

**Solidified floating organic drop microextraction for the determination  
of cadmium in water samples  
by electrothermal atomic absorption spectrometry**

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**ABSTRACT**

In the present work, a method for determining cadmium (Cd) in water samples was developed by solidified floating organic drop microextraction (SFODME) with 1-(2-Pyridylazo)-2-naphthol (PAN) as a chelating reagent and detected by electrothermal atomic absorption spectrometry (ETAAS). Under the optimized conditions, the calibration graph was linear in the range of 0.1 – 5.0  $\mu\text{g L}^{-1}$  with a detection limit (LOD) of 0.053  $\mu\text{g L}^{-1}$ . The relative standard deviation (%RSD) for 6 replicate measurements (1.0  $\mu\text{g L}^{-1}$ ) was  $\pm 2.67\%$ . The proposed method was applied to tap water and drinking water samples. The accuracy of the proposed method as percentage recovery gave satisfactorily results.

*Keywords: Solidified floating organic drop microextraction / electrothermal atomic absorption spectrometry / 1-(2-Pyridylazo)-2-naphthol (PAN) / cadmium*

**INTRODUCTION**

The determination of cadmium in water samples is of substantial importance for environmental monitoring, because cadmium has high toxicity and damaging effects on both plants and humans (da Silva et al. 2003). Cadmium is considered a toxic heavy metal because it is associated with many diseases of the kidneys and heart (Erie et al. 2005). Due to its toxicity to both humans and animals, cadmium concentration in the environment are monitored and should fall within the guideline values; for drinking water they are as follows: WHO 3  $\mu\text{g L}^{-1}$  (Organization 2004) and EU 5  $\mu\text{g L}^{-1}$  (Water 2012).

Following the literature survey, different techniques such as ICP-MS (Filipiak-Szok, Kurzawa, and Sztyk 2015), ICP-OES (Lech and Mondragón 2014), AAS (Junior et al. 2014) and UV-VIS spectroscopy (Xu et al. 2014) have been developed for the simultaneous determination of Cd in different samples. However, in most cases, determination of low concentrations of these ions required a preconcentration step. Various techniques have been used for separation and preconcentration of Cd such as liquid-liquid extraction (LLE) (Anthemidis et al. 2004), solid-phase extraction (Dadfarnia et al. 2007) and cloud point extraction (Coelho and Arruda 2005).

However, traditional procedures are time-consuming, tedious and consume large amounts of expensive and toxic organic solvents. Thus, resulting in the development of microextraction techniques such as single drop microextraction

(SDME) (Gil, de Loos-Vollebregt, and Bendicho 2009), homogenous liquid–liquid microextraction (HLLME) (Ghiasvand et al. 2005), solid phase microextraction (SPME) (Dietz, Sanz, and Cámara 2006) and dispersive liquid–liquid microextraction (DLLME) (Rezaee et al. 2010). Notwithstanding, these techniques have limitations in terms of organic solvent that are toxic and unfriendly to the environment, such as, chlorobenzene ( $C_6H_5Cl$ ), chloroform ( $CHCl_3$ ) and carbon tetrachloride ( $CCl_4$ ).

In 2007, Khalili Zanjani et al. (Zanjani et al. 2007), reported a new liquid–liquid microextraction method based on solidified floating organic drop. In this method termed solidified floating organic drop microextraction (SFODME), a free microdrop of the organic solvent, which has a melting point near room temperature in the range of 10–30 °C is transferred to the surface of an aqueous sample, while being agitated by a stirring bar in the bulk of the solution. Under the proper stirring conditions, the suspended microdrop can remain in the top-center position of the aqueous sample. After the completion of the extraction, the sample vial is cooled and the solidified microdrop is transferred into a conical vial, where it melts immediately. This technique has also been successfully applied to the analysis of various metal in aqueous samples.

The aim of the present work was to develop SFODME coupled with ETAAS for determination of Cd, 1-(2-Pyridylazo)-2-naphthol (PAN) was used as a chelating reagent. In order to obtain a high enrichment factor, the influence of some experimental parameters affecting the complex formation and extraction conditions, were studied and optimized.

