

Cloud Point Extraction and Flame Atomic Absorption Spectrometric Determination of Cd(II) in Industrial and Environmental Samples¹

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Abstract—A micelle-mediated separation/preconcentration technique was used for the determination of trace Cd(II) in solid and liquid samples by flame atomic absorption spectrometry. Cadmium ions reacted with ammonium pyrrolidine dithiocarbamate to form a chelate that was extracted from aqueous medium by a non-ionic surfactant Tergitol NP-7 at pH 7. Values of pH, concentrations of ammonium pyrrolidine dithiocarbamate and Tergitol NP-7, temperature, incubation time, sample volume and matrix ions were optimized. The enrichment factor of the method was found to be 25, and the detection and quantitation limits were 1.5 and 3.8 µg/L, respectively. Assessment of the method was performed with a certified reference material, and the observed concentration of Cd(II) was in good agreement with the certified value. The method was also applied to the determination of Cd(II) in waters and industrial samples. Cd(II) concentrations in two industrial ZnO composite samples were determined between 59 and 69 µg/g.

Keywords: cadmium, cloud point extraction, flame atomic absorption spectrometry, Tergitol NP-7

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Heavy metals above their permissible concentrations are hazardous contaminants for waters and living organisms. Hazardous metals are environmentally persistent, non-biodegradable, toxic and accumulative. Cadmium is classified as a toxic metal even at very low concentration; it has destructive effects on the humans and nature. Various methods were developed for the separation and preconcentration of cadmium such as solid phase extraction (SPE) [1], cloud point extraction (CPE) [2] and liquid-liquid extraction (LLE) [3]. Among these methods, CPE is a safe, environmentally friendly, easy, fast, and inexpensive technique for separation/removal of harmful metal ions from aqueous media [4].

When the temperature rises above a certain point, surfactants form micelles, the solution becomes turbid and separates in two liquid phases. One of the phases is the surfactant-rich phase which includes micelles and analyte ions surrounded by micelles (micelles are capable to interact with many soluble analyte species in aqueous solutions) in a much smaller volume than the other phase. The other phase is aqueous solution [5, 6]. The target analytes surrounded by hydrophobic micelles can be separated at the bottom of a tube by centrifugation. It is known that ammonium pyrrolidine dithiocarbamate (APDC) forms stable complexes

with divalent metal cations such as Cd(II), Pb(II) and Cu(II) [7].

The aim of the study was to preconcentrate and determine cadmium in solubilized solid and liquid samples. For this purpose, Tergitol Type NP-7 (TNP7) non-ionic surfactant, an alkylaryl polyether alcohol, was used to entrap cadmium ions. Cadmium was complexed with APDC and extracted by pH-dependent cloud point extraction method. The TNP7 surfactant has not been used so far for the preconcentration of cadmium ions by cloud point extraction to our best literature survey.

EXPERIMENTAL

Chemicals and Reagents

TNP7 surfactant, APDC, metal nitrate salts, hydrochloric acid, nitric acid and methanol were purchased from Sigma-Aldrich (Germany). All chemicals were of analytical grade and used without further purification. Distilled water was used for preparation and dilution of stock solutions. Cd(II) stock solutions were prepared from the crystalline hydrate nitrate salt by dissolving in distilled water. Cadmium nitrate and other metal nitrates were dried in an oven before weighing.

¹ The article is published in the original.

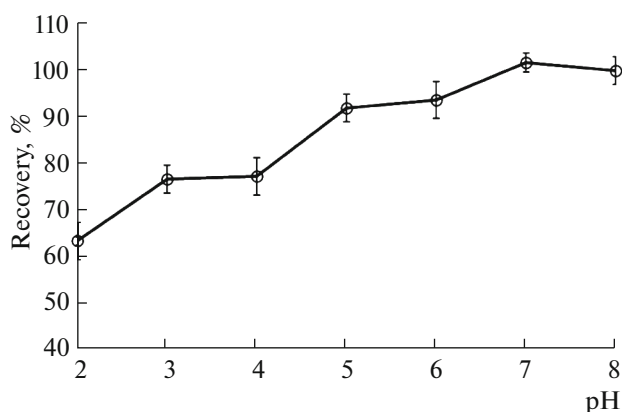


Fig. 1. Effect of solution pH on the recovery of Cd(II) ions ($n = 4$).

