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An environment-Friendly Cloud Point Extraction Method for preconcentration and determination of Lead and Cadmium in Water Samples

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ABSTRACT

A new, cost-effective, and environmental-friendly cloud point extraction methodology was described for enrichment of lead and cadmium in real water samples. The method involves the complexation of lead or cadmium with 2-nitro-6-(1,3-thiazol-2-diazeyl)-phenol at pH 8.5 and 7.0 for cadmium and lead, respectively, then extraction into Triton X-114. After dilution of the surfactant-rich phase with acidified methanol, the enriched analytes concentration was estimated by spectrophotometric measurements at 590 and 540, respectively. Parameters that influenced cloud point extraction, such as pH, reagent, surfactant and nitric acid concentrations, centrifuge rate and time, temperature, incubation time, as well as interferences were evaluated and optimized. The preconcentration factor was 50 and the detection limits were 1.64 and 1.62 $\mu\text{g L}^{-1}$ for lead and cadmium, respectively. The method presented relative standard deviation as precision were 2.28% and 1.96% for lead and cadmium, respectively. The accuracy of the new preconcentration procedure was checked by the analysis of the standard reference materials, and successfully applied to determine lead and cadmium in real water samples with relative recovery values in the range of 95.40%–101% for the spiked samples.

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INTRODUCTION

In environmental samples, heavy metals are considered to be hazardous materials due to their toxicity for animals and humans even at low concentration levels [1]. Lead (Pb(II)) and cadmium (Cd(II)) have acute and chronic effects on humans and other living organisms. Pb(II) and Cd(II) can cause harmful gastrointestinal, cardiovascular, hematological, renal, kidney and reproductive effects. Therefore, the determination of trace levels of Pb(II) and Cd(II) ions as an important heavy metals in the environmental samples is a very significant goal for chemists working in the fields of analytical chemistry and environmental analytical chemistry [2-4]. The precise estimation of heavy metals in environmental samples at trace quantities requires the use of modern analytical measurement techniques with low detection limits such as flame atomic absorption spectrometry (FAAS) [5, 6]. A separation/enrichment step is necessary prior to the measurements to increase the sensitivity and enhances the accuracy of estimation.

Recently, the development of various methods for the separation and enrichment of trace levels of Pb(II) and Cd(II) ions were reported in the literature, such as solid-phase [7-9], dispersive liquid-liquid microextractions [10-13], single-drop microextractions [14, 15], cloud point extraction [16-18] and co-precipitation [19-22].

For separation and enrichment of trace levels of heavy metals, green CPE procedure was used due to it uses inexpensive and not toxic non-ionic surfactants and reducing extraction time [23-25]. CPE is based on the distribution of the analyte between two phases at the cloud point temperature. One phase includes a surfactant at a concentration \leq a critical micelle concentration; the other phase which extract metal ions present in the solution as metal complexes.

In the proposed work, ecofriendly, selective and sensitive CPE extraction method for enrichment and quantification of trace levels of Pb(II) and Cd(II) ions in real water samples was described. The factors influencing the efficiency of CPE procedure were optimized. 2-nitro-6-(1,3-thiazol-2-diazeyl)-phenol (TANP) was synthesized as a selective chelating agent by our

group and it was used preconcentration of the studied analytes by CPE in the presence of Triton X-114.

EXPERIMENTAL

Apparatus

All absorption spectra were made using Varian UV-Vis spectrophotometer (Cary 100 Conc., Australia) equipped with a 5.0 mm quartz cell was used for absorbance measurements. This spectrophotometer has a wavelength accuracy of ± 0.2 nm with a scanning speed of 200 nm/min and a bandwidth of 2.0 nm in the wavelength range of 200–900 nm. The pH-meter (Thermo scientific, USA) was utilized for pH measurements. A thermostated water bath (Memmert WNB7-45 WNB 22, Germany) was used. Centrifuge (Isolab, Germany) was used to centrifuge the samples.

Chemicals and reagents

All chemicals used in this work were of analytical grade and were obtained from Merck (Darmstadt, Germany) or Fluka (Bunch., Switzerland), and deionized/bidistilled water was used in all experiments. All the plastic and laboratory glass wares were cleaned by soaking in 5.0% (v/v) HNO₃ solution for 24 hours and then rinsed and cleaned with deionized water at least three times prior to use.