## EXPERIMENTAL

### Apparatus

All experiments were carried out in a Zeeman electrothermal atomic absorption spectrometer (Varian, model Spectra AA220Z) equipped with an autosampler (Varian, model AS-50). All measurements were performed in the peak area mode. A cadmium hollow cathode lamp was operated at 10.0 mA and a wavelength of 228.8 nm with a spectral bandwidth of 0.5 nm. The graphite furnace temperature program is listed as follows in Table 1.

### Reagent

All reagents used were of the highest purity and analytical reagent grade. The stock standard solutions of Cd(II) ( $1000 \text{ mg L}^{-1}$ ) were prepared by dissolving Cadmium nitrate (QReC Chemical, England) in distilled deionized water. Working solutions were prepared daily by appropriate dilution of the stock solutions. Solution ( $5.0 \text{ mmol L}^{-1}$ ) of 1-(2-Pyridylazo)-2-naphthol (PAN, Acros Organics, USA) was prepared in Ethanol (Merck, Germany). 1-undecanol and 1-dodecanol (Merck, Germany), were used as the extraction solvents. Buffer solutions of ammonium acetate (pH 4,  $0.2 \text{ mol L}^{-1}$ ), phosphate (pH 7.0,  $0.2 \text{ mol L}^{-1}$ ), and ammonium chloride (pH 9,  $0.2 \text{ mol L}^{-1}$ ) were used for pH adjustments.

### SFODME extraction

SFODME device used in this work for extraction of analytes was similar to that described in literature (Zanjani et al. 2007). A sample solution of 13 mL containing analytes (Cd(II)  $0.5 \text{ } \mu\text{g L}^{-1}$ ) was adjusted to the desired pH values using ammonium chloride buffer solution (pH 9), 0.50 mL of  $5.0 \text{ mmol L}^{-1}$  PAN. Stir bar

and 90  $\mu\text{L}$  of 1-undecanol were added. The magnetic stirrer was turned on at 1000 rpm, and the solution was stirred for a 20 min at 65  $^{\circ}\text{C}$ . In this step, analytes react with PAN to form hydrophobic complexes, which are extracted into the 1-undecanol. After the extraction process, the sample vial was transferred into an ice bath around 5 mins until organic solvent was solidified. The solidified solvent was then transferred into a vial where it melted immediately at room temperature. The extract was diluted with 500  $\mu\text{L}$  of ethanol. Finally, 10  $\mu\text{L}$  of the extract was injected into electrothermal atomic absorption spectrometer.

**Table 1** Atomic absorption spectrometer instrumental temperature program for cadmium determination

Step	Temperature ( $^{\circ}\text{C}$ )	Step time (s)	Flow rate of argon ( $\text{L min}^{-1}$ )
Drying	85	35.0	0.3
Pyrolysis	250	8.0	0.3
Atomization	1800	2.8	0.0
Clean up	1800	2.0	0.3

### Sampling

Tap and drinking water (Phitsanulok, Thailand) were collected and filtered through a 0.45  $\mu\text{m}$  Whatman filter membrane, then kept at 4  $^{\circ}\text{C}$  before use.

## RESULTS AND DISCUSSION

### Selection of Extraction solvent

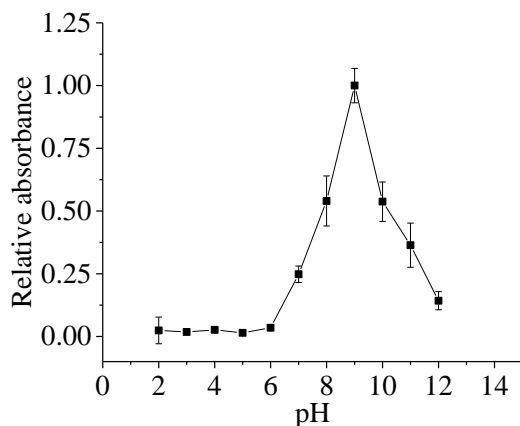
Selection of an appropriate extraction solvent is importance for optimizing SFODME processes. The extraction solvent has to satisfy four requirements: (1) to be immiscible with water and have low volatility in order to be stable during the extraction period. (2) can extract the analytes well, (3) have a lower density than water and (4) have a melting point near room temperature (in the range of 10–30  $^{\circ}\text{C}$ ). For this paper, two solvents: 1-dodecanol (density: 0.8309  $\text{g mL}^{-1}$ ; melting point: 24  $^{\circ}\text{C}$ ) and 1-undecanol (density: 0.8298  $\text{g mL}^{-1}$ ; melting point: 19  $^{\circ}\text{C}$ ) (Ghambarian et al. 2010) were investigated. From the results obtained, 1-undecanol was selected as extraction solvent in this study because of its sensitivity, stability, low water solubility, and low vapor pressure.

