheaper than the extractants. The most commonly used surfactants are commercially available and, since it is not necessary to evaporate off the solvents, no analyte is lost in the process. The experimental operations involved in CPE methodology are very simple.

In this study, the use of micellar systems as an alternative to other techniques of separation and pre-concentration offers several advantages including low cost, safety and high capacity to pre-concentration various elements with high recoveries and very good extraction efficiency. The results for this work demonstrate the possibility of using the (Na-DDTC)-TritonX-100 system for the pre-concentration of Mercury and later analysis by spectrophotometer.

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