

# A Strategy Based on the Dispersive Liquid-Liquid Microextraction of Cadmium in Environmental Samples Prior to Its Determination by Flame Atomic Absorption Spectrometry

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## INTRODUCTION

Our environment is becoming ever more polluted by heavy metals due to advances in industry, rapid population growth, and urbanization. This leads to land, water, and soil pollution, which in turn is negatively impacting living organisms (1). Within this context, identifying heavy metals in environmental samples has become one of the most important subject areas within analytical chemistry. One of the single most dangerous and toxic heavy metals is cadmium (Cd) (2). Sources of cadmium within our environment include cadmium-based paints, cigarette smoke, and plastic products (as an additive) (3). The by-products of these industrial activities pollute natural water sources and ultimately, cadmium enters the human body. Cigarette smoke enters the lungs, and then circulates into the bloodstream and throughout the rest of the body. Cadmium leads to serious damage of renal tissue and renal capillary vessels and is a cause of osteoporosis by damaging bone tissue (4-6). Cadmium furthermore is known to cause various other health problems such as stomach aches, vomiting, the breakage/decay of bones, reproductive issues, infertility, both nervous and immune system damage, mental health issues, and damage to the DNA, and cancer (especially of the lungs) (7, 8).

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## ABSTRACT

A simple method was developed by combining dispersive liquid-liquid microextraction (DLLME) and flame atomic absorption spectrometry (FAAS). For the pre-concentration of trace amounts of cadmium, a new complexation chelate of 2-[(4-phenylpiperazine-5-thioxo-4,5-dihydro-1,3,4-oxadiazole-2-yl)methyl]-5-methyl-4-[2-(1H-indole-3-yl)ethyl]-2,4-dihydro-3H-1,2,4-triazole-3-one (PPTOMDT) was used and mixed with the solvents of chloroform and methanol. The mixture of the extraction solutions was then directly injected into an aqueous solution containing Cd<sup>2+</sup> ions. After centrifugation, the settled phase was diluted with 500 µL of ethanol/nitric acid and aspirated into the FAAS. The limit of detection (LOD) was found at 0.69 µg L<sup>-1</sup> under optimum conditions. The relative standard deviation (RSD) for 15 replicates at a 3.75 µg L<sup>-1</sup> Cd<sup>2+</sup> concentration level was 3.21%. The calibration plot was linear within the range of 2.5–15 µg L<sup>-1</sup> of Cd<sup>2+</sup>. After the analytical characteristics were determined, the CRM-TMDW-500 Drinking Water and CRM-SA-C Sandy Soil C, both certified reference materials, were analyzed in order to validate the method. The application of the DLLME method has been successfully tested for the determination of cadmium in solid and liquid samples. The recoveries of the spiked sample ranged between 92-96%.

This means that being informed of cadmium concentrations in environmental samples is of utmost importance. The United States Environmental Protection Agency (EPA) has stated the maximum containment level of cadmium in drinking water to be 5.0 µg L<sup>-1</sup> (9). Inductively coupled plasma mass spectrometry (ICP-MS) (10) and graphite furnace atomic absorption spectrometry (GFAAS) (11) are the two techniques used to determine cadmium. However, these techniques are rather expensive. Consequently, flame AAS (FAAS) is a preferred means of designating cadmium and is comparatively lower in cost, faster, and easy to use (12, 13).

However, the matrix is a challenge for all spectroscopic techniques (14). In order to resolve this problem, separation and enrichment-based methods are applied which aim to conveniently change the analyte by collecting it within a lower volume. To date, several enrichment methods have been developed and modified in combination with AAS. Among these, solid phase extraction (SPE) (15), co-precipitation (16), and cloud point extraction (17) are commonly used. But, these methods require the use of a significant amount of chemicals and are very time-consuming, the solvents are going to waste and release secondary waste (from excess quantities) into the environment.

In recent years, a shift has started towards microextraction

methods that lower their consumption of organic solvents to an utmost minimum, simplify the steps involved in preparing the samples, have a high rate of evaporation, and are convenient for automation (18). Liquid-phase microextraction (LPME) (19), single-drop microextraction (SDME) (20), solid phase microextraction (21), and dispersive liquid-liquid microextraction (DLLME) can be included within these methods. Of these extraction procedures, DLLME is an especially simple and fast method and was first developed in 2006 by Rezaee and his team in order to determine organic types (22). As of late, its use has been expanded to also determine inorganic types (23).

DLLME is a solvent-based extraction method that has been modified by shrinking the extraction phase rates. When solvents are of significantly heavier water and non-mixed with water such as chlorobenzene, carbon tetrachloride and tetrachloroethylene are used as an extraction solvent, polar solvents mixed with water such as acetone, ethanol, MeOH, and ACAN are used as diffusion solvents (24). In this method, both a dispersive liquid as well as an extraction liquid mixed with water are rapidly poured into the solvent. This produces a cloudy solvent in which the analyte ions become enriched within the extraction solvent (25). This method's simplicity, efficiency in terms of time and cost, low sample volume, and high preconcentration factor are among the most important advantages diffusion-based liquid-liquid microextraction carries (26).

