

## Ultrasound-assisted emulsification dispersive liquid-liquid microextraction for preconcentration and determination of cadmium in natural water samples by spectrophotometric technique

Jintana Klamtet

Department of chemistry, Faculty of science, Naresuan University,  
Phitsanulok, 65000, Thailand

Corresponding author. E-mail: jintanakl@nu.ac.th

### Abstract

The aim of this work was to develop ultrasound-assisted emulsification dispersive liquid-liquid microextraction for preconcentration cadmium in water samples using 4-(2-Pyridylazo) resorcinol (PAR) as complexing agent. In the preconcentration step, the amount of 3 mL acetone (dispersive solvent) containing 150  $\mu$ L of tetrachloroethylene (extraction solvent) was injected rapidly into the sample solution containing cadmium solution, 4.00 mL 3.0 mmol L<sup>-1</sup> of 4-(2-pyridylazo) resorcinol (chelating agent) and 4.00 mL buffer solution pH 10 by using a syringe. In this step, the cadmium/PAR complexes were extracted into the fine droplets of tetrachloroethylene. Then, the fine droplets of tetrachloroethylene were emulsified by ultrasonic bath before centrifugation (5 min at 3000 rpm). Finally, the organic phase containing enriched analytes was separated and determined by UV-Visible spectrometer. Under these optimum conditions, the limit of detection (LOD) was 0.14 mg/L and limit of quantitation (LOQ) was 0.47 mg/L with sensitivity enhancement factor (EF) of 1.26. The proposed method showed the relative standard deviation (RSD) less than 5% and was successfully to apply for the recovery and determination of cadmium in different water samples around Naresuan University. The results showed that the 3 collected samples have an amount of cadmium in the range 0.00 – 0.60 mg L<sup>-1</sup> and the percentage recovery was in the range 90.3-105.30 %.

*Keywords: Cadmium, preconcentration, dispersive liquid-liquid extraction*

### INTRODUCTION

Cadmium is one of the toxic element, which could damage organs such as kidneys, liver and lungs, even in minute concentration (Wen, Yang et al., 2011; Şahin and Durukan, 2011). Cadmium is widely used metallurgical alloying, the manufacture of batteries and paints, ceramics, metal plating, photograph development, pigment works and textile printing industries (Şahin and Durukan, 2011). One of the pathways that the cadmium enters human body is through daily intake of water and food, thus, the determination of cadmium concentrations in these samples is a great importance. Moreover, content of cadmium in some matrices such as foods, sediment or water can provide the pollution of the surrounding environment (Gama, Lima and Lemos, 2006; Wen, Deng et al., 2011). The maximum tolerable level for cadmium(II) in drinking water has been strictly regulated. Recommended cadmium concentration in drinking water by the World Health Organization (WHO) is smaller than 0.005 mg L<sup>-1</sup> (Şahin and Durukan, 2011).

Due to low concentration of cadmium in environmental samples, a preconcentration step is generally required prior to determination. Several enrichment procedures has been reported in the literature for cadmium determination involving different analytical techniques such as solid phase extraction [Tsoegas, Giokas and Vlessdis, 2009; Burham et al., 2009; Ensafi and Ghaderi, 2007], cloud point extraction (Silva et al., 2009), single drop extraction (Wen, Deng et al., 2011) and dispersive liquid-liquid extraction (Wen, Yang et al., 2011; López, I. et al., 2013). In this work,