The standard stock solutions of Pb(II) and Cd(II) ions (1000 mg L⁻¹) were prepared by dissolving the appropriate weight of high purity Cd(NO₃)₂·4H₂O and Pb(NO₃)₂ in 1.0 mol l⁻¹ HNO₃. Working solutions were prepared by appropriate dilution of the stock solutions. Buffer solutions were prepared to adjust the pH values. Acetate buffer (3.0-6.0); phosphate buffer (pH 7.0) and ammoniacal buffer (8.0–10) [26].

Triton X-114 (Fluka, Buches, Switzerland) was used without further purification. Aqueous 1.0 % (v/v) solution of Triton X-114 was prepared by dissolving 1.0 mL of Triton X-114 in 100 ml of deionized water in 100 ml volumetric flask with stirring.

Nitric acid solutions were prepared by direct dilution with deionized water from the concentrated solutions. Methanol, acetone, and

ethanol (Merck) were used to decrease the viscosity of surfactant-rich phase. The solutions of various cations and anions used for the interference study were obtained from the respective high purity inorganic salts (Sigma-Aldrich, USA) by proper dilution in bi-distilled water.

A stock solution (1.0×10^{-3} mol l⁻¹) of TANP was prepared by dissolving an appropriate amount of the synthesized reagent [27] in a minimum amount of absolute ethanol and diluting the mixture to 100 ml with ethanol in a 100 ml measuring flask. The working solution was prepared by its appropriate dilution with the same solvent. The accuracy of the proposed method was assessed by analyzing the certified reference material (TMDA-53.3 and TMDA-51.3) fortified water (National Water Research Institute, Environment Canada, Burlington, Canada).

Procedure for CPE

An aliquot of Pb(II) and Cd(II) ions standard solutions were transferred to 50 mL centrifuge tube, 2.5 and 1.5 mL of the 1.0×10^{-3} mol L⁻¹ TANP solution and 3.5 and 4.0 mL of universal buffer solution (pH 7.0) and 8.5) for Pb(II) and Cd(II), respectively were added. After that, 1.5 and 2.0 mL of 0.3% (v/v) Triton X-114 solution for Pb(II) and Cd(II), respectively were added. This system was heated in a water bath at 40°C for 10, 5.0 min for Pb(II) and Cd(II). To separate the two phases, the mixture was centrifuged for 10 min at 4000 rpm. Then, it was cooled in an ice-bath for 5.0 min. The surfactant-rich phase became a viscous phase, which could then be separated by inverting the tubes to discard the aqueous phase. A volume of 0.5 mL DMF was added to the surfactant-rich phase to reduce its viscosity and to facilitate sample handling prior to spectrophotometric assay of Pb(II) and Cd(II) at 590 and 540 nm. Calibration was performed by using different standard solutions of Pb(II) and Cd(II) submitted to the same preconcentration and determination procedures. Blank solution was also submitted to a similar procedure and measured in parallel to the sample solutions.

Applications in real water samples and certified reference materials

The proposed method was applied to different water samples. The tap, mineral, well and wastewater samples were collected from Zagazig city, Egypt and sea water samples from Red Sea, Egypt, River water samples collected from Shobra, Egypt. The samples stored in polyethylene bottles. The samples were filtered through a cellulose membrane filter (Millipore) of 0.45 µm pore size and acidified with 1.0 % (v/v) HNO₃ and were subsequently stored at 4.0 °C in a refrigerator. The organic content of the water samples was oxidized in the presence of 1.0% H₂O₂ and by the addition of concentrated nitric acid. The pH of the samples was adjusted to 7.0 with a buffer solution. Then the preconcentration CPE procedure given above was applied to understudy water samples. The Pb(II) and Cd(II) concentrations in the samples were determined by spectrophotometry. Another application of the presented CPE procedure was performed using certified reference materials (TMDA-53.3 and TMDA 51.4) fortified water (National Water Research Institute, Environment Canada, Burlington, Canada).

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of a standard solution of Pb(II) and Cd(II) complex with TANP which extracted by CPE at pH= 7.0 and 8.5 and has a maximum absorbance at 590 and 540 nm in surfactant-rich phase and the complex formed without CPE was measured at 561 and 535 nm against a reagent blank (**Figures 1 and 2**).