### Effect of pH

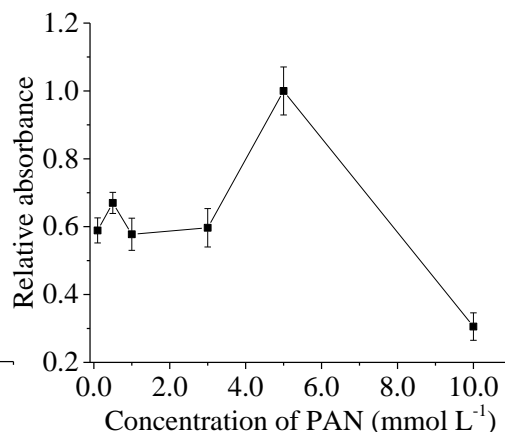
The pH of the sample has a consider effect on the formation of chelate and the amount that can be extracted into the small volume of the organic phase. Therefore, the effect of the pH in the range of 2 – 12 on the extraction was investigated. The results are shown in Fig. 1, in order to have high selectivity, a pH of 9 was selected for the subsequent work and the real sample analysis.

### Effect of 1-(2-pyridylazo)-2-naphthol concentration

The influence of PAN concentration on SFODME extraction of Cd(II) was studied by evaluated in the concentration range of PAN were 0.1 – 10.0  $\text{mmol L}^{-1}$ . The results in Fig. 2 indicated that the relative absorbance were increased by increasing of the concentration of PAN up to 5.0  $\text{mmol L}^{-1}$ . At high concentration of PAN may cause saturation of extracting solvent, which results in the extraction into



**Fig. 1** Effect of pH on extraction of Cd(II). (Conditions: 15 mL of  $1.0 \mu\text{g L}^{-1}$  Cd(II) solution, 500  $\mu\text{L}$  of  $3.0 \text{ mmol L}^{-1}$  PAN solution, 90  $\mu\text{L}$  1-undecanol, extraction at room temperature, stirring rate: 325 rpm and extraction time: 30 min.



**Fig. 2** Effect of concentration of PAN on extraction of Cd(II). (Conditions: 13 mL of  $0.5 \mu\text{g L}^{-1}$  Cd(II) solution, pH 9, 90  $\mu\text{L}$  1-undecanol, extraction at room temperature, stirring rate: 325 rpm and extraction time: 30 min.

the aqueous phase. Thus,  $5.0 \text{ mmol L}^{-1}$  PAN was used at the optimum concentration in this work.

### Effect of extraction time

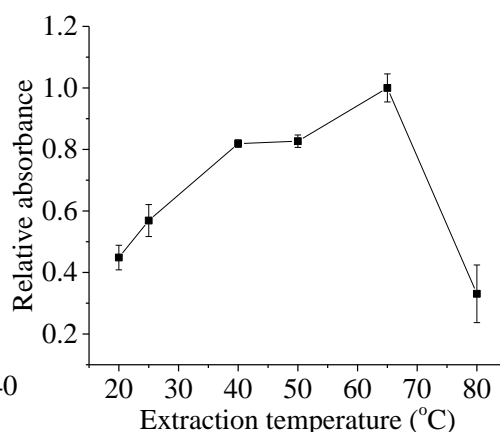
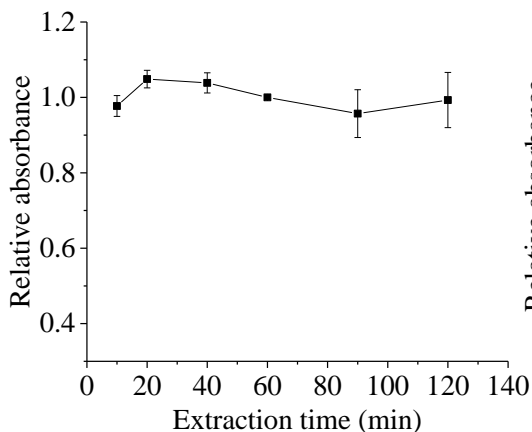
Extraction time is another important factor effecting the extraction efficiency and sensitivity of analysis (Ghambarian et al. 2010). In SFODME systems, an optimum extraction time is a time that guarantees the achievement of equilibrium between the aqueous and organic phases. The dependence of extraction efficiency was studied within a range of 10 – 120 min. The results in Fig. 3 showed that absorbance increased with increased time up to 20 min and then remained fairly constant but with a small increase from 10 – 20 min. Therefore, the extraction time of 20 min was selected for this experiments.