dispersive liquid-liquid microextraction (DLLME) was investigated due to its simplicity, easy to operate, rapidness, and high extraction efficiency (Zhou, Zhao and Xie, 2011). This method based on the use of an appropriate extractant, i.e., a few microlitres of an organic solvent and a disperser solvent with high miscibility in both extractant and aqueous phase such as methanol, ethanol, acetonitrile and acetone (Wen, Yang et al., 2011; Wen, et al., 2012). DLLME method depends on rapid injection of appropriate of mixture of extractant and disperser solvent into the aqueous sample to form a cloudy solution. The cloudy state results from the formation of fine droplets of the extraction solvent which disperse in the sample solution (Wen, Yang et al., 2011; Wen et al., 2012). The cloudy solution is centrifuged and the fine droplets are settled at the bottom of the conical test tube. The analytes of interest are extracted from the initial solution and concentrated to a small volume of the settled phase (Tabrizi, 2010). The analyte in the settled phase can be determined by various analytical techniques such as ETAAS (López et al., 2013; Naseri et al., 2008), AFS (Zhou, Zhao and Xie, 2011), ICP-OES (Sereshti, Khojeh and Samadi, 2011), FAAS [Rouhollah, Farzaneh and Behrooz, 2011], *etc.* Recently, ultrasound-assisted DLLME has been reported (Molaakbari, Mostafavi and Afzali, 2011; Cortada, Vidal and Canals, 2011; Zhang et al., 2012; Berton et al., 2012) and most of them focused on advanced analytical instruments. Therefore, this work will carry out the ultrasound-assisted emulsification dispersive liquid-liquid microextraction (UAE-DLLME) coupled with UV-Visible spectrophotometer for cadmium determination. Because UV-Visible spectrophotometry is simple method and much more cost-efficient. The UAE-DLLME preconcentration technique can considerably improve the analytical performance of ordinary spectrophotometer (Wen, et al., 2012). The UAE-DLLME was very simple and rapid for sample extraction. The effect of various parameters affecting the extraction efficiency such as type and volume of extraction and disperser solvent, pH, extraction time and concentration of the chelating agent was studied and optimized to achieve high recovery.

## METHODOLOGY

### 1. Instrumentation

UV-Visible spectrophotometer model V-650 (Jasco, Japan) was used for the determination. A centrifuge model EBA 3S (HettichZentrifugan, USA) was used to assist phase separation. The ultrasound extraction process was carried out by ultrasonic cleaner model Transsonic 460/H (Elma, Germany). The pH values were measured by pH meter model Eutech instrument pH 700 (thermos Fisher Scientific, Singapore).

### 2. Reagent

Cadmium (BDH PROLABO, Belgium) working standard solutions were prepared by appropriate dilutions from standard stock solutions ( $1000 \text{ mg L}^{-1}$ ) in deionised water. The 4-(2-Pyridylazo) resorcinol monosodium salt hydrate (PAR) (Fluka, Switzerland) was used as a complexing agent for cadmium and was prepared daily by dissolving the required amount of PAR in deionised water. A potassium dihydrogen orthophosphate (Ajax Finchem, Australia) and a di-sodium hydrogen phosphate (Merck, Germany) buffer solutions were used in the pH range of 3.0-7.0 and the buffer solution in the range of 8.0-11.0 was prepared by using sodium tetraborate (Ajax Finchem, New Zealand) and sodium carbonate (Fluka, Switzerland). All the

other reagents including extractants and disperser solvent were analytical reagent grade, as well as the reagents mentioned above.

### 3. Ultrasound-assisted emulsification dispersive liquid-liquid microextraction procedure

In this work, 10 mL of sample solution containing cadmium adjusted to pH 10 using carbonate buffer was placed in a glass test tube. Then, 4 mL of  $3 \times 10^{-3}$  mol L<sup>-1</sup> 4-(2-pyridylazo) resorcinol (chelating agent, PAR) was added into the sample solution. In this step, the cadmium ions reacted with the chelating agent to form the related complexes. 3.00 mL of acetone (disperser solvent) containing 150  $\mu$ L tetrachloroethylene (extraction solvent) was injected rapidly into the sample solution. After the injection, the extraction was accomplished under the effect of ultrasound in an ultrasonic bath for 5 min. A cloudy solution was formed and cadmium ions were extracted into the fine droplets of tetrachloroethylene. Then, the solutions were centrifuged at 3000 rpm for 5 min, and the dispersed fine droplets of tetrachloroethylene were sedimented at the bottom of centrifuge tube. The upper aqueous phase was removed with a syringe, and acetone was adapted to dilute the concentrated samples to 5 mL. Finally, the enriched analytes were determined by spectrophotometer.