The separation of metal ions by CPE methods involves prior formation of a metal complex by an appropriate complexing agent, with sufficiently hydrophobic character, and subsequent extraction into a small volume of surfactant-rich phase. The required hydrophobic character of the extracted copper complexes is guaranteed by the high lipophilic nature of the complexing agent (TANP) used. In the present work, this characteristic was confirmed by the application of TANP as a complexing agent in a cloud point extraction.

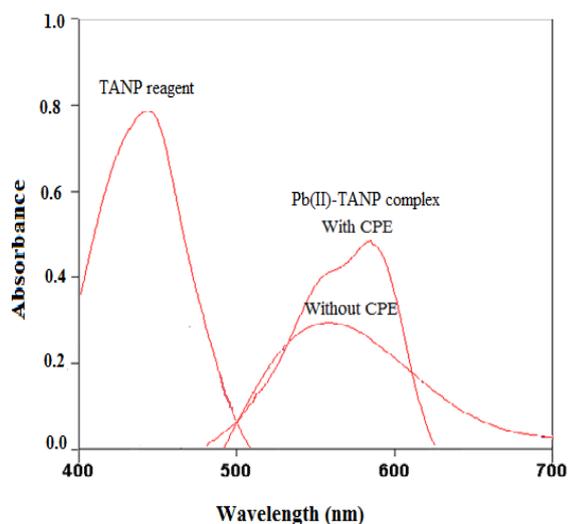


Figure 1. Absorption spectrum of Pb(II)-TANP complex with and without CPE procedure against TANP reagent blank.

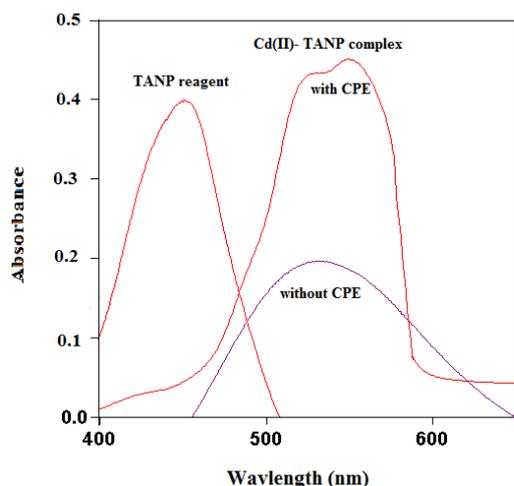


Figure 2. Absorption spectrum of Cd(II)-TANP complex with and without CPE procedure against TANP reagent blank.

Optimization of the experimental conditions

Effect of pH

Cloud point extraction of Pb(II) and Cd(II) were carried out in buffer solutions at different pH. The extraction yield depends on the pH at which complex formation is carried out. **Figure 3** shows the effect of pH on the absorbance of Pb(II) and Cd(II) complexes. It is seen that the absorbance increases with an increase in pH up to 7.0 and 8.5 (universal buffer) for Pb(II) and Cd(II) were chosen as the optimum pH value for further experiments. In addition, the influence of the buffer amount was assessed, while the other experimental variables remained constant. The results have shown that if 3.5 and 4.0 mL or larger volume of buffer solution were added for

Pb(II) and Cd(II), no obvious variation took place in the absorbance. Therefore, it was concluded that 3.5 and 4.0 mL for Pb(II) and Cd(II) of buffer solution were chosen as the optimum volume. (**Figure 4**)

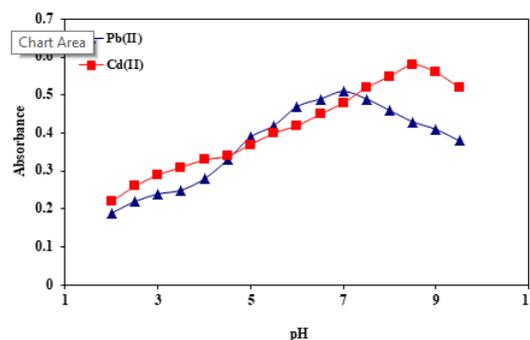


Figure 3. Effect of pH on the cloud point extraction of Pb(II) and Cd(II) using TANP reagent.

