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An application of coacervate-based extraction for the separation and preconcentration of cadmium, lead, and nickel ions prior to their determination by flame atomic absorption spectrometry in various water samples

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Abstract: Cloud point extraction (CPE), which is the most popular coacervate-based extraction method, was utilized for the separation and preconcentration of trace amounts of cadmium, lead, and nickel. Quinalizarin was used as complexing agent and Triton X-114 was used as surfactant. After extraction, analyte ions were determined by flame atomic absorption spectrometry. The detection limits ($3s$) of 1.8 μg L^{-1} for Cd(II), 3.2 μg L^{-1} for Pb(II), and 2.8 μg L^{-1} for Ni(II) were obtained using 50 mL of solutions. The relative standard deviation was calculated as 4.3% for 10 μg L^{-1} Cd(II), 4.9% for 50 μg L^{-1} Pb(II), and 4.6% for 50 μg L^{-1} Ni(II). Obtained enrichment factors of Cd(II), Pb(II), and Ni(II) were 144, 129 and 92, respectively. In addition, the method was successfully implemented for the determination of Cd(II), Pb(II), and Ni(II) in water samples and standard reference materials and satisfactory recovery values were obtained.

Key words: Cloud point extraction, coacervate-based extraction, atomic absorption spectrometry, preconcentration, trace analysis, cadmium, lead, nickel

1. Introduction

Due to heavy metal contaminated water produced by several industries, all living organisms that have the ability of bioaccumulation encounter serious health problems even at very small concentrations of heavy metals. For surface waters, heavy metal pollution is one of the five basic types of important pollutions.[1] Nevertheless, some heavy metals are known to be essential for life and some are known to be nonessential for biological activity.[2] Cadmium and lead are nonessential, extremely toxic elements and cause several adverse effects on health, even at minute concentrations.[3] For a biological system, long-term exposure to cadmium leads to deterioration of calcium regulation and this causes cell damage and death. Prolonged intake of lead causes cumulative poisoning, which leads to central nervous system damage, hematological disorder, anemia, and kidney disorder.[4] Although compared with lead and cadmium, nickel is essential and moderately toxic, it has many negative effects on human health and an allergic reaction is the most important of these effects.[5–7] In addition, inhalation of nickel compounds causes serious health problems such as cancer, eczema, and skin diseases.[8] Therefore, in order to minimize the negative impact of heavy metals, it is important to measure and continuously monitor their levels in environmental samples. From an analytical standpoint, the concentrations of heavy metals in most samples are generally close to the detection limits of most analytical techniques and this is a significant

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problem on which analytical chemists work. Because of these reasons, the development of an accurate, sensitive, and economical detection method for trace amounts of heavy metals is a very important task.[9,10]

When considering speed, cheapness, and ease of use, flame atomic absorption spectrometry (FAAS) is one of the most popular spectroscopic methods. However, FAAS suffers from unsatisfactory sensitivity and interference effects.[11] In order to eliminate these handicaps a preconcentration/separation step is applied before analysis. However, the preconcentration technique should be environmentally friendly, inexpensive, and simple to use. These requirements are met by using a coacervate (a surfactant rich liquid and an extraction medium) during sample preparation. Cloud point extraction (CPE) is one of the most popular coacervate-based extraction techniques. Formation of micellar aggregates in aqueous solutions of nonionic surfactants lies at the basis of the CPE technique. CPE involves three steps: (1) dissolution of analytes: analytes present in sample bound to micelles; (2) clouding: by heating to a certain temperature called cloud point temperature (CPT) a cloudy solution is obtained; (3) separation of phases: at a temperature above the CPT the micellar solution separates into two phases (one is an analyte containing, small volume of surfactant rich phase and the other is aqueous phase).[12,13]

Quinalizarin (1,2,5,8-tetrahydroxyanthracene-9,10- dione) is a hydroxyl anthraquinone reagent and anthraquinone derivatives are very popular chelating agents for the sensitive and selective determination of metals in analytical chemistry.[14] The reactions between quinalizarin and metal ions to form complexes are very rapid.[14]

In the present study, a simple and selective CPE method for preconcentration and FAAS determination of Cd(II), Pb(II), and Ni(II) in aqueous sample was proposed. For this purpose quinalizarin was used as complexing agent and octylphenoxypolyethoxyethanol (Triton X-114) as surfactant. In order to improve the efficiency of the method several parameters such as pH, amounts of quinalizarin and Triton X-114, temperature, and duration were explored. The method was also adapted to the determination of the metal ions studied in different water samples and standard reference materials.