### 4. Sample collection and preparation

All real water samples were collected from the pond, canal and reservoir around the Naresuan University in Phitsanulok province, Thailand, in cleaned polyethylene bottles. All samples were filtered through Whatman No. 42 paper filters after sampling. Then, the proposed method was applied to extraction of cadmium ions from the water samples.

## RESULTS AND DISCUSSION

### 1. The study of absorption spectra

The UV-Vis spectrophotometry was used in this work to determine the enriched samples after extraction. The maximum wavelength of first derivative absorption was investigated due to eliminate the absorption effect of chelating agent. The complex of Cd-PAR was determined in the range of wavelength between 490 and 600 nm. The absorption spectra were showed in Figure 1. The results indicated that the maximum absorption wavelength was 532 nm.

### 2. Effect of UAE-DLLME parameters

#### 2.1 Effect of sample pH

The sample pH plays an important role in a DLLME extraction procedure because the complexation and extraction efficiencies of metal ion are closely related to the pH of the solution system (Wen et al., 2012; Qingxiang, Na, and Guohong, 2011). In order to obtain the desired preconcentration efficiencies, the pH values were carried out in the range of 6.5-11.0. The result shown in Figure 2 indicated that the derivative absorbance signal increased from pH 8.5 to 10.0, and decreased when pH was over pH 10.0. Thus, the sample pH was set at pH 10.0 in the following experiments.

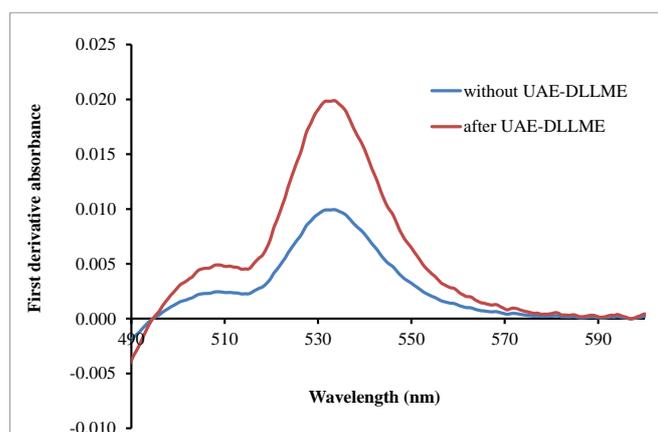


Figure 1 Absorption spectra of cadmium determination with/without UAE-DLLME. UAE-DLLME condition:  $1.20 \text{ mg L}^{-1} \text{ Cd}$ ,  $3.0 \times 10^{-3} \text{ mol L}^{-1} \text{ PAR}$ , pH 10, ultrasound extraction time 5 min., dilution solvent – acetone. Without UAE-DLLME condition:  $1.20 \text{ mg L}^{-1} \text{ Cd}$ ,  $3.0 \times 10^{-3} \text{ mol L}^{-1} \text{ PAR}$ , pH 10.

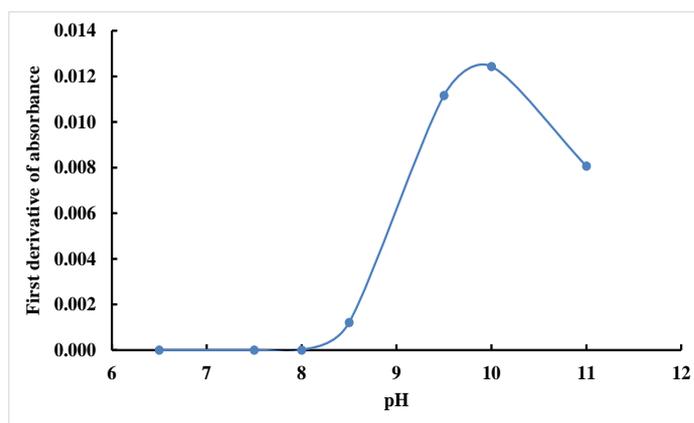


Figure 2 Effect of pH on the first derivative absorbance. UAE-DLLME condition:  $1.00 \text{ mg L}^{-1} \text{ Cd}$ ,  $3.0 \times 10^{-3} \text{ mol L}^{-1} \text{ PAR}$ , pH 10, extraction solvent  $100 \mu\text{L}$  tetrachloroethylene, ultrasound extraction time 1 min., dilution solvent – methanol