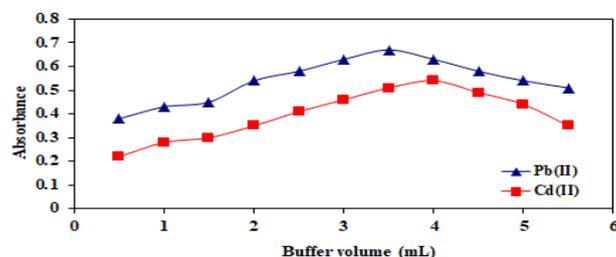


Figure 4. Effect of buffer volume on the cloud point extraction of Pb(II) and Cd(II) using TANP reagent.

Effect of TANP concentration

A solution containing Pb(II) and Cd(II), 0.3 % Triton X-114 and at a medium buffer of pH 7.0 and 8.5 containing various amounts of TANP were subjected to the cloud point preconcentration process. In order to study the influence of TANP concentration on the extraction and determination of Pb(II) and Cd(II) complexes different concentrations of the chelating reagent in the range of 1.0×10^{-5} – 1.0×10^{-4} mol L⁻¹ was used, and the general procedure was applied. **Figure 5** shown that the absorbance increased up to a TANP concentration of 5.0×10^{-5} mol L⁻¹ and 3.0×10^{-5} which was selected as the optimum concentration for Pb(II) and Cd(II), respectively.

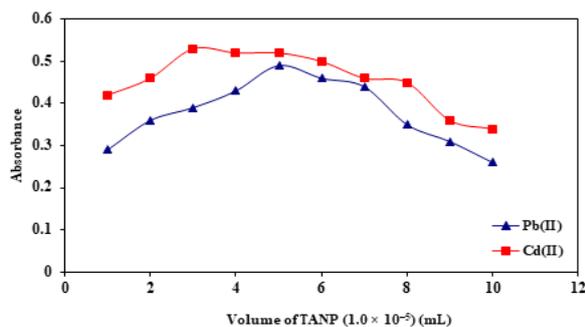


Figure 5. The effect of TANP concentration on the cloud point extraction of Pb(II) and Cd(II).

Effect of Triton X-114 concentration

The effect of non-ionic surfactant concentration within the Triton X-114 concentration range from 0.05–0.5% (v/v), on the CPE efficiency of Pb(II) and Cd(II) ions. As shown in **Figure 6**, the absorbance of the complex was increased by increasing the Triton X-114 concentration up to 0.3% (v/v) for both metal ions. A considerable decrease in the absorbance is observed with increasing the surfactant amounts higher than 0.3% (v/v). This can be attributed to an increase in volume and viscosity of the micellar phase. At concentrations below this value, the extraction efficiency of complexes was low because there are few molecules of the surfactant to entrap the metal-TANP complex quantitatively. Thus, Triton X-114 concentration of 0.3% (v/v) was selected for subsequent experiments. Therefore, it was concluded that 1.5 and 2.0 mL for Pb(II) and Cd(II) of ligand were chosen as the optimum volume for the CPE of Pb(II) and Cd(II).

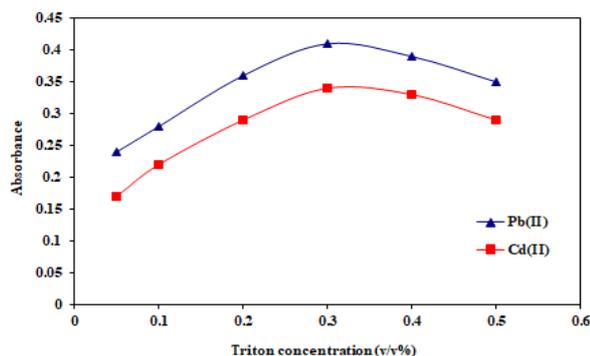


Figure 6. Effect of Triton X-114 concentration on the cloud point extraction of Pb(II) and Cd(II) using TANP reagent.

Effects of incubation time and temperature

In order to achieve easy phase separation and efficient preconcentration in cloud point

extraction processes, it is impart 4e to optimize the incubation time and temperature. It was desirable to employ the shortest incubation time and the lowest possible incubation temperature, as a compromise between completion of extraction and efficient separation of phases. The influence of the incubation time and temperature was investigated in the ranges 5.0-20 min and from 30-60 °C. The results demonstrate that in the incubation time of 10 and 5 min for Pb(II) and Cd(II) (**Figure 7**) and the temperature of 40°C (**Figure 8**) were chosen for further experiments. The extraction efficiency for the Pb(II)–TANP and Cd(II)–TANP complexes were constant. Therefore, an incubation temperature of 40°C was chosen for the separation process. Higher temperatures lead to the decomposition of TANP and the reduction of extraction yield. A centrifuge time period of 10 min at 4000 rpm was selected as optimum, as complete separation occurred within this time and no appreciable improvements were observed for longer periods.