2. Results and discussion

In coacervate-based techniques, determination of optimum parameters has prime importance. For example, appropriate pH specifies formation of complex and coacervate and efficiency of extraction.[12] In addition, working at a suitable temperature is also very important for phase separation. Therefore, to enhance extraction efficiency and thus enrichment factor, several parameters that affect the formation of metal–ligand complex and the CPE conditions were explained. Each optimization experiment was performed twice. Fifty milliliters of Cd(II), Pb(II), and Ni(II) standard solutions containing 10 μg L^{-1}, 50 μg L^{-1}, and 50 μg L^{-1} of the ions, respectively, were used during these optimization experiments. Then optimized conditions (given in Table 1) were used to analyze the metal ions of interest in certified reference materials and natural water samples.

2.1. Effect of pH

Extraction efficiency is dependent on the pH at which metal–ligand interactions occur.[15,16] The role of pH in the formation and extraction of metal–quinalizarin complex was studied by changing pH in the range of 3–11 while other parameters were set at their optimum values. To adjust the pH to the desired value appropriate buffer solutions were used. The results obtained are shown in the Figure. The extraction efficiency of each metal ion with quinalizarin into Triton X-114 was maximized and remained nearly constant at a pH value of around 8.0. The decrease in the absorbance value of metal ions at low pH may be because of the competition of hydrogen ions with target ions for the reaction with quinalizarin. Hence the optimum pH value was chosen as 8.0 for further studies.

Table 1. Optimum conditions for the CPE of Cd, Pb, and Ni ions.

Optimum conditions for CPE of Cd, Pb, and Ni	Value
Concentration of chelating agent	0.25% (w/v)
Concentration of surfactant	0.02% (v/v)
pH	8
Equilibrium temperature (°C)	70
Equilibrium time (min)	30
Centrifugation rate (rpm)	3000
Centrifugation time (min)	1
Diluent	0.1 mol L^{-1} HNO_3 in ethanol

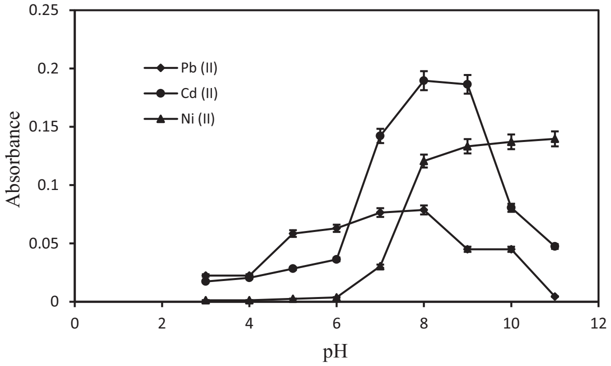

Figure. Influence of pH on the absorption of Cd, Pb, and Ni by CPE. Analyte concentration: 10 μg L^{-1} Cd(II), 50 μg L^{-1} Ni(II), and 50 μg L^{-1} Pb(II); Sample volume, 50 mL; surfactant, 0.02% Triton X-114; ligand, 0.25% Quinalizarin; dilution solvent, ethanolic HNO_3; equilibration temperature, 70 °C; equilibration time, 30 min.