## 2.2 Selection of extraction solvent and its volume

The type of extraction solvent and its volume are crucial parameters in liquid phase microextraction because it influences the extraction efficiency of the analytes. The extraction solvent was selected based on higher density than water, extraction capability for the compounds of interest, and low solubility in water (Jahromi et al., 2007). In this work, three organic solvents such as dichloromethane, trichloromethane and tetrachloroethylene were investigated. The results demonstrated in Figure 3. The results showed that higher signal of first derivative absorbance was obtained when tetrachloroethylene was used as the extraction solvent. So tetrachloroethylene was selected as the extraction solvent in further experiments. After the extractant type selection, the volume of tetrachloroethylene was carried out in the range of 50-200  $\mu\text{L}$  and the results were shown in Figure 4. As can be seen, the first derivative absorbance increased along with the increased volume of tetrachloroethylene from 50  $\mu\text{L}$  to 150  $\mu\text{L}$ , and then decreased when the volume of tetrachloroethylene higher than 150  $\mu\text{L}$ . The increased signals were due to the increased volume of tetrachloroethylene which can dissolve more cadmium complex. But the decrease of signal of first derivative absorbance was due to some of tetrachloroethylene could not be dispersed into the aqueous solution as infinitesimal drops and existed as larger drops which decreased the contact area between cadmium complex and organic drop, that is reduced the transfer of cadmium complex into the tetrachloroethylene phase (Qingxiang, Na, and Guohong, 2011). Therefore, 150  $\mu\text{L}$  tetrachloroethylene was chosen for subsequent determination.

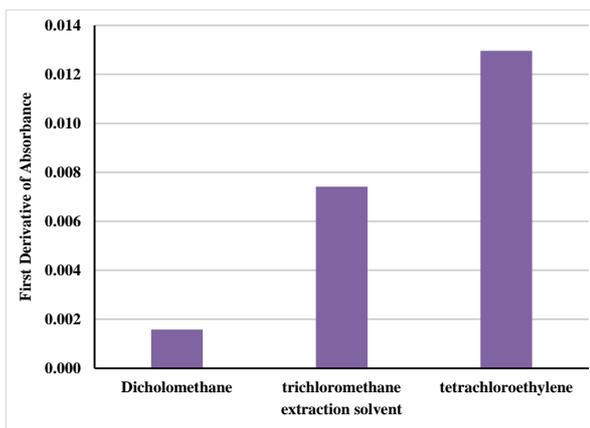


Figure 3 Effect of types of extraction solvent. UAE-DLLME condition: 1.00  $\text{mg L}^{-1}$  Cd,  $3.0 \times 10^{-3}$   $\text{mol L}^{-1}$  PAR, pH 10, ultrasound extraction time 1 min., dilution solvent – methanol.

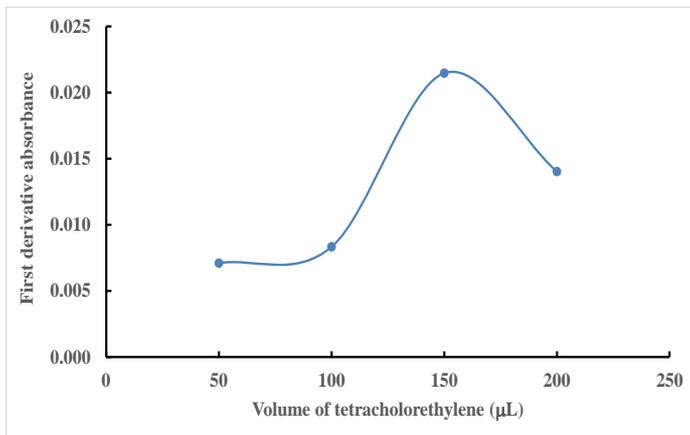


Figure 4 Effect of tetrachloroethylene volume on first derivative absorbance. UAE-DLLME condition: 1.00 mg L<sup>-1</sup> Cd, 3.0×10<sup>-3</sup> mol L<sup>-1</sup> PAR, pH 10, ultrasound extraction time 1 min., dilution solvent – methanol.