In this study, DLLME has been refined to accurately determine cadmium ions in solid and aqueous environmental samples. This approach is reported for the very first time and uses a 2-[(4-phenylpiperazine-5-thioxo-4,5-dihydro-1,3,4-oxadiazole-2-yl)methyl]-5-methyl-4-[2-(1H-indole-3-yl)ethyl]-2,4-

dihydro-3H-1,2,4-triazole-3-one (PPTOMDT) compound substance as a complexation agent in order to convert cadmium ions into an organic phase. All experimental parameters have been carefully optimized in order to obtain the highest possible recovery.

## EXPERIMENTAL

### Instrumentation

A PerkinElmer® AAnalyst™ 400 flame atomic absorption spectrometer, equipped with deuterium background correction, was used for the experiments (PerkinElmer, Inc., Shelton, CT, USA). A cadmium hollow-cathode lamp was used. The air-acetylene flame flow rate was set between 2.5 and 17 L min<sup>-1</sup> for the conventional working parameters. The instrumental operating parameters are listed in Table I.

The absorption spectra of the synthesized reagent were read using a Specord 210 Plus model spectrophotometer (Analytik Jena AG, Jena, Germany). A Merck-Millipore® Direct-Q® 8UV system was used to obtain ultrapure water (Merck, Germany). The pH values were measured with a Hanna 211 pH meter (Sigma-Aldrich Chemie GmbH, Germany). Digestion of the samples was performed using a Milestones Ethos D (Milestone Inc., Italy) with a closed vessel microwave system. A Sigma 3-16P model centrifuge (Sigma Laborzentrifugen GmbH, Germany) was used to form the sediment phase.

**TABLE I**  
**FAAS Instrumental Operating Conditions for Cadmium**

Element	Cd
Wavelength	228.8 nm
Slit Width	1.5 nm
Lamp Current	6 mA

## Chemicals and Solutions

In order to prepare each of the solutions for the experiments, ultrapure water was used. For cadmium, stock solutions were prepared daily from a 1000-mg L<sup>-1</sup> standard cadmium solution (Merck, Darmstadt, Germany). Acetic acid/sodium acetate buffer (0.1 mol L<sup>-1</sup>, pH 6.5) was used for pH adjustment. The other chemicals used include carbon tetrachloride, chloroform, dichloromethane, and carbon disulphide (each as extraction solvents) as well as ethanol, methanol, acetone, and acetonitrile as a disperser solvent, all obtained from Merck, Germany. The PPTOMDT compound was synthesized in accordance with the scientific literature at Karadeniz Technical University's Organic Chemistry Research Laboratory (27). The chelating agent, 0.2 g/50 mL PPTOMDT solution in dimethyl sulfoxide/methanol (1:4), was prepared and then stored in a dark bottle.

The steam, sea, and tap water samples, collected from the Turkish province of Trabzon, were kept in polytetrafluoro-ethylene (PTFE) containers. In order to block metallic ions from breaking down, the water samples were acidified with nitric acid before analysis. The liquid samples were stored in the dark at 4 °C after being filtered with a 0.45 µm pore-size membrane. The certified reference materials CRM-SA-C Sandy Soil and CRM-TMDW-500 Drinking Water (High-Purity Standard Inc., Charleston, SC, USA) were used for DLLME method validation.

## Procedure

An amount of 20 mL of a solution containing 3.75 µg L<sup>-1</sup> of cadmium was stored in a plastic tube, calibrating its pH to 6.5. Then, a mixture of 1000 µL of methanol, 250 µL of chloroform, and 0.5 mg of PPTOMDT (% 0.4 m/v, 125 µL) was swiftly poured into the solu-

tion, which formed a white cloudy solution. The solution was then centrifuged for 3 minutes at 3000 rpm. By doing this,  $\text{Cd}^{2+}$  ions form a complex with the PPTOMDT compound upon entering a chloroform phase. After the decantation procedure, the obtained organic phase (to which 0.5 mL of  $\text{HNO}_3$  was added), the Cd concentration was determined by FAAS. The same DLLME method was also performed for the blank solutions. All experimental measurements were repeated three times.

### Preparation of the Samples

Water samples in 20 mL amounts (stream, sea, spring, and tap) were collected from different parts of Trabzon, Turkey. The water samples were filtered through a 0.45- $\mu\text{m}$  micropore membrane filter, an appropriate amount of acetate buffer was added to adjust the pH to 6.5, and the DLLME procedure was applied. Commercial solid samples were purchased from a local market. With the aim of getting a cadmium content response, 0.45 g amounts of dried rice, noodles, cracked wheat, black tea, ground coffee, tobacco leaves, and cigarettes as well as a plastic toy weighing 0.20 g were stored by weight in sensitive Teflon<sup>®</sup> containers. Then 8.0 mL of concentrated nitric acid as well as 2.0 mL of  $\text{H}_2\text{O}_2$  were added to break down each of the samples. Digestion was performed using a microwave system with a maximum pressure of 46 bar, maximum temperature of 300 °C, and 650 W of electric power. Twenty minutes were allowed for cooling time. After the digestion process, the solutions were evaporated to near dryness. The remnants were filtered through blue filter paper and the samples diluted to 25 mL (stock solutions) with ultra-pure water for each solid sample. The stock solutions were diluted two-fold for the plastic toy and four-fold for the remaining solid samples

before analysis. The diluted samples were then analyzed using the proposed procedure as mentioned in the "Procedure" section.