2.2. Effect of amount of quinalizarin

The distribution ratio of the metal–ligand complex between micellar phase and aqueous phase determines the extraction efficiency of metal ions.[17] If the pH of the aqueous phase is kept constant, the distribution ratio and thus extraction efficiency improve by increasing complexing agent concentration. The effect of complexing agent amount on the extraction efficiency of the metal ions of interest was studied in the range of 0.05%–1.0% (w/v). According to the results obtained after optimization experiments, for all metal ions studied, the recovery value obtained increased with the increase in quinalizarin concentration up to 0.25%, and then remained constant, which indicates complete complexation. Therefore, 0.25% (w/v) quinalizarin concentration was chosen as the best value for subsequent experiments.

2.3. Effect of Triton X-114 concentration

Triton X-114 was used as extractant and the concentration of this surfactant affects both the extraction efficiency and the volume of the surfactant-rich phase. In order to obtain easy phase separation and maximum extraction efficiency the optimum amount of Triton X-114 should be determined.[18] For this purpose, the change in the analytical signal of the metal ion of interest within the Triton X-114 concentration range of 0.0%–0.5% (v/v) was studied. When the concentration of Triton X-114 was greater than 0.02% (v/v) extraction was quantitative.

It can be assumed that when the concentration was lower than 0.02% (v/v) the hydrophobic complex was not quantitatively entrapped by insufficient number of surfactant molecules. With an increase in Triton X-114 concentration above 0.20% (v/v), extraction efficiency decreases. This can be explained by increasing the volume and viscosity of the surfactant rich phase. Hence, a concentration of 0.02% (v/v) was chosen for subsequent experiments.

2.4. Effects of the equilibrium temperature and time

In order to achieve convenient phase separation with maximum efficiency, equilibration temperature and incubation time should be applied. To optimize the equilibration temperature and extraction time a series of experiments were performed in the range of 25–90 °C and 5–90 min, respectively. Based on the results obtained, 70 °C and 30 min were chosen as optimal.

2.5. Effect of viscosity

After performing CPE the extraction phase obtained has high viscosity, because of a very high concentration of Triton X-114. In order to make sample transfer to the FAAS nebulizer easy, the viscosity of the surfactant rich phase should be reduced. For this purpose, ethanol, methanol acetone, and acidic solutions of ethanol and methanol were tested in order to increase the analytical signals and sensitivity. The results proved that 500 μL of ethanol solution containing 0.1 mol L^{-1} nitric acid was the best choice. For conventional aspiration this amount of solution was sufficient to ensure a sufficient volume of sample. However, at smaller volumes, the reproducibility of the signals was very poor, and, for higher volumes, there was a decrease in the signal because of dilution.

2.6. Effect of salt addition

According to the literature, addition of salt to the CPE medium can lower the value of CPT and enhance the density of the surfactant rich phase, facilitating the separation of aqueous and surfactant rich phases.[19,20] To explore the ionic strength effect caused by the addition of salt on performance of CPE, a series of experiments were performed by adding different amounts of NaCl in the range of 0% and 4% (w/v) to each metal ion solution of interest. The results indicated ionic strength has no considerable effect upon extraction efficiency or sensitivity. This result is consistent with some studies in the literature.[10,21]

2.7. Effect of interfering ions

In order to explore the effects of possible matrix ions in natural water samples, several interfering ions were added individually to a solution containing 10 μg L^{-1} Cd(II), 50 μg L^{-1} Ni(II), and 50 μg L^{-1} Pb(II). A set of 50 mL of solutions containing varying amounts of interferent ions and the metal ion of interest was taken and the same CPE procedure was applied. If an added foreign ion caused ±5% variation in the absorbance value of analyte, it was considered an interfering species. The results obtained are summarized in Table 2. The table shows that the ions that usually exist in water samples do not interfere under the experimental conditions used.