### 2.3 Selection of type and volume of disperser solvent

In DLLME, the selection of disperser solvent is critical and its affects the efficiency of extraction and the enhancement factor. During the extraction procedure, the disperser solvent functions as a bridge to disperse the extraction reagent dissolved in it to form dispersed fine droplets. As a result, the solution becomes turbid and the contact area between extractant and target analyte could be largely increased thus to improve the extraction efficiency (Wen, Yang et al., 2011). In order to achieve better dispersing, methanol, ethanol and acetone were tested. The results were shown in Figure 5 and indicated that acetone was the best disperser solvent for the extraction of cadmium.

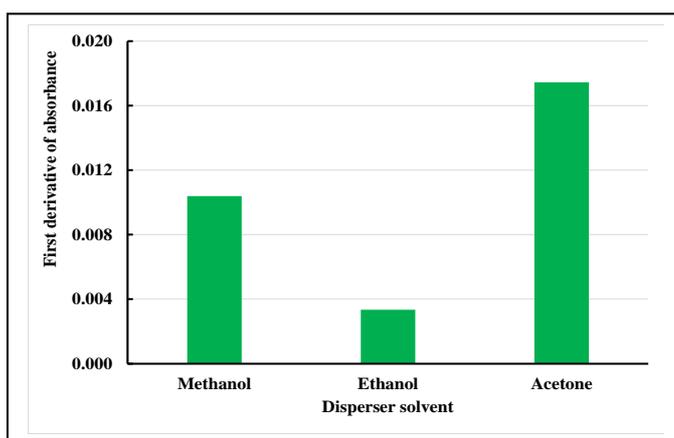


Figure 5 Selection of type of disperser solvent. UAE-DLLME condition: 1.00 mg L<sup>-1</sup> Cd, 3.0×10<sup>-3</sup> mol L<sup>-1</sup> PAR, pH 10, extraction solvent 150 µL tetrachloroethylene, ultrasound extraction time 1 min., dilution solvent – methanol.

The volume of disperser solvent is also an important factor for achieving good extraction performance. So, the influence of acetone volume on the first derivative absorbance of cadmium was also investigated. Because different volume of acetone gave different volume of sedimented phase when the volume of extraction solvent is constant (Rouhollah, Farzaneh and Behrooz, 2011). The volume of acetone was optimized in the range 1.0-5.0 mL and the results showed that the derivative absorbance signal increased with increasing acetone volume from 1.0 to 3.0 mL and then decrease when volume of acetone over 3.0 mL. It should be noted that the cloudy solution was not formed well when using small volume of acetone. When acetone volume was increased over 3.0 mL, the solubility of complex in water increased, therefore the first derivative absorbance decreased. Therefore, 3.0 mL of acetone was used in further experiment.

#### 2.4 Concentration of 4-(2-pyridylazo) resorcinol (PAR)

In this work, 4-(2-pyridylazo) resorcinol was used to form Cd-PAR complex. The effect of PAR concentration on the first derivative absorbance was studied in the range of  $0.10 \times 10^{-3}$  -  $5.00 \times 10^{-3}$  mol L<sup>-1</sup> which was shown in Figure 6. As can be seen that the first derivative absorbance increased with the increasing of PAR concentration from  $0.10 \times 10^{-3}$  to  $3.00 \times 10^{-3}$  mol L<sup>-1</sup> and at PAR concentration higher than  $3.00 \times 10^{-3}$  mol L<sup>-1</sup>, the first derivative absorbance slightly decreased. This could be due to co-extract of excessive chelating agents into organic phase, thus the extraction efficiency decreased (Wen et al., 2012). Therefore,  $3.00 \times 10^{-3}$  mol L<sup>-1</sup> of PAR concentration was selected as the optimal condition for subsequence determination.