Apparatus

Absorbance measurements were performed using a Shimadzu AA-7000F (Japan) flame atomic absorption spectrometer equipped with deuterium background corrector. Air-C₂H₂ gas mixture was used with a flow rate of 1.8 L/min. 228.8 nm wavelength, 8 mA lamp current and 7 mm of burner height was employed. Berghof Speedwave II (Germany) microwave digestion was used to digest solid samples. Hanna HI-2211 (USA) model digital pH-meter was used to measure pH. A Nuve BM-402 (Turkey) temperature and time controlled digital thermostatic water bath was used to achieve desired temperature. Separation of micelle and aqueous phase was performed with using Nuve NF-400 (Turkey) centrifuge. A Velp RX3 (Italy) model vortex mixture was used to dissolve surfactant rich phase.

Cloud Point Extraction Method

1.4 mL of 1×10^{-3} M APDC solution, 1 mL of 0.8 $\mu\text{g/mL}$ Cd(II) stock solution and 1.2 mL of 2% (w/v) TNP7 solutions were mixed in a 50 mL polyethylene tube. The pH of the solution was adjusted to 7 by using digital pH-meter and adding 0.1 M ($\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$) buffer solution. The spiked solution was kept in a thermostatic water bath for 10 min at 25°C. After micelle formation, the mixture was centrifuged for 5 min at 4000 rpm. Aqueous phase was removed and surfactant rich phase was dissolved with 0.5 mL of 1.0 M HNO₃ in methanol by using a vortex mixer. This solution was transferred into a 2 mL volumetric glass and diluted to 2 mL by adding 1.0 M HNO₃. Cd(II) concentration of the final solution was determined by flame atomic absorption spectrometry (FAAS).

Preparation of Standard Reference Materials and Real Samples

Three water samples were prepared to determine their Cd(II) content. The tap water samples were taken from Nigde city drinking water pipeline network, the lake water samples were taken from Akkaya Lake Nigde. The wastewater samples were collected from a textile factory in Nigde. Water samples were filtered using filter paper, transferred to a 50-mL centrifuge tube, and the proposed extraction method was applied with and without adding cadmium. Solid standard reference material GBW 07310 (stream sediment) and two different zinc oxide samples collected from a zinc oxide production factory in Nigde were analyzed. A 0.50 g of oven-dried GBW 07310 sediment was weighed and 6 mL of concentrated HCl and 2 mL of concentrated HNO₃ were added to it. The samples were digested by using microwave digestion system. After digestion the samples were diluted to 25 mL with distilled water, pH values of the solutions were adjusted by buffer solutions and the proposed method was carried out. The zinc oxide samples were digested using the same procedure but after dilution to 50 mL with distilled water, only 0.5 mL of sample was analyzed.

RESULTS AND DISCUSSION

Effect of pH

Solution pH plays an important role both in the micelle formation of surfactant monomers and the formation and extraction of Cd-APDC complexes. Experiment was conducted in order to find out the optimum pH in the range of 2.0 to 8.0. Desired pH values were obtained by using appropriate buffer solutions. Results are given in Fig. 1. The results showed that the recovery values of Cd(II) enhanced up to pH 7.0. This value was selected as optimum for further experiments.

Effects of Other Variables

In our experiments the optimal values of solution temperature, surfactant and ligand concentration, incubation time and sample volumes were identified for quantitative separation and determination of Cd(II). The extraction procedure was applied by changing one variable at one time. In order to determine the optimum concentration of APDC which required for quantitative recoveries the ligand concentrations were changed and the results were given in Fig. 2.

The recovery of the metal ions increased with increasing concentrations of APDC and reached a constant value at 3.6×10^{-5} M APDC. This value was chosen as optimum for quantitative extraction of Cd(II) in further experiments.

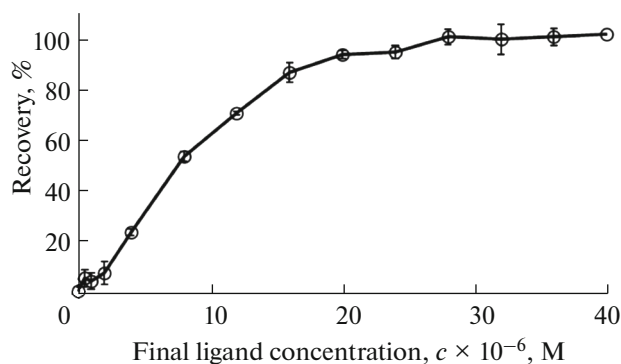


Fig. 2. Effect of APDC amount on the recovery of Cd(II) ions ($n = 4$).