2.8. Analytical features

Using the optimized conditions of the CPE procedure, calibration graphs prepared for cadmium (2.5–25 μg L^{-1}), nickel (5.0–200 μg L^{-1}), and lead (5.0–200 μg L^{-1}) were found to be linear. The enrichment factor, calculated as the ratio of the slope of calibration curves of the analyte after CPE to that of prior CPE, was 144 for cadmium, 92 for nickel, and 129 for lead. In order to prove the precision, the relative standard deviation (RSD), calculated for 10 replicate measurements from 50-mL sample solutions containing 10 μg L^{-1} Cd^{2+}, 50 μg L^{-1} Pb^{2+}, and 50 μg L^{-1} Ni^{2+}, was 4.3% (n = 10), 4.9% (n = 10), and 4.6% (n = 10), respectively. The limit of detection (LOD), defined as the concentration equivalent to three times the standard deviation ($3s$) of 10 measurements of the blank, was 1.8 μg L^{-1} for Cd^{2+}, 3.2 for μg L^{-1} Pb^{2+}, and 2.8 μg L^{-1} Ni^{2+}. The limit of quantification (LOQ) was defined as 10 times the standard deviation ($10s$) of 10 measurements. The LOQ was calculated as 5.8 μg L^{-1} for Cd^{2+}, 10.6 for μg L^{-1} Pb^{2+}, and 9.3 μg L^{-1} Ni^{2+}. Table 3 summarizes some analytical figures of the method.

Table 2. Effect of interfering ions on enrichment of 10 μg L^{-1} Cd(II), 50 μg L^{-1} Ni(II), and 50 μg L^{-1} Pb(II).

Interfering ion, M	Added as	[Cd^{2+}]:[M]	[Pb^{2+}]:[M]	[Ni^{2+}]:[M]
Na$^+$	NaNO$_3$	$> 1:5000$	$> 1:5000$	$> 1:5000$
NH$_4^+$	NH$_4$NO$_3$	$> 1:2000$	$> 1:2000$	$> 1:2000$
Ca^{2+}	CaCl$_2$	$> 1:2000$	1:1000	1:1000
Cd^{2+}	Cd(NO$_3$)$_2$	-	1:100	$> 1:2000$
Cu^{2+}	Cu(NO$_3$)$_2$	1:100	1:500	1:500
Pb^{2+}	Pb(NO$_3$)$_2$	1:100	-	1:100
Mn^{2+}	MnCl$_2$	$> 1:1000$	$> 1:2000$	$> 1:2000$
Zn^{2+}	Zn(NO$_3$)$_2$	1:1000	$> 1:2000$	1:2000
Co^{2+}	Co(NO$_3$)$_2$	$> 1:2000$	$> 1:2000$	1:1000
Ni^{2+}	Ni(NO$_3$)$_2$	$> 1:2000$	$> 1:2000$	-
Mg^{2+}	MgSO$_4$	$> 1:2000$	$> 1:2000$	1:2000
Sn^{2+}	SnCl$_2$	1:500	1:500	1:500
Al^{3+}	Al(NO$_3$)$_3$	1:1000	1:1000	1:1000
Fe^{3+}	Fe(NO$_3$)$_3$	$> 1:1000$	1:2000	$> 1:2000$
Cr^{3+}	Cr(NO$_3$)$_3$	1:1500	1:1000	1:1000
CH$_3$COO$^-$	NH$_4$CH$_3$COO	1:5000	1:5000	1:5000
Cl$^-$	NH$_4$Cl	1:1500	1:1000	1:2000
NO$_3^-$	KNO$_3$	1:1000	1:2000	1:2000
CO$_3^{2-}$	Na$_2$CO$_3$	1:1500	1:2000	1:1000
SO$_4^{2-}$	Na$_2$SO$_4$	1:5000	1:5000	1:5000

Table 3. Analytical characteristics of the method.