### Preparation of CRMs

In order to confirm the accuracy of the developed method, CRM-SA-C Sandy Soil C and CRM TMDW-500 Drinking Water were used. Portions (0.10 g) of CRM-SA-C Sandy Soil C were transferred into a Teflon vessels, and a mixture of 3.5 mL of  $\text{HNO}_3$ , 3.5 mL of  $\text{HCl}$ , 1.0 mL of  $\text{HF}$ , and 1.0 mL of  $\text{H}_2\text{O}_2$  was added. After digestion, the solutions were heated to near dryness. Then, the solutions were cooled, diluted to 20 mL volume with deionized water in a calibrated flask, and the pH adjusted to 6.5. Then, the obtained solutions were analyzed following the experimental procedure listed above. This procedure was also used to analyze the drinking water reference samples.

## RESULTS AND DISCUSSION

Several parameters were examined in terms of what affects the cadmium ion recovery values. In order to obtain a high extraction recovery, the main analytical parameters affecting the complex formation between the PPTOMDT and the cadmium are summarized below. After each of the values was optimized, a calibration graph for the method was created and applied successfully to the liquid and the solid samples.

### Characterization of the Complex

The influence of the  $\text{Cd}^{2+}$  ions on the spectroscopic properties of the complex formed by the PPTOMDT was also studied. First, a  $6.0 \times 10^{-5}$  mol  $\text{L}^{-1}$  solution was prepared in order to dissolve the PPTOMDT compound in methanol-dimethyl sulfoxide (24.0/1.0 mL). Then,  $6.0 \times 10^{-4}$  mol  $\text{L}^{-1}$  was calibrated for the cadmium ion solution. A

total volume of 4 mL was mixed together by using 2.0 mL from each of the two prepared solutions. For a 4.0-mL mixture containing 10 mol  $\text{L}^{-1}$  equivalents of the metal, the absorbance was measured using a 1 cm long absorption cell in the Specord 210 Plus model spectrophotometer (Analytik Jena AG, Jena, Germany).  $\text{Cd}^{2+}$  ions found in the PPTOMDT compound are shown in Figure 1. An absorbance value decrease between 250 and 350 nm in terms of the presence of metal in the compound was discovered.

The mole ratio method was applied for the determination of the stoichiometric ratios of PPTOMDT with  $\text{Cd}^{2+}$  (28). Figure 1b shows the molar-ratio plot for  $\text{Cd}^{2+}$ . The absorption decrease was observed at 270 nm with an increase in the  $\text{Cd}^{2+}$  ion concentration.  $A_0$  and  $A$  are the absorbance of free ligand and absorbance of the solution involving  $\text{Cd}^{2+}$  cation, respectively. The inflection point was 0.5 ( $[\text{Cd}^{2+}]/[\text{L}]$ ). It can thus be concluded that PPTOMDT formed a stable 1:2 (M:L) complex with  $\text{Cd}^{2+}$ .

### Effect of pH

The pH plays a substantial role on the formation of the metal chelate and its subsequent extraction (5, 29). By increasing the pH of the solutions, different molecular forms of metallic species with neutral, anionic, or cationic character are formed. These hydrolysis products formed in the solution help to select the optimum pH and/or suitable pH working range (30). The influences of pH on the extraction of cadmium from both the water as well as the solid samples were studied within the 2.0–10.0 range using phosphate, acetate, and ammonium chloride as the buffer solutions. Figure 2 shows the effect of pH on the extraction of  $\text{Cd}^{2+}$ . The sharp increase in the recovery values of the cadmium ion in the range of pH

2 to 5 indicates that increasing the pH has a high effect on the enrichment method. The extraction efficiency maximum pH is 6-7 (92%). Interactions between the positively charged metal ions and the ligand will increase with an increase in pH. Because the relevant functional groups are completely deprotonated, the negative charge density on the ligand surface increases and thus the recovery efficiency of the metal ions increases (Figure 2). The metal-ligand interaction is probably less efficient at low pH values

owing to proton competition with cadmium. Therefore, pH 6.5 was selected for further study.

### Influence of the Amount of PPTOMDT

The effect of the amount of PPTOMDT (0.2 g/50 mL) on the preconcentrated cadmium was studied using various volumes of the reagent ranging from 50.0 to 175.0  $\mu\text{L}$ . The results are shown in Figure 3. The extraction efficiency was stable when the PPTOMDT

concentration was higher than 0.4 mg (100  $\mu\text{L}$ ), indicating complete complexation. Thus, the amount of 0.5 mg (125  $\mu\text{L}$ ) PPTOMDT was selected as the best choice for subsequent experiments.