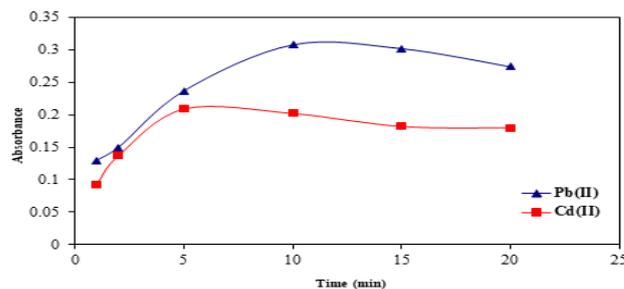


Figure 7. Effect of time on the cloud point extraction of Pb(II) and Cd(II) using TANP reagent.

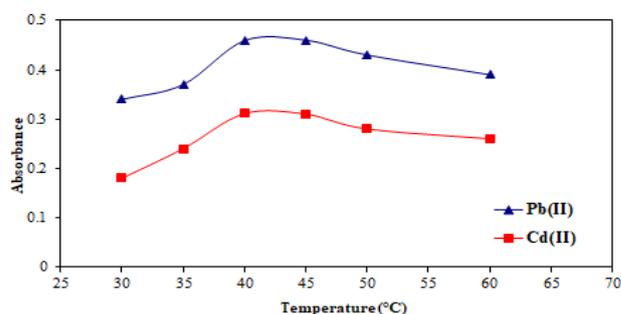


Figure 8. Effect of temperature on the cloud point extraction of Pb(II) and Cd(II) using TANP reagent.

Effects of diluent

In order to decrease the viscosity of the surfactant-rich phase a diluting agent was used. The addition of a diluent into the surfactant-rich phase is often needed to obtain a homogeneous solution with compatible viscosity. Different

solvent including methanol, ethanol, acetone, DMF and acetonitrile were tested as diluent solvents. Surfactant-rich phase was found to be freely soluble in DMF. Hence 500 μL of DMF was used as diluent for the surfactant-rich phase. Therefore, the preconcentration factor which defined as the ratio of the initial solution volume to the volume of surfactant rich phase was 100 using the proposed method.

Interference studies

The effect of foreign ions on the absorbance was tested. Different amounts of common ions were added to the test solution containing 200 ng mL^{-1} of Pb(II) and Cd(II) and the developed

procedure was applied. The tolerance limits were determined for a maximum error of $\pm 5.0\%$ and the results are given in **Table 1**. These results demonstrate that the common coexisting ions did not have a significant effect on the separation and determination of Pb(II) and Cd(II). Since commonly present ions in water samples did not affect significantly the recovery of Pb(II) and Cd(II), the method can therefore be applied to determination of Pb(II) and Cd(II) in water samples.

Table 1. Effect of interfering ions on preconcentration and recoveries of 200 ng mL^{-1} Pb(II) and Cd(II) (n=3).

Ions	Added as	Pb(II)		Cd(II)	
		Maximum tolerable amount (mg L^{-1})	Recovery (%) \pm SD ^a	Maximum tolerable amount (mg L^{-1})	Recovery (%) \pm SD ^a
K⁺	KCl	10	96.0 \pm 3.0	10	95.0 \pm 2.0
Na⁺	NaCl	10	95.0 \pm 2.0	10	96.0 \pm 4.0
Al³⁺	Al (NO₃)₃	2.0	96.0 \pm 1.0	2.0	96.0 \pm 3.0
Cr³⁺	Cr(NO₃)₃	1.0	97.0 \pm 4.0	1.0	97.0 \pm 3.0
Fe³⁺	FeCl₃	2.0	95.0 \pm 3.0	3.0	95.0 \pm 2.0
Ca²⁺	CaCl₂	3.0	96.0 \pm 3.0	2.0	97.0 \pm 4.0
Mg²⁺	MgCl₂	2.0	96.0 \pm 2.0	1.0	95.0 \pm 2.0
Pb²⁺	Pb(NO₃)₂	1.0	97.0 \pm 4.0	1.0	96.0 \pm 3.0
Mn²⁺	Mn(NO₃)₂	1.0	96.0 \pm 2.0	1.0	97.0 \pm 2.0
Zn²⁺	ZnSO₄	0.5	95.0 \pm 2.0	2.0	96.0 \pm 3.0
Cd²⁺	Cd(NO₃)₂	0.5	95.0 \pm 4.0	0.5	96.0 \pm 3.0
Cu²⁺	CuSO₄	0.5	96.0 \pm 2.0	0.5	97.0 \pm 2.0
NO₃⁻	KNO₃	10	97.0 \pm 3.0	5.0	95.0 \pm 2.0
SO₄²⁻	Na₂SO₄	10	96.0 \pm 2.0	5.0	96.0 \pm 3.0
Cl⁻	NaCl	10	95.0 \pm 2.0	10	95.0 \pm 2.0
F⁻	NaF	10	96.0 \pm 3.0	10	96.0 \pm 34.0