Parameter	Analytical feature		
	Cd	Pb	Ni
Enrichment factor	144	129	92
Sample volume, mL	50	50	50
Limit of detection, μg L^{-1} ($3s$)	1.8	3.2	2.8
Limit of quantification, μg L^{-1} ($10s$)	5.8	10.6	9.3
Precision RSD (%) (for 10 μg L^{-1} Cd(II), 50 μg L^{-1} Ni(II), and 50 μg L^{-1} Pb(II); n = 10)	4.3	4.9	4.6
Linear range, μg L^{-1}	2.5–50	5–200	5–200
Calibration equation	$A = 1.27 \times 10^{-2} C + 3.76 \times 10^{-2}$	$A = 9.94 \times 10^{-4} C + 1.14 \times 10^{-2}$	$A = 1.70 \times 10^{-3} C + 4.22 \times 10^{-2}$
Linear regression coefficient, R^2	0.9929	0.9815	0.9621

2.9. Accuracy of the method

In order to explore the performance of the study the CPE method was applied to two different reference materials, i.e. TMDA 51.3 (fortified water) and SPS-SW2 (surface water), for the assessment of Cd^{2+}, Pb^{2+}, and Ni^{2+} ions. The certified and calculated values for the analysis of certified reference materials are given in Table 4. The results given in Table 4 are the average of three parallel experiments. A t-test for 2 degrees of freedom and at the 95% confidence level showed that there was good agreement between the estimated content by the proposed method and the certified values for the analyte ions studied. Considering the results obtained one can conclude that the developed method is free from interferences of the various constituents and is successful for the quantitation of the metal ions studied.

Table 4. Determination of analyte ions in certified reference materials using the proposed methodology (n = 3).

CRM*	Ion	Certified (μg L^{-1})	Found (μg L^{-1})	Recovery %
SPS-SW2 (surface water)	Cd(II)	2.5	2.6 ± 0.1	104
TMDA 51.3 (fortified water)	Pb(II)	36.6	34.9 ± 0.3	95
TMDA 51.3 (fortified water)	Ni(II)	68.3	67.8 ± 0.3	99

*Certified reference material

2.10. Analysis of real samples

To evaluate the accuracy of the proposed study, recovery experiments were performed by spiking different water samples such as tap (Ankara, Turkey) and sea (Black Sea, Turkey) water samples. The results are given in Table 5 and 6. As can be seen from the tables, the recovery values for spiked water samples are quantitative.

Table 5. Determination of analyte ions in tap water samples using the proposed methodology (n = 3).

Ion	Added (μg L^{-1})	Found (μg L^{-1})	Recovery (%)
Cd(II)	-	1.6 ± 0.2	-
	10	11.9 ± 0.2	103
	25	27.5 ± 0.5	103
	40	39.8 ± 0.4	96
Pb(II)	-	11.8 ± 0.3	-
	5	16.5 ± 0.3	94
	10	22.1 ± 0.3	103
	50	61.8 ± 0.5	100
Ni(II)	-	29.8 ± 0.2	-
	5	34.3 ± 0.4	90
	10	39.6 ± 0.4	98
	50	78.1 ± 0.6	97

2.11. Comparison with the literature

As a type of coacervate-based extraction technique CPE is a simple, rapid, inexpensive, and nonpolluting methodology and because of these properties it is a great alternative to conventional preconcentration methods. The obtained high recoveries and low detection limits by the developed study provide an ideal occasion to preconcentrate trace metals in aqueous solutions. Table 7 gives a comparison of the proposed method with other CPE methods for the determination of Cd^{2+}, Pb^{2+}, and Ni^{2+} ions in the literature.[21–26] The obtained detection limits and enhancement factors by the proposed study are higher than those reported in the literature.

Table 6. Determination of analyte ions in sea water (Black Sea) samples using the proposed methodology (n = 3).

Ion	Added (μg L^{-1})	Found (μg L^{-1})	Recovery (%)
Cd(II)	-	4.6 ± 0.3	-
	10	14.9 ± 0.2	102
	25	28.4 ± 0.4	96
	40	44.1 ± 0.3	99
Pb(II)	-	35.3 ± 0.3	-
	5	39.8 ± 0.7	90
	10	44.7 ± 0.6	94
	50	83.7 ± 0.8	97
Ni(II)	-	38.5 ± 0.2	-
	5	43.3 ± 0.4	96
	10	47.9 ± 0.4	94
	50	88.8 ± 0.9	101

Table 7. Comparison of the characteristic data between recently published CPE methods and the presented method.