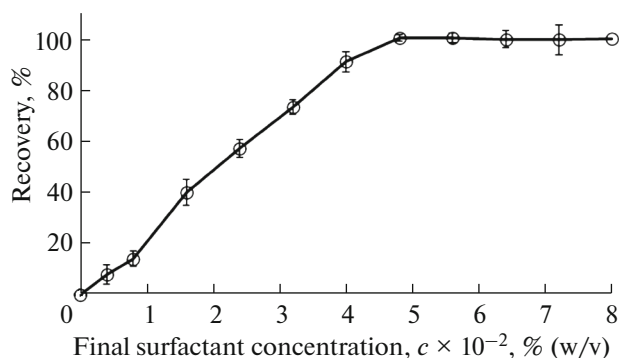


Fig. 3. Effect of surfactant concentration on the recovery of Cd(II) ions ($n = 4$).

One of the most important parameters in cloud point extraction for the preconcentration of metal complexes is the surfactant concentration. Figure 3 shows the effect of surfactant concentration on the recovery of Cd(II). Initially, the recovery values increased sharply with increasing surfactant concentration and then kept constant with its further increase. The obtained results showed that a surfactant concentration of 0.056% was sufficient to gain quantitative extraction of Cd(II) into the surfactant-rich phase.

The temperature was varied between 20 and 50°C. Because of low cloud point temperature of the TNP7 surfactant, the micelle formation was successfully completed, and recoveries were quantitative at all temperatures. So, temperature of 25°C was chosen as optimum.

The incubation time was investigated between 5–50 min. The results were quantitative even after 10 min of incubation time. For more than ten minutes no considerable difference was observed in terms of quantitative recoveries.

Limitation on the centrifuge volume allowed to treat up to 50 mL of sample solution at a time. Three total sample volumes were investigated: 10, 25 and 50 mL. The obtained recovery values for Cd(II) (%) were 99 ± 2 , 99 ± 2 and 97 ± 1 , respectively. A preconcentration factor of 25 could be gained for 50 mL sample, and further all experiments were conducted at 50 mL.

Effect of Matrix Ions

The effects of different cations and anions on the FAAS signal of cadmium and the selectivity of the method was investigated. The CPE procedure was performed in the presence of these ions. Table 1 shows tolerance limits of each interfering ion and recovery values. Table 2 indicates that most of the coexisting ions did not show a serious effect on the separation and determination of Cd(II). The interference of some cations in high intereferent-to-ana-

lyte ratios could be avoided by increasing the ligand concentration in the preconcentration step [8]. The results supported that the developed CPE method may be considered as reasonably selective for extraction of cadmium at pH 7.

Table 1. Effect of inorganic ions on the recovery of cadmium ($n = 4$)

Ion	Added species	Tolerance ratio	Recovery, % ^a
Na ⁺	NaNO ₃	1.25×10^4	98 ± 4
K ⁺	KNO ₃	1.25×10^4	95 ± 4
Ca ²⁺	Ca(NO ₃) ₂ · 4H ₂ O	1250	99 ± 2
Mg ²⁺	Mg(NO ₃) ₂ · 6H ₂ O	1250	102 ± 2
Ni ²⁺	Ni(NO ₃) ₂ · 6H ₂ O	125	100 ± 2
Co ²⁺	Co(NO ₃) ₂ · 6H ₂ O	125	98 ± 3
Pb ²⁺	Pb(NO ₃) ₂	1250	107 ± 1
Cu ²⁺	Cu(NO ₃) ₂ · 3H ₂ O	1250	98 ± 2
Zn ²⁺	Zn(NO ₃) ₂ · 6H ₂ O	125	109 ± 2
Bi ³⁺	Bi(NO ₃) ₃ · 5H ₂ O	125	98 ± 5
Fe ³⁺	Fe(NO ₃) ₃ · 9H ₂ O	125	98 ± 5
Cr ³⁺	Cr(NO ₃) ₃	1250	105 ± 3
Al ³⁺	Al(NO ₃) ₃ · 9H ₂ O	1250	106 ± 2
Cl ⁻	NaCl	1.25×10^4	98 ± 4
NO ₃ ⁻	NaNO ₃	1.25×10^4	95 ± 4
NO ₂ ⁻	NaNO ₂	1250	106 ± 2
SO ₄ ²⁻	Na ₂ SO ₄	1250	107 ± 2
PO ₄ ³⁻	Na ₃ PO ₄	1.25×10^4	98 ± 3

^aMean \pm standard deviation; Cd(II) amount 0.8 μ g.