^a Mean \pm standard deviation.

Analytical characteristics

The calibration graphs were linear in the ranges 10–250 $\mu\text{g L}^{-1}$ Pb(II) and 10–210 $\mu\text{g L}^{-1}$ Cd (II) under the optimum conditions of the general procedure. The regression equations for

Pb(II) and Cd(II) determination were $A = 2.49 \times 10^{-4} + 7.5 \times 10^{-3}C$ ($R^2 = 0.9995$) and $A = 4.32 \times 10^{-4} + 9.35 \times 10^{-3}C$ ($R^2 = 0.9998$), respectively, where A is the absorbance and C is the metal concentration in solution ($\mu\text{g L}^{-1}$). By

using direct measurement in spectrophotometry without the preconcentration procedure, the linear equations were $A = 7.0 \times 10^{-4} + 5.0 \times 10^{-5}C$ ($R^2 = 0.9994$), and $A = 2.0 \times 10^{-4} + 6.0 \times 10^{-5}C$ ($R^2 = 0.9997$), for Pb(II) and Cd(II), respectively. The limit of detection, defined as $C_L = 3S_B/m$ (where C_L , S_B and m are limit of detection, standard deviation of the blank, and the slope of the calibration graph, respectively). The enhancement factor was calculated as the ratio of the slope of the calibration graph with preconcentration CPE procedure to the slope of the calibration graph without CPE was also approximately 2.1 and 2.3 for Pb(II) and Cd(II), respectively. The consumptive index is defined

as the sample volume, in milliliters, consumed to reach a unit of enrichment factor (EF): $CI = V_s$ (mL)/EF, where V_s is the sample volume. The precision of the procedure was determined as the relative standard deviation (RSD) and relative error for six replicate measurements carried out in solutions containing $200 \mu\text{g mL}^{-1}$ of Pb(II) and Cd(II). Table 2 summarizes the analytical characteristics under the optimum conditions such as limits of detection and quantification, reproducibility, preconcentration and enhancement factors and consumptive index (CI). Table 3. The results obtained using the presented method are in good agreement with the certified values.

Table 2. Analytical characteristics of the proposed CPE method for determination of Pb(II) and Cd(II).

Parameters	Pb(II)		Cd(II)	
	With CPE	Without CPE	With CPE	Without CPE
Calibration range ($\mu\text{g L}^{-1}$)	10–250	200-4000	10–210	300-3000
Regression equation ($n=6$) ^a				
Slope	0.0019	0.0007	0.0023	0.001
Intercept	0.0314	0.007	0.0269	0.002
Correlation coefficient (r)	0.9995	0.9992	0.9998	0.9991
Limit of detection ($\mu\text{g L}^{-1}$)	1.64	60	1.62	85
Limit of quantification, ($\mu\text{g L}^{-1}$)	5.46	200	5.4	283
Reproducibility (RSD%) ($n=6$)	2.28	2.60	1.96	2.40
Preconcentration factor (PF)	100		100	
Enrichment factor (EF)	2.1		2.3	
Sample volume (mL)	25		25	
Consumptive index (CI)	11.90		10.87	

^a $A = a + bC$, where C is the concentration of Pb(II) and Cd(II) in $\mu\text{g L}^{-1}$.