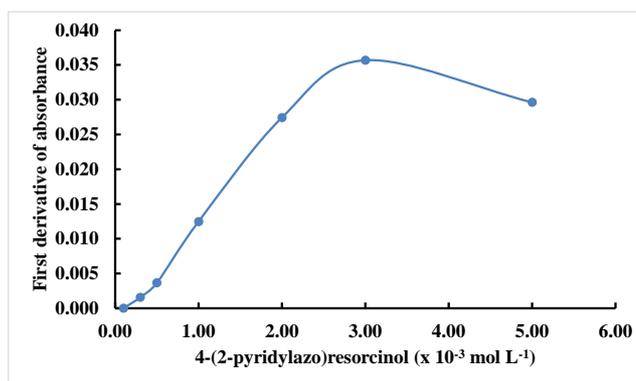


Figure 6 Effect of PAR concentration. UAE-DLLME condition: 1.00 mg L<sup>-1</sup> Cd,  $3.0 \times 10^{-3}$  mol L<sup>-1</sup> PAR, pH 10, extraction solvent 150  $\mu$ L tetrachloroethylene, ultrasound extraction time 1 min., dilution solvent – methanol.

### 2.5 Effect of ultrasound extraction time

The ultrasound was used in this work for improving in extraction efficiency due to increasing mass transfer and emulsification of solution. The ultrasound extraction time was optimized over 0-10 min. It was found that the first derivative absorbance was increased when the ultrasound extraction time was changed from 1 to 5 min and decreased slightly when the ultrasound extraction time was longer than 5 min. The longer ultrasound extraction time could lead to increase the temperature of solution, and the complexation of Cd-PAR would be affected thus the extraction efficiency decreased (Wen et al., 2012). According to these, 5 min ultrasonic extraction time was chosen in the following study.

### 2.6 Effect of centrifugation time

Centrifugation time has influenced the separation of tetrachloroethylene from water phase. In this experiment, the centrifugation time was studied from 1 to 15 min. The results indicated that centrifugation time was 5 min (3000 rpm) suitable for extraction. The short centrifugation time could not insure the preferable phase separation, and longer centrifugation time would have generated heat which may enhance the dissolving the metal complex into the aqueous phase (Qingxiang, Na and Guohong, 2011). This resulted in the decrease in first derivative of absorbance. So, 5 min was selected for further use.

### 2.7 Effect of type of dilution solvent

The type of dilution solvent could affect the detection such as the ratio of volumes between water phase and organic phase and the enrichment factor (Wen, Yang et al., 2011). In this experiment, some conventional solvents including methanol, ethanol, acetone and pure water were studied. The results showed that acetone was the best dilution solvent for determination of cadmium.

### 2.8 Interferences

Many metal ions existing in natural waters would form stable chelating complexes with PAR with in the wide range and may be co-extracted along with analytes. This could decrease the extraction efficiency. Therefore, the experiments have been designed using standard solution of  $1 \text{ mg L}^{-1}$  Cd(II) under the above optimized conditions. The effect of each species was considered to be interference when the signal in the presence of the species resulted in an absorbance deviation of more than  $\pm 5\%$ . The results showed that less than  $100 \text{ } \mu\text{g L}^{-1}$  of Mg(II) and Zn(II) and up to  $500 \text{ } \mu\text{g L}^{-1}$  of Ca(II) and Pb(II) did not cause interference in the determination of Cd(II), see Table 1. Thus, the pH for the determination of Cd(II) must be strictly controlled to enhance its specificity, coupled with using a solution containing phosphate and citrate to mask several interferences (Klamtet, Suprom and Wanwat, 2008).