### Effect of Type and Volume of the Disperser Solvent

The selection of an appropriate disperser phase is crucial in DLLME. The selection of the disperser solvent is based on the miscibility of the solvent in both

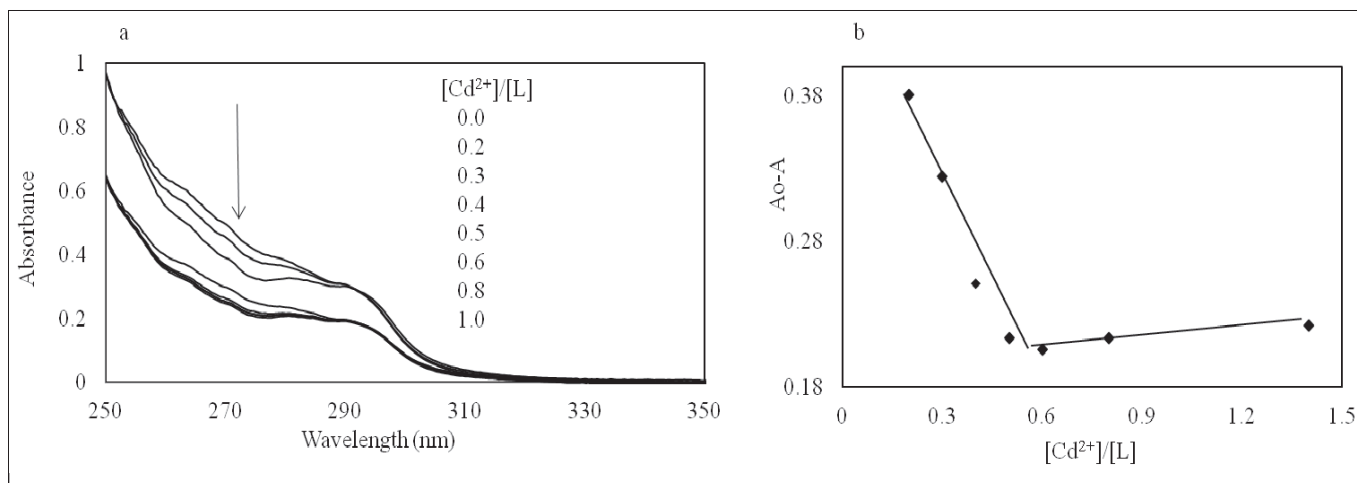


Fig. 1 (a and b). Absorption spectra of the PPTOMDT (a) and its complex stoichiometry with  $\text{Cd}^{2+}$ , (b), Insets: Measurements were obtained at 270 nm.

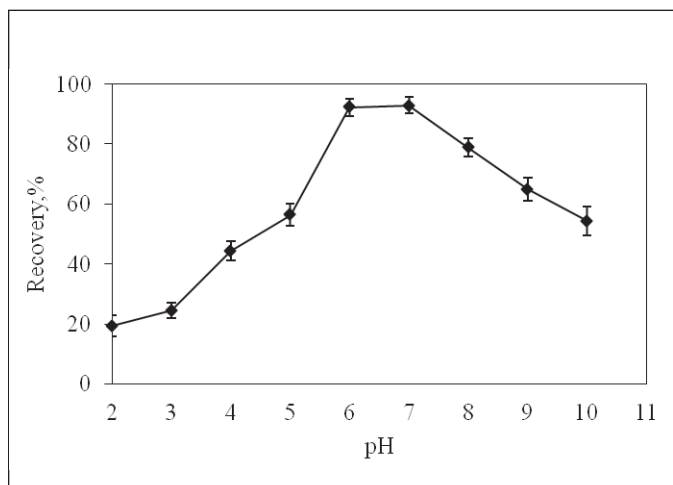


Fig. 2. The effect of pH on the preconcentration of cadmium using DLLME. Amount of chelating agent: 125  $\mu\text{L}$ , 0.4% (w/v); sample volume: 20.0 mL ( $3.75 \mu\text{g L}^{-1} \text{Cd}^{2+}$ ); volume of  $\text{CHCl}_3$ : 250  $\mu\text{L}$ ; volume of methanol: 1000  $\mu\text{L}$ ; ( $n=3$ ).

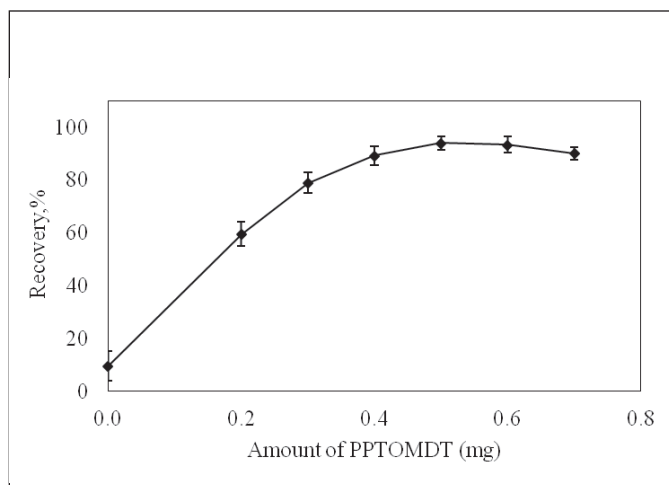


Fig. 3. Effect of amount of the PPTOMDT: Sample volume: 20.0 mL ( $3.75 \mu\text{g L}^{-1} \text{Cd}^{2+}$ ); pH: 6.5; methanol: 1000  $\mu\text{L}$ , ( $n=3$ ).

the aqueous phase (sample solution) and the extraction solvent. For this purpose, different solvents were tested, including methanol, acetonitrile acetone, ethanol, and tetrahydrofuran. A series of sample solutions were studied using 1000  $\mu\text{L}$  of each disperser solvent containing 250  $\mu\text{L}$  of chloroform ( $\text{CHCl}_3$ ). The maximum extraction recovery was obtained using methanol (Figure 4a).