Reagent	Surfactant	Element	Sample volume (mL)	EF[a]	LOD[b] (μg L^{-1})	Sample	Ref.
Methyl Green	Triton X-114	Cd	9	13.5	3	Food	22
1-Phenylthio semicarbazide	Triton X-114	Pb	50	25	3.42	Food and drinks	23
1-(2-Pyridilazo)-2-naphthol	Triton X-114	Cd Ni	15	40 42	0.37 2.6	Water	24
Dithizone	Triton X-114, Octanol	Pb	40	39	4.3	Water	25
2,2'-Furyldioxime	Triton X-114, Octanol	Ni	25	45	0.6	Food	21
Dithizone	TX-114	Cd Ni	10	58 43	0.27 1.02	Water	26
Quinalizarin	Triton X-114	Cd Pb Ni	50	144 129 92	1.8 3.2 2.8	Water	This study

[a] Enrichment factor, [b] Limit of detection

3. Experimental

3.1. Instrumentation

A PerkinElmer (USA) model AAnalyst 800 Atomic Absorption Spectrometer equipped with deuterium background correction and an air/acetylene burner with 17 and 2 L min^{-1} flow rates was used for absorbance measurements. As a source, hollow cathode lamps were used. The working current/wavelength values for cadmium, lead, and nickel were 4 mA/228.8 nm, 10 mA/283.3 nm, and 25 mA/232.0 nm, respectively. A 0.2-nm slitwidth was used for all analytes. A Fisher Scientific Accumet 15 model pH meter was used for pH adjustments and a Clifton NE1-22 model thermostatic bath was used to heat solutions for CPE. A Hettich EBA 21 model centrifuge was used to facilitate the separation of phases.

3.2. Reagent and solutions

Standard stock solutions of 1000 mg L^{-1} Cd^{2+}, Pb^{2+}, or Ni^{2+} were separately prepared from $Pb(NO_3)_2$, $Cd(NO_3)_2 \cdot 4H_2O$, or $Ni(NO_3)_2 \cdot 6H_2O$ (Merck, Darmstadt, Germany) in deionized water. Diluted solutions of the metal ions of interest were prepared daily from standard stock solutions. Deionized water with a resistivity of 18.1 MΩ cm^{-1} was obtained from a Banstead, Nanopure Diamond purification system. The chelating reagent, 0.25% (w/v) quinalizarin, was prepared daily by dissolving the necessary amounts of quinalizarin (Merck Chemicals, Germany) in acetone. Triton X-114 (Sigma, St. Louis, MO, USA) was used without further purification. Phosphate buffer solutions (Merck Chemicals, Germany) were prepared and used for pH adjustment. For validation of the proposed method the certified reference materials TMDA 51.3 (fortified water, LGC, Teddington, UK) and SPS-SW2 (surface water, LGC) were used.

3.3. CPE procedure

For CPE, sample or standard containing 50 mL of solutions of the metal ions of interest was prepared and taken in a conical graduated tube. pH was adjusted to 8 using 2 mL of phosphate buffer. Next 250 μL of quinalizarin (0.25% m/v) and 500 μL of Triton X-114 (0.02% v/v) were added and mixed well with the aid of a vortex and kept in a thermostated bath at 70 °C for 30 min. Subsequently the tubes were centrifuged at 3000 rpm for 1 min to facilitate phase separation. After centrifugation the initial solution was divided into two phases: one of the phases was the analyte containing a small volume of surfactant rich phase and the other was the aqueous phase. Then, in order to obtain denser surfactant rich phase, the mixture was inserted into an ice bath. After the aqueous phase was carefully transferred with the aid of a pipette, 500 μL of ethanol containing 0.1 mol L^{-1} nitric acid was added to the surfactant rich phase to reduce its viscosity and the solution obtained was aspirated to FAAS for determination of the metal ions of interest.

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