Analytical applications

The validity of the present CPE procedure was checked by analyzing certified reference

materials (TMDA-53.3 and TMDA-51.4) fortified water. The results are given in

Table 3. Determination of Pb(II) and Cd(II) content in the certified reference materials (N=3)

Sample	Pb(II)			Cd(II)		
	Observed ($\mu\text{g L}^{-1}$)	Certified value ($\mu\text{g L}^{-1}$)	Recovery (%)	Observed ($\mu\text{g L}^{-1}$)	Certified value ($\mu\text{g L}^{-1}$)	Recovery (%)
TMDA-53.3 fortified water	340.0 ± 4.0	349.0	97.40	116.0 ± 3.4	118.0	98.30
TMDA-51.4 fortified water	66.0 ± 1.4	68.90	95.80	25.0 ± 1.0	25.6	97.70

In order to test the reliability of the proposed method, it was applied to the determination of Pb(II) and Cd(II) from different water (tap, mineral, well, river and sea) samples.

The results are described in **Table 4**. According this table, the added Pb(II) and Cd(II) can be quantitatively recovered from the water samples by the proposed procedure. Recoveries (R) of

spike additions (100 or 200 $\mu\text{g L}^{-1}$) to water samples were quantitative. The percentage recovery (R) was calculated by using the equation:

$$R \% = \{(C_m - C_0)/m\} \times 100.$$

Where C_m is a value of the metal in a spiked sample, C_0 is a value of the metal in a sample and

m is the amount of metal spiked. The results indicated that the recoveries were reasonable for trace analysis, in a range of 95.60– 100.60% and 95.40-101.0% for Pb(II) and Cd(II), respectively and confirm the validity and efficiency of the proposed method for metal determination in water samples.

Table 4. Spiked recoveries of Pb(II) and Cd(II) from real water samples after being applied the proposed method ($N= 3$).

Samples	Added ($\mu\text{g L}^{-1}$)	Pb(II)		Cd(II)	
		Found \pm SD ($\mu\text{g L}^{-1}$)	Recovery ^a (%)	Found \pm SD ($\mu\text{g L}^{-1}$)	Recovery ^a (%)
Tap water ^c	0.0	<LOD ^b	-	<LOD	-
	100	99.50 \pm 0.60	99.50	101.0 \pm 0.30	101.0
	150	151.0 \pm 0.50	100.60	148.50 \pm 0.60	99.0
Mineral water ^c	0.0	<LOD	-	<LOD	-
	100	100.3 \pm 0.24	100.30	99.80 \pm 0.20	99.80
	150	148.9 \pm 0.50	99.20	149.30 \pm 0.50	99.50
Well water ^c	0.0	<LOD	-	<LOD	-
	100	98.30 \pm 0.20	98.30	97.8 \pm 0.15	97.80
	150	148.90 \pm 0.60	99.10	146.9.0 \pm 0.40	97.60
Sea water ^d	0.0	10.0 \pm 0.12	-	8.0 \pm 0.08	-
	100	106.0 \pm 0.40	96.36	103.0 \pm 0.16	95.40
	150	154.0 \pm 0.70	96.25	155.0 \pm 0.25	98.10
River water ^e	0.0	6.0 \pm 0.10	-	5.0 \pm 0.07	-
	100	102.0 \pm 0.17	96.23	102.0 \pm 0.19	97.14
	150	151.0 \pm 0.35	97.44	148.0 \pm 0.42	95.50
Wastewater	0.0	12.5 \pm 0.40	-	11.0 \pm 0.20	-
	100	108.0 \pm 0.80	96.0	107.0 \pm 0.32	96.40
	150	159.0 \pm 0.90	97.85	157.0 \pm 0.40	97.52

^a Average of three determinations with 95% confidence level;

^b <LOD: Below limit of detection.

^c Collected from Zagazig, Egypt.

^d Collected from Alexandria, Egypt.

^e Collected from Shobra, Egypt.

CONCLUSIONS

The proposed cloud point extraction was successfully applied for preconcentration and determination of trace amounts of Pb(II) and Cd(II) in water samples using TANP as a complexing reagent and spectrophotometric detection. This study allowed the development of a new, fast, easy to use, sensitive, and safe, environmentally friendly methodology alternative to other separation or preconcentration techniques. The procedure is inexpensive, because it consists of many low equipment and running costs, such as FAAS which is available in most laboratories.

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