The disperser solvent volume can directly affect both the formation of the extraction efficiency and the degree of the dispersion of the extraction solvent in the aqueous phase. For this purpose, the effects of methanol were investigated in the range of 200–2000  $\mu\text{L}$  at the constant volume of chloroform (extraction solvent). The results showed that the cloudy suspension of droplets did not form well at lower volumes of methanol, resulting in a decrease in extraction efficiency. The extraction efficiency increased slightly upon increasing the volume of methanol from 200 to 1200  $\mu\text{L}$  (Figure 4b). It is clear that by increasing the volume of methanol, the solubility of the

complex in water increased. The amount of 1000  $\mu\text{L}$  of methanol ( $93.5\% \pm 2.5$ ) was thus employed to extract cadmium from the aqueous samples.

#### Effect of Type and Amount of Extraction Solvent

The volume and type of extraction solvent are important to the DLLME process. The extraction solvent should have a higher density than of water, an extraction capability for compounds of interest, and low solubility in water. The effects of certain solvents including carbon tetrachloride, chloroform, carbon disulfide, and dichloromethane were tested and examined using the 20-mL cadmium solution with a  $3.75 \mu\text{g L}^{-1}$  concentration. The results are provided in Figure 5a. Chloroform was found to provide a higher extraction efficiency.

The influence of the extraction solvent volume was investigated in the 100–400  $\mu\text{L}$  range. The extraction efficiency reached from 61% to 96% with an increase in volume of chloroform from 100 to 200  $\mu\text{L}$ . Consequently, in subsequent stud-

ies, 250  $\mu\text{L}$  chloroform was chosen to extract the cadmium from the aqueous samples (Figure 5b).

#### Volume of Sample Solution

The volume of the sample solution is another important factor in obtaining a high enrichment factor from the DLLME-based preconcentration. The effects of the sample volume on the cadmium recovery values were investigated while keeping other conditions constant. For this purpose, at optimum conditions, 0.075  $\mu\text{g}$  of cadmium was extracted at the range between 10.0 and 50.0 mL. The extraction efficiency was observed to be constant up to 20.0 mL. Then, by increasing the volume of the sample from 20.0 mL to 50 mL, the extraction efficiency decreased. Therefore, 20.0 mL ( $96.7\% \pm 2.6$ ) was used as the optimum sample volume. During the analysis of both the model solution and the real water samples, the final sample volume was 0.5 mL. Since the analyte was concentrated 40 times (from 20.0 mL to 0.5 mL), the enrichment factor was 40.

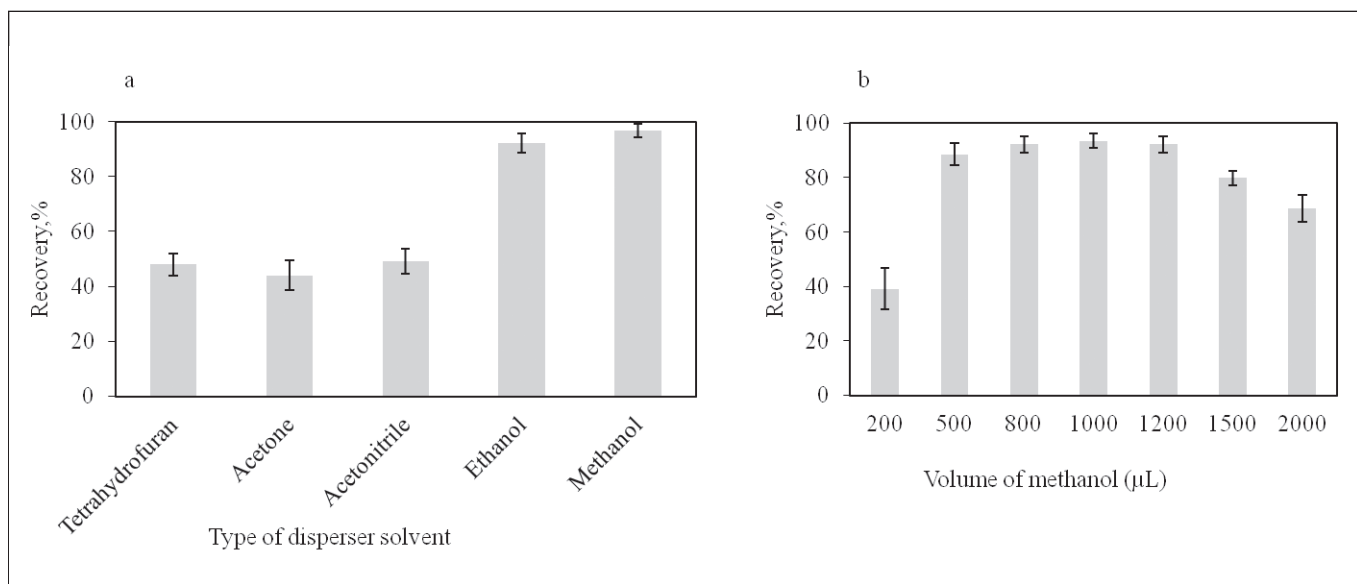


Fig. 4 (a and b). The effect of type of disperser solvent (a) and volume of methanol (b): Sample volume: 20.0 mL ( $3.75 \mu\text{g L}^{-1} \text{Cd}^{2+}$ ); pH: 6.5; amount of chelating agent: 125  $\mu\text{L}$ , 0.4% (w/v); volume of methanol: 1000  $\mu\text{L}$ , ( $n=3$ ).