Table 1 Tolerance limit of coexisting ions for determination of Cd(II) (1 mg L<sup>-1</sup>)

Interfering ions	Tolerance limit ( $\mu\text{g L}^{-1}$ )
Ca	$\leq 500$
Mg	$< 100$
Zn	$< 100$
Pb	$\leq 500$

### 3. Analytical Performance

The analytical performance of UAE-DLLME couple with UV-Visible spectrometry for preconcentration and determination of Cd in natural water was investigated under the optimal conditions. The results indicated that linear calibration graph was in the range 0.20-1.40 mg L<sup>-1</sup> ( $A = 0.0091C_{\text{Cd}} + 0.0039$   $r^2 = 0.9902$ ). The precision of this method was 4.50% (RSD, n=7) at the spiked concentration of 0.80 mg L<sup>-1</sup>. The limit of detection (LOD), which is defined as the concentration corresponding to three times the standard deviation of the blank samples, was 0.14 mg L<sup>-1</sup> and the limit of quantitation (LOQ) was 0.46 mg L<sup>-1</sup>. The enrichment factor, obtained from the slope ratio of the calibration graph after and before the extraction, was 1.26 for 10 mL of the sample solution.

### 4. Analysis of real water samples

In order to demonstrate the applicability and reliability of the proposed method for real samples, 3 natural water samples were collected. The analytical results are given in Table 2. These results showed the recovery of spiked samples were in the acceptable in the range of 90.3- 105.3%.

Table 2 Analytical results for cadmium determination in real samples (Avg.  $\pm$  SD, n=3)

Real samples	Added (mg L <sup>-1</sup> )	Found (mg L <sup>-1</sup> )	Recovery (%)
Sample 1	0	$0.36 \pm 0.18$	$105.3 \pm 9.0$
	0.20	$0.57 \pm 0.16$	
Sample 2	0	$0.11 \pm 0.04$	$100.1 \pm 0.5$
	0.20	$0.31 \pm 0.04$	
Sample 3	0	$0.19 \pm 0.05$	$90.3 \pm 10.1$
	0.20	$0.37 \pm 0.03$	

## CONCLUSION

The ultrasound-assisted emulsification dispersive liquid-liquid microextraction method was developed for preconcentration and determination of cadmium in water samples coupled with spectrophotometry. The results demonstrated that the proposed method is simple, rapid, sensitive, cost effective and low consumption of organic solvents. The proposed method showed good limit of detection with the enhancement

factor of 1.26. The developed method was applied to the determination of real samples with satisfactory analytical results.

## ACKNOWLEDGMENTS

The authors are grateful for the financial support of the office of Naresuan University, Thailand (Project, 2015) for financial support in the form of research project. Thank to chemistry department, Faculty of science, Naresuan University for support some analytical instruments and all facility.

## REFERENCES

- Berton, P. et al. (2012). Selective determination of inorganic cobalt in nutritional supplements by ultrasound-assisted temperature-controlled ionic liquid dispersive liquid phase microextraction and electrothermal atomic absorption spectrometry, *Anal. Chim. Acta.*, 713, 56-62.
- Burham, N. et al. (2009). Removal of Pb and Cd from aqueous media and fish liver using novel polyurethane foam functionalized with pyrazolone as new metal ion collector, *Cent. Eur. J. Chem.*, 7(3), 578-585.
- Cortada, C., Vidal, L. and Canals, A. (2011). Determination of nitroaromatic explosives in water samples by direct ultrasound-assisted dispersive liquid–liquid microextraction followed by gas chromatography–mass spectrometry, *Talanta*, 85, 2546-2552.
- Ensafi A.A. and Ghaderi, A.R. (2007). On-line solid phase selective separation and preconcentration of Cd(II) by solid phase extraction using carbon active modified with methy thymol blue, *J. Hazard. Mater.*, 148, 319-325.
- Gama, E. M., Lima, A.D.S. and Lemos, V.A. (2006). Preconcentration system for cadmium and lead determination in environmental samples using polyurethane foam/Me-BTANC, *J. Hazard. Mater. B.*, 136, 757-762.
- Jahromi, E. Z. et al. (2007). Dispersive liquid-liquid microextraction combined with graphite furnace atomic absorption spectrometry: ultra trace determination of cadmium in water samples, *Anal. Chim. Acta.*, 585, 305-311.
- Klamt, J., Suprom, N. and Wanwat, C. (2008). flow injection system for the spectrophotometric determination of lead after preconcentration by solid phase extraction onto Amberlite XAD-4, *Mj. Int. J. Sci. Tech.*, 2(02), 408-417.
- López, I. et al. (2013). Determination of lead and cadmium using an ionic liquid liquid and dispersive liquid-liquid microextraction followed by electrothermal atomic absorption spectrometry, *Talanta*, 110, 46-52.
- Molaakbari, E. Mostafavi, A. and Afzali, D. (2011). Ionic liquid ultrasound assisted dispersive liquid–liquid microextraction method for preconcentration of trace amounts of rhodium prior to flame atomic absorption spectrometry determination, *J. Hazard. Mater.*, 185, 647-652.
- Naseri, M. T. et al. (2008). Rapid determination of lead in water samples by dispersive liquid-liquid microextraction coupled with electrothermal atomic absorption spectrometry, *Talanta*, 75, 56-62.
- Qingxiang, Z., Na, Z. and Guohong, X. (2011). Determination of lead in \ environmental waters with dispersive liquid-liquid microextraction prior to atomic fluorescence spectrometry, *J. Hazard. Mater.*, 189, 48-53.
- Rouhollah, K., Farzaneh, S. and Behrooz, M. (2011). Combination of dispersive liquid-liquid extraction and flame atomic absorption spectrometry for

