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**Article**

# Preconcentration and Determination of Cadmium in Water and Food Samples by *in situ* Surfactant-Based Solid-Phase Extraction and Flame Atomic Absorption Spectrometry

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A extração em fase sólida baseada em tensoativos *in situ* (ISS-SPE) é proposta como um procedimento de pré-concentração na determinação de cádmio em amostras de água e comida por espectrometria de absorção atômica de chama. No presente trabalho, utilizou-se brometo de cetiltrimetilamônio como um tensoativo catiônico, íon hexafluorfosfato como um agente par-iônico e 4-benzilpiperidinaditiocarbamato de potássio (K-4-BPDC) como um agente quelante. Várias variáveis que afetam as eficiências de extração foram investigadas e otimizadas, como pH, tipo e quantidade de tensoativo, concentração do agente par-iônico, concentração do agente quelante, força iônica e tempo de extração. Após a otimização das condições de complexação e extração, obteve-se um fator de enriquecimento de 40. A curva de calibração mostrou ser linear na faixa de 1-50 µg $L^{-1}$ e o limite de detecção era 0,3 µg $L^{-1}$. O desvio padrão relativo para 20 µg $L^{-1}$ de cádmio era menor que 2,2%. A validação da metodologia foi feita pelo método de adição de padrão e análise de materiais de referência certificados. O método foi aplicado com sucesso na determinação de cádmio em diversas amostras de água e comida.

*In situ* surfactant-based solid-phase extraction (ISS-SPE) is proposed as a preconcentration procedure for the determination of cadmium in water and food samples by flame atomic absorption spectrometry. In the present work, cetyltrimethylammonium bromide was used as a cationic surfactant, hexafluorophosphate ion as an ion-pairing agent and 4-benzylpiperidinedithiocarbamate potassium salt (K-4-BPDC) as a chelating agent. Several variables that affect the extraction efficiencies such as pH, type and amount of surfactant, concentration of ion-pairing agent, concentration of chelating agent, ionic strength and extraction time were investigated and optimized. After optimization of the complexation and extraction conditions, an enrichment factor of 40 was obtained. The calibration curve was linear in the range of 1-50 µg $L^{-1}$ and the limit of detection was 0.3 µg $L^{-1}$. The relative standard deviation for 20 µg $L^{-1}$ of cadmium was lower than 2.2%. Validation of the methodology was performed by standard addition method and analysis of certified reference materials. The method was successfully applied to the determination of cadmium in various food and water samples.

**Keywords:** *in situ* surfactant-based solid-phase extraction, cadmium determination, food and water samples, preconcentration, flame atomic absorption spectrometry

## Introduction

The increasing use of heavy metals over the past few decades has inevitably led to an increased pollution of metallic substances in natural water, and posed serious ecological and health risks. The toxic heavy metals could gradually accumulate in the human body through the food chain and cause damage to human health. Cadmium is a well-known toxic and persistent pollutant that is naturally present at very low levels in common aquatic environments.[1] Cadmium can be accumulated in several organs, producing carcinogenic effect.[2] The Food and Agriculture Organization (FAO) of the United Nations and the World Health Organization (WHO) Joint Expert Committee on Food Additives recommended provisional maximum tolerable daily intake of cadmium from all sources (water, food and air) of 1.0-1.2 µg $kg^{-1}$ of body mass.[3] According to WHO the upper permissible level of cadmium in drinking water is 3.0 µg $L^{-1}$.[4] For humans, the main sources of cadmium are from water and food. Therefore, sensitive, reproducible and accurate analytical methods are required for the determination of trace

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amount of cadmium in such samples. Several spectral and electrochemical methods have been used for determination of heavy metal ions.[5-11]