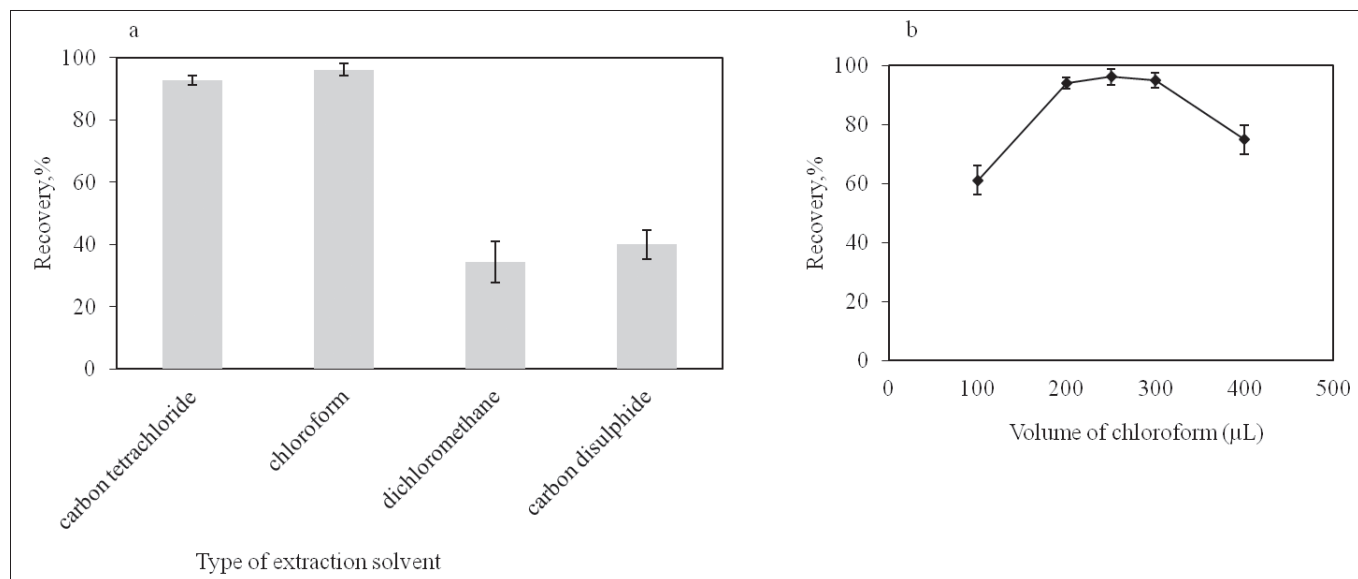


Fig. 5. The effect of type of extraction solvent (a) and volume of  $\text{CHCl}_3$  (b): Sample volume, 20.0 mL ( $3.75 \mu\text{g L}^{-1} \text{Cd}^{2+}$ ); pH, 6.5; amount of chelating agent: 125  $\mu\text{L}$ , 0.4% (w/v); volume of methanol: 1000  $\mu\text{L}$ , ( $n=3$ ).

### Effect of Foreign Ions

Environmental samples usually have a complex matrix system. These matrix systems in the sample may affect the recovery of the analyte. Therefore, the effect of foreign ions was examined by using the model solutions containing a fixed quantity of  $\text{Cd}^{2+}$  ion and different interfering ions as listed in Table II. In these experiments, 20.0-mL solutions containing 0.075  $\mu\text{g}$  of cadmium as well as various amounts of interfering ions were treated according to the recommended procedure. As shown in Table II, there is no important interference from the foreign ions in the environmental samples for the determination of cadmium.

### Analytical Performance

The proposed method was evaluated under the selected experimental conditions by controlling the calibration range, limit of detection (LOD), and precision. Linearity was observed over the range of 2.5–15.0  $\mu\text{g L}^{-1}$  with a correlation coefficient ( $R^2$ ) of 0.9962. The limit of detection (LOD) is determined by utilizing both the measured limit

of the blank (LOB) and the test replicates of a sample known to contain a low concentration of the analyte (Eq. (1)) (31). The mean and Standard deviation (SD) of the low concentration sample is then calculated according to the following equations:

#### Eq. 1

$$\text{LOD} = \text{LOB} + 1.645 (\text{SD low concentration sample})$$

The LOB is estimated by measuring replicates of a blank sample and calculating the mean result and the SD (see Eq. 2).