### Effect of extraction temperature

The extraction temperature influences the solubility of the organic solvent in water and also affects the mass-transfer process and the extraction efficiency. In this paper different temperatures were studied ranging from 20 to 80 °C. The results are shown in Fig. 4, the analytical signal increased with increasing extraction temperature up to 60 °C, but a further increase in temperature caused a decrease in analytical signal, which might be due to an increase of pressure in extraction system at higher temperatures, hence, 60 °C was chosen for this study.

### Salt effect

The influence of ionic strength was evaluated at 0 – 5% (w/v) NaCl and KCl, the results showed that when increasing salt concentration, the relative absorbance were decreased. Therefore, no addition of salt was chosen in this study.



**Fig. 3** Effect of extraction time on extraction of Cd(II). (Conditions: 13 mL of 0.5 µg L<sup>-1</sup> Cd(II) solution, pH 9, 500 µL of 5.0 mmol L<sup>-1</sup> PAN solution 90 µL 1-undecanol, extraction at room temperature and stirring rate: 325 rpm

**Fig. 4** Effect of extraction temperature on extraction of Cd(II). (Conditions: 13 mL of 0.5 µg L<sup>-1</sup> Cd(II) solution, pH 9, 500 µL of 5.0 mmol L<sup>-1</sup> PAN solution 90 µL 1-undecanol, stirring rate: 1000 rpm and extraction time: 30 min.

**METHOD PERFORMANCE**

Under the optimum conditions, the proposed method gave line equations compared between ETAAS and SFODME-ETAAS procedure,  $y = 0.0212x + 0.0172$ ;  $r^2 = 0.9984$  and  $y = 0.1629x + 0.2258$ ;  $r^2 = 0.9981$ , respectively. The analytical curves were linear in the range of 0.1 – 5.0 µg L<sup>-1</sup>. The LOD and LOQ were 0.053 and 0.177 µg L<sup>-1</sup>, respectively, based on 20 times the blank SD. The relative standard deviation (RSD) was ±2.67% for Cd(II) (1.0 µg L<sup>-1</sup> and n=6) and the preconcentration factor was 22.03 when using 13 mL sample volume.

**Table 2** Analytical results and recoveries of the analytes in water samples

Sample	Added (µg/L)	Found (µg/L ± RSD)	Recovery (% ± RSD)
Drinking water	0.0	0.34 ± 0.07	-
	1.5	1.62 ± 0.08	100.48 ± 0.05
	3.0	3.65 ± 0.07	117.83 ± 0.12
Tap water	0.0	0.70 ± 0.09	-
	1.5	1.99 ± 0.03	86.54 ± 0.05
	3.0	3.80 ± 0.05	103.44 ± 0.07

**ANALYSIS OF SAMPLES**

In general, the amount of cadmium present in the water samples was at very low levels. Reliability of this method was checked by determining Cd concentration spiked in the sample with calibration method. The results for the recovery of the spiked samples are given in Table 2.

The procedure was applied to ten water samples, including, five-bottled mineral water and tap water. The samples were spiked with 1.5 and 3.0 µg L<sup>-1</sup> with Cd, the amount recovered was in the range of 85.79 – 121.12%. The cadmium contents in this report for bottled mineral water and tap water ranged from 0.26 – 0.34 and 0.37 – 0.70 µg L<sup>-1</sup>, respectively.

## CONCLUSIONS

This study demonstrates the solidified floating organic drop microextraction with electrothermal atomic absorption spectrometry for determination of cadmium in water samples, using 1-(2-pyridylazo)-2-naphthol; PAN as the chelating reagent. The advantages of this method are its simplicity, selectivity, safety, low cost and minimum consumption of organic solvent. The proposed method has the potential to be used for miniaturized sample pretreatment procedures for the separation, preconcentration and determination of ultra-trace elements in various samples.

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