Among the spectral methods, flame atomic absorption spectrometry (FAAS) method is simple, rapid, reliable, low cost, highly selective (as atomic lines are sharp) and present in almost all analytical laboratories. Despite these advantages, its sensitivity is lower than inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP OES) and graphite furnace atomic absorption spectrometry (GF AAS). Hence, combining a preconcentration step prior to FAAS determination is often resorted by various researchers.[12-17] In recent years, different procedures such as coprecipitation,[18,19] liquid-liquid extraction (LLE),[20-22] cloud-point extraction,[23,24] solid-phase extraction (SPE)[25-31] and dispersive liquid-liquid microextraction[32] have been developed for the separation and preconcentration of cadmium from different matrices. However, some of these pretreatment methods need large amounts of sample and/or organic solvents, are time-consuming and expensive, and have unsatisfactory enrichment factors. These problems could be addressed by the development of modular and compact processes that provide adequate separation and preconcentration without complex processes.

SPE is more flexible and efficient than LLE in terms of simplicity, low consumption of the organic solvents, flexibility to choose the adsorbent and high enrichment factor. Recently, SPE has been increasingly used for the preconcentration and separation of ultra-trace amounts of inorganic and organic species from complex matrices.[33,34] Solid-phase extraction techniques are surface-dependent processes as their efficiency directly depends on the particle size and the surface area of the sorbent.[35] Recently, Yousefi and Shemirani developed a novel solid phase extraction technique that is based on in situ formation of very fine solid particles as sorbent that was named *in situ* surfactant-based solid-phase extraction (ISS-SPE).[36] In this *in situ* sorbent formation extraction method, a cationic surfactant with a proper alkyl group is dissolved in the aqueous sample and then hexafluorophosphate as ion-pairing agent is added. Due to the interaction between the surfactant and the ion-pairing agent, very fine solid particles are formed. The alkyl group of the surfactant (on the sorbent particles) can act to extract hydrophobic analyte(s) from aqueous samples. Extraction occurs via hydrophobic bonding of the alkyl group of the sorbent with the hydrophobic parts of the extracted analyte molecules. After centrifugation, the solid particles are sedimented at the bottom of the centrifuge tube and the aqueous phase is removed by a simple decantation of the centrifuge tube. The sedimentary sorbent can be either dissolved in ethanol (or other organic solvent) or leached with acid in order to recover the analyte(s).[36] Its major advantages are low cost, simple experimental procedures, high preconcentration factors, short extraction time and personal and environmental safety.[36,37]

In the present study, *in situ* surfactant-based solid-phase extraction method was developed for determination of trace amount of cadmium by using FAAS in food and water samples. 4-Benzylpiperidinedithiocarbamate potassium salt (K-4-BPDC) (Figure 1) was used as a chelating agent.[38-41] The experimental parameters, such as pH of the solution, type and amount of surfactant, concentration of ion-pairing agent, amounts of chelating agent, ionic strength, extraction time and the effect of diverse ions were investigated.

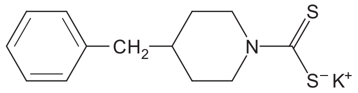

**Figure 1.** Structure of 4-benzylpiperidinedithiocarbamate potassium salt (K-4-BPDC).

## Experimental

### Apparatus

A PG-990 (PG instrument Ltd., United Kingdom) atomic absorption spectrophotometer, equipped with deuterium background correction, cadmium hollow cathode lamp and an air-acetylene flame was used for cadmium determination. All data acquisition was made according to peak height with the equipment software. The operating conditions were: wavelength 228.8 nm, spectral resolution 0.4 nm, applied lamp current 5.0 mA, air flow rate 10.0 L min$^{-1}$, acetylene flow rate 1.0 L min$^{-1}$, and aspiration flow rate 5 mL min$^{-1}$. A Hettich centrifuge (Model Universal 320R, Germany) was used for centrifugation. The pH values were measured with a Metrohm pH-meter (model 827) supplied with a glass-combination electrode.