**TABLE II**  
Effect of Some Foreign Ions on the Recovery of  $3.75 \mu\text{g L}^{-1} \text{Cd}^{2+}$  ( $n=3$ )

Ion	Added as	Concentration ( $\text{mg L}^{-1}$ )	Recovery (%)
$\text{Na}^+$	NaCl	15000	$94 \pm 3$
$\text{K}^+$	KCl	5000	$93 \pm 2$
$\text{Ca}^{2+}$	$\text{CaCl}_2$	500	$93 \pm 2$
$\text{Mg}^{2+}$	$\text{Mg}(\text{NO}_3)_2$	300	$94 \pm 2$
$\text{Ba}^{2+}$	$\text{BaCl}_2$	20	$95 \pm 2$
$\text{Mn}^{2+}$	$\text{Mn}(\text{NO}_3)_2$	10	$95 \pm 3$
$\text{Zn}^{2+}$	$\text{Zn}(\text{NO}_3)_2$	10	$94 \pm 1$
$\text{Al}^{3+}$	$\text{Al}(\text{NO}_3)_3$	15	$96 \pm 2$
$\text{Pb}^{2+}$	$\text{Pb}(\text{NO}_3)_2$	10	$95 \pm 2$
$\text{Cu}^{2+}$	$\text{Cu}(\text{NO}_3)_2$	5	$95 \pm 2$
$\text{Fe}^{3+}$	$\text{Fe}(\text{NO}_3)_3$	15	$94 \pm 2$
$\text{Ni}^{2+}$	$\text{Ni}(\text{NO}_3)_2$	10	$95 \pm 3$
$\text{Cr}^{3+}$	$\text{Cr}(\text{NO}_3)_2$	10	$94 \pm 2$
$\text{SO}_4^{2-}$	$\text{Na}_2\text{SO}_4$	750	$95 \pm 2$
$\text{HCO}_3^-$	$\text{NaHCO}_3$	1500	$95 \pm 2$
$\text{PO}_4^{3-}$	$\text{Na}_3\text{PO}_4$	50	$94 \pm 3$

**Eq. 2**

LOB = mean(blank) + 1.64 (SD blank)

The enrichment factor (EF) was 40 times, and calculated as the ratio between the volume of the aqueous phase (20 mL) and the final volume (500 µL). The relative standard deviation (RSD) for the analysis of 10 replicate measurements of a 20-mL solution containing 3.75 µg L<sup>-1</sup> Cd<sup>2+</sup> was 3.21%.

**Analysis of Environmental Samples**

To verify the accuracy of the proposed method, the cadmium concentrations were determined using the present method for CRM-SA-C Sandy Soil C and CRM-TMDW-500 Drinking Water after the appropriate dilution was made. As can be seen in Table III, recoveries were obtained between 95% and 96.3%, respectively. The method was also applied for Cd determination in various water samples taken from the Turkish city of Trabzon.

**TABLE III**  
**Determination of Cadmium in Certified Reference Materials (n=3)**

Sample	Certified	Found	Recovery
CRM-SA-C Sandy Soil C <sup>a</sup>	109 ± 8.0 µg g <sup>-1</sup>	105 ± 2.8 µg g <sup>-1</sup>	96.3± 3.1%
CRM TMDW-500 Drinking Water	10.0 ± 0.1 µg L <sup>-1</sup>	9.5 ± 0.3 µg L <sup>-1</sup>	95.0± 2.6%

<sup>a</sup>Diluted 57-fold for Cd analysis.

Stream and seawater samples were filtered using 0.45-µm membrane filters, and the pH solutions were adjusted to 6.5. To show the applicability of the presented DLLM, the tap, stream, spring, and seawater as well as samples of burghul, noodles, rice, black tea, coffee, tobacco, cigarettes, and plastic toys were analyzed for their cadmium content. The recoveries of the spiked samples and the results obtained from the analysis of the environmental samples are presented in Tables IVa, IVb, and V.

**Comparison to Other Extraction and Preconcentration Methods**

A comparison of the proposed method with other reported extrac-

tion and preconcentration methods for Cd<sup>2+</sup> determination is given in Table VI (12, 32-37). The DLLME method has several advantages and includes short extraction time, negligible consumption of extraction solvents, and simplicity. It can be observed that the detection limit obtained in this study is compatible with studies that use FAAS as the detection system (35, 36). The limits of detection are lower than that of the previously reported methods except for reference 36 and reference 37. In addition, the DLLME technique is competitive in terms of sensitivity when compared with widely used sample preparation techniques, such as solid-phase extraction (SPE) and cloud point

**TABLE IVa**  
**Determination of Cadmium in Spiked Samples (n=3)**

Sample	Added (µg)	Found (µg)	Recovery (%)
	0	<LOD	-
Tap water	0.075	0.071 ± 0.001	94.6 ± 2.1
	0.150	0.143 ± 0.003	95.3 ± 2.2
	0	<LOD	-
Stream water	0.075	0.070 ± 0.001	93.3 ± 2.1
	0.150	0.014 ± 0.005	93.3 ± 3.1
	0	<LOD	-
Spring water	0.075	0.079 ± 0.002	96.0 ± 2.4
	0.150	0.144 ± 0.004	96.0 ± 3.1
	0	<LOD	-
Sea water	0.075	0.070 ± 0.003	93.3 ± 3.0
	0.150	0.141 ± 0.005	94.0 ± 3.1
	0	<LOD	-
Burghul	0.075	0.070 ± 0.002	93.3 ± 2.7
	0.150	0.143 ± 0.004	95.3 ± 2.4
	0	<LOD	-
Noodle	0.075	0.069 ± 0.001	92.0 ± 2.0
	0.150	0.142 ± 0.002	94.6 ± 2.2
	0	<LOD	-