Table 2. Recent cadmium extraction and determination methods using cloud point extraction

Detection system	Surfactant	Metals determined	Ligand	Incubation	LOD, $\mu\text{g/L}$	LDR, $\mu\text{g/mL}$	PF	Reference
FAAS	Tween 80	Cd, Cr, Pb, Cu, Ni, Bi	Ligandless	60 min at 60°C	1.7	0.2–2	10	[9]
UV-Vis	Triton X-114	Cd	VBB	15 min at 45°C	3.8	0.01–0.5	24	[10]
FAAS	Triton X-114	Cd	BIMPI	20 min at 55°C	3.5	0.034–1.67	33	[11]
FAAS	Triton X-114	Cd	Ligandless	20 min at 60°C	1.0	0.003–0.3	5	[12]
FAAS	Triton X-114	Cd, Pb, Pd, Ag	BIES	10 min at 50°C	1.4	–	30	[13]
GF-AAS	Triton X-114	Cd, Pb	DDTP	20 min at 50°C	6.0	–	129	[14]
FAAS	Triton X-114	Cd	DDTP	15 min at 40°C	0.9	0.003–0.4	–	[15]
FAAS	Triton X-114	Cd	TTDM	25 min at 65°C	2.0	0.007–0.33	25.6	[16]
FAAS	Tergitol NP-7	Cd	APDC	10 min at 25°C	1.5	0.09–1.4	25	Present study

Notations: PF—preconcentration factor, LDR—linear dynamic range, UV-Vis—ultraviolet-visible spectrophotometer, GF—graphite furnace, VBB—victoria blue B, BIES—bis((1H-benzo [d] imidazol-2yl)ethyl) sulfane, DDTP—O,O-diethylthiophosphate, BIMPI—2-((2-((1H-benzo[d]imidazole-2yl)methoxy)phenoxy)methyl)-1Hbenzo[d]imidazole, TTDM—3,3',3'',3'''-tetraindolyl(terephthaloyl)dimethane.

Analytical Performance of the Method

The analytical performance of CPE method coupled with FAAS was determined at optimal conditions. The results revealed that the linear dynamic range of the method was linear with a correlation coefficient (R^2) of 0.9988 at the concentration range of 0.0038–1.4 $\mu\text{g/mL}$ of Cd(II). The equation of the line

for Cd(II) was $A = 0.2448c + 0.0033$, where A is the absorbance and c is the concentration of cadmium in $\mu\text{g/mL}$ in the final solution. The limits of detection and quantification were calculated as the concentration equivalent to three and ten times the standard deviation ($n = 20$) of the blank solutions for LOD (1.5 $\mu\text{g/L}$) and LOQ (3.8 $\mu\text{g/L}$), respectively. The relative standard deviation was 5.5% at 16 $\mu\text{g/L}$ of Cd(II)

Table 3. Analysis of real samples ($n = 4$)

Sample	Added Cd, μg	Found Cd, μg	Recovery, %	Content, $\mu\text{g/g}$
Standard reference material GBW 07310	1.12*	1.15 ± 0.06	103 ± 6	1.12
ZnO composite I	–	0.30 ± 0.02^a	–	59 ± 4
	0.25	0.55 ± 0.02	100 ± 4	–
	0.50	0.79 ± 0.03	99 ± 4	–
ZnO composite II	–	0.35 ± 0.03	–	69 ± 6
	0.25	0.61 ± 0.02	102 ± 3	–
	0.50	0.87 ± 0.03	103 ± 3	–
Wastewater from leather industry	–	ND**	–	ND
	0.40	0.40 ± 0.04	106 ± 3	–
	0.80	0.84 ± 0.02	105 ± 3	–
Tap water	–	ND	–	ND
	0.40	0.40 ± 0.02	99 ± 5	–
	0.80	0.82 ± 0.02	103 ± 3	–
Lake water	–	ND	–	ND
	0.40	0.38 ± 0.01	95 ± 3	–
	0.80	0.77 ± 0.01	97 ± 1	–

* Certified value.

** Not detectable.

($n = 10$). The preconcentration factor of the method as a ratio of the highest sample volume to the lowest volume was equal to 25.

A comparison of the investigated CPE method with some of recent reported studies for Cd(II) by different CPE procedures is given in Table 2. The proposed CPE method exhibits better or comparable analytical characteristics with some of those studies.

Advantages of the Method

Tergitol NP-7 (a surfactant with low cloud point temperature) enabled improving and expanding the analytical performance of the traditional CPE technique by shortening the times of micelle formation, equilibrium and analysis. Analytical characteristics of the method are comparable with other studies. Moreover, as TNP7 has the lowest cloud point temperature among the common surfactants, the method is less energy consuming. In addition, surfactant micelles appear in as little as 5 min incubation time, which saves energy and time.

Analysis of Certified Reference Material and Real Samples

The procedure was validated by applying it to standard reference material GBW 07310 (stream sediment). The result was in good agreement with the certified value. Cadmium concentrations of three real water samples and two industrial solid samples were determined by the proposed CPE method (Table 3).

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