- preconcentration and determination of copper in water samples, *Desalination*, 266, 238-243.
- Şahin, Ç. A. and Durukan, İ. (2011). Ligandless-solidified floating organic drop microextraction method for the preconcentration of trace amount of cadmium in water samples, *Talanta*, 85, 657-661.
- Sereshti, H., Khojeh, V. and Samadi, S. (2011). Optimization of dispersive liquid-liquid extraction coupled with inductively coupled plasma-optical emission spectrometry with the aid of experimental design for simultaneous determination of heavy metals in natural waters, *Talanta*, 83, 885-890.
- Silva, E.L. et al. (2009). Simultaneous preconcentration of copper, zinc, cadmium, and nickel in water sample by cloud point extraction using 4-(2-pyridylazo)-resorcinol and their determination by inductively coupled plasma optical emission spectrometry, *J. Hazard. Mater.*, 171, 1133-1138.
- Tabrizi, A.B. (2010). Development of a dispersive liquid-liquid microextraction method for iron speciation and determination in different water samples, *J. Hazard. Mater.*, 183, 688–693.
- Tsogas, G.Z., Giokas, D. L. and Vlessdis, A.G. (2009). Graphite furnace and hydride generation atomic absorption spectrometric determination of cadmium, lead, and tin traces in natural surface waters: Study of preconcentration technique performance, *J. Hazard. Mater.*, 163, 988-994.
- Wen, X.D., Yang Q. et al. (2011). Determination of cadmium and copper in water and food samples by dispersive liquid-liquid microextraction combined with UV-vis spectrophotometry, *Microchem. J.*, 97, 249-254.
- Wen, X.D., Deng, Q. et al. (2011). Ultra-sensitive determination of cadmium in rice and water by UV-vis spectrophotometry after single drop microextraction, *Spectrochim. Acta. Part A*, 79, 508-512.
- Wen, X.D. et al., (2012). A new coupling of spectrophotometry determination with ultrasound-assisted emulsification dispersive liquid-liquid microextraction of trace silver, *Spectrochim Acta Part A: Molecular and biomolecular spectroscopy*, 97, 782-787.
- Zhang, J. et al., (2012). Simultaneous determination of four synthesized metabolites of mequindox in urine samples using ultrasound-assisted dispersive liquid-liquid microextraction combined with high-performance liquid chromatography, *Talanta*, 88, 330-337.
- Zhou, Q., Zhao, N. and Xie, G. (2011). Determination of lead in environmental waters with dispersive liquid-liquid microextraction prior to atomic fluorescence spectrometry, *J. Hazard. Mater.*, 189, 48-53.