**TABLE IVb**  
**Determination of Cadmium in Spiked Samples (n=3)**

Sample	Added (µg)	Found (µg)	Recovery (%)
	0	<LOD	-
Rice	0.075	0.070 ± 0.002	93.3 ± 2.6
	0.150	0.146 ± 0.001	97.3 ± 2.5
	0	<LOD	-
Black tea	0.075	0.068 ± 0.002	90.6 ± 2.1
	0.150	0.140 ± 0.005	93.3 ± 3.0
	0	<LOD	-
Coffee	0.075	0.069 ± 0.002	92.0 ± 3.0
	0.150	0.141 ± 0.001	94.0 ± 2.0
	0	<LOD	-
Tobacco	0.075	0.164 ± 0.005	94.6 ± 2.2
	0.150	0.237 ± 0.007	96.0 ± 2.4
	0	0.079 ± 0.003	-
Cigarette	0.075	0.150 ± 0.004	94.6 ± 2.1
	0.150	0.224 ± 0.004	96.6 ± 2.3
	0	0.064 ± 0.003	-
Plastic toys	0.075	0.136 ± 0.003	94.6 ± 2.4
	0.150	0.209 ± 0.003	96.6 ± 2.4
	0	<LOD	-

**TABLE V**  
**Results of Determination of Cadmium in Solid and Water Samples (n=3)**

Solid Samples	Cd <sup>2+</sup> (µg g <sup>-1</sup> )	Water Samples	Cd <sup>2+</sup> (µg L <sup>-1</sup> )
Burghul	<LOD	Tap water	<LOD
Noodle	<LOD	Stream water	<LOD
Rice	<LOD	Spring water	<LOD
Black tea	<LOD	Seawater	<LOD
Coffee	<LOD		
Tobacco	1.03 ± 0.02		
Cigarette	0.88 ± 0.03		
Plastic toys	0.80 ± 0.03		

**TABLE VI**  
**Comparison of DLLME with Other Methods for Determination of Cadmium**

Method	LOD	EF/PF (µg L <sup>-1</sup> )	Linear Range(µg L <sup>-1</sup> )	Sample Type	Ref.
USAEME-FAAS	0.91	15.3	10-600	Tap, sea, river, wastewater	12 12
SPE-FAAS	1.44	50	216-3000	Tap water, tea leaves	32
CPE-FAAS	0.75	15.1-20.3	2.5-500	Mineral, river, lake	33
HFRLM-FAAS	1.5	107	5-30	River water	34
SPE-FAAS	5.5	-	5-150	Alcohol fuel samples	35
USAE-SFODME-FAAS	0.66	81	10-450	Tap, sea, river water	36
IL-UADMMME-FAAS	0.40	100	10-500	Lake and wastewater, onion, tomato, green chilli, peppermint, hair samples	37
DLLME-FAAS	0.69	40	2.5-15	Tap, stream, spring, Spring, seawater; burghul, noodle, rice, black tea, coffee, tobacco, cigarette, plastic toy samples	Present Work

LOD: limit of detection.

EF: Enhancement factor.

PF: preconcentration factor.

USAEME: Ultrasound assisted emulsification microextraction.

CPE: Cloud point extraction.

HFRLM: Hollow fiber renewal liquid membrane extraction.

IL-UADMMME: Ionic liquid-based ultrasound-assisted dual magnetic microextraction.

USAE-SFODME : Ultrasound-assisted emulsification solidified floating organic drop microextraction.

extraction (CPE). Also, the developed method has an advantage in that it can be applied to different types of samples compared with the other methods described in Table VI. However, the preconcentration factor of the proposed method is lower than that of the previously reported methods except for reference 12 and reference 33. Thus, the analytical characteristics of the recommended method could be a good cadmium detection alternative for analytical laboratories.

## CONCLUSION

In this method, a dispersive liquid liquid microextraction (DLLME) method is presented for the preconcentration of cadmium in water and solid samples and FAAS-based analysis. The PPTMODT compound of 2-[(4-phenylpiperazine-5-thioxo-4,5-dihydro-1,3,4-oxadiazole-2-yl)methyl]-5-methyl-4-[2-(1H-indole-3-yl)ethyl]-2,4-dihydro-3H-1,2,4-triazole-3-on was successfully used for the first time in the determination of cadmium ions in environmental samples. A mixture comprised of 1000 µL of methanol (dispersive solvent) and 250 µL of chloroform (extraction solvent) was able to quantitatively extract cadmium ions. This method also has several merits which includes simplicity of operation, good repeatability, high recoveries, and low consumption of organic solvent. The measured analytical performance demonstrates that this method is a good alternative for the determination of Cd in both water and solid samples in the low µg L<sup>-1</sup> range with good accuracy and good reproducibility.

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