### Reagents and materials

All reagents used were of analytical reagent grade. Deionized water was used throughout the experiments. A stock solution of 1000 mg L$^{-1}$ of cadmium was prepared by dissolving appropriate amount of $Cd(NO_3)_2$ (Merck, Darmstadt, Germany) in 1% nitric acid solution. Working solutions were prepared daily from the stock solution by serial dilution. All standard solutions for FAAS instrument calibration were prepared in mixture of acetone-ethanol (1:1). K-4-BPDC was prepared according to the procedure described by Andac *et al.*.[38] Fresh 0.01 mol L$^{-1}$ solution of K-4-BPDC was prepared daily by dissolving an appropriate amount of reagent in deionized water. *N*-cetyltrimethylammonium bromide (CTAB), tetra-*n*-butylammonium bromide (TBAB), *N*-dodecyltrimethylammonium bromide (DTAB), *N*-alkyl-*N*,*N*-dimethyl-*N*-benzylammonium chloride (ADBAC, $C_{12}$-$C_{14}$ alkyl), ethanol and sodium chloride were purchased from Merck (Darmstadt, Germany). Sodium hexafluorophosphate ($NaPF_6$) was purchased from ACROS (Geel, Belgium). A buffer solution (pH 6.0, 1.0 mol $L^{-1}$) was prepared by mixing an appropriate amount of acetic acid with sodium acetate solution. Water standard reference material SRM 1643e (trace elements in water) and SRM-1640a (trace elements in natural water) from National Institute of Standards and Technology (NIST) were both employed to test the proposed methodology. Pipettes and glass vessels used for trace analysis were stored in 10% nitric acid for at least 24 h and washed four times with deionized water before use.

### Preparation of the real samples

Spinach, lettuce, black tea and fish samples were purchased at a local market. Spinach sample was washed with deionized water, cut and oven-dried at 90 ºC for 24 h. Next, it was ground in a household grinder. One gram of the sample was placed in a 100 mL beaker, and 10 mL of concentrated $HNO_3$ (65% m/m) was added to the beaker. The mixture was evaporated near to dryness on a hot plate at about 130 ºC for 30 min. After cooling to room temperature, 5 mL of concentrated hydrogen peroxide (30%, m/m) was added. The mixture was again evaporated near to dryness. The resulting solution was diluted to 25 mL with deionized water. The result was filtered and the pH of the solution was adjusted at 6.0 by adding NaOH solution (1 mol $L^{-1}$). Finally, the solution was diluted to 50 mL by deionized water. The same digestion procedure was used for lettuce, black tea and fish samples. Fish muscle sample was used and was oven dried at 60-65 $^{o}$C. A blank digest was carried out in the same way for each sample.

All of the collected water samples (tap, mineral, river and sea water) were filtered through a cellulose membrane filter (Millipore) of pore size 0.45 µm and, after acidification to 1% with concentrated nitric acid, were stored in polyethylene bottles.

### *In situ* surfactant-based solid phase extraction procedure

An aliquot of 40 mL sample or standard solution containing cadmium in the concentration range of 1-50 µg $L^{-1}$ and $2.0 \times 10^{-4}$ mol $L^{-1}$ K-4-BPDC was adjusted to pH 6.0 (1 mL of acetate/acetic acid buffer solution) and was poured in a screw cap conical-bottom glass centrifuge tube. Then, 0.8 mL of CTAB solution (0.05 mol $L^{-1}$) was added into the sample solution and the tube was manually shaken to ensure complete homogenization of the CTAB in the aqueous solution. Then, 4.0 mL of $NaPF_6$ solution (1.0 mol $L^{-1}$) was quickly added by using a syringe. A cloudy solution (very fine particles of the dispersed $CTAB^+PF_6^-$ salt) was formed. In order to accelerate phase separation, the cloudy solution was centrifuged for 5 min at 5000 rpm. As a result, fine particles of the sorbent were sedimented at the bottom of the centrifuge tube. The aqueous phase was then separated completely by a syringe. Afterwards, the sorbent was dissolved in 1.0 mL of acetone-ethanol mixture (1:1 v/v). The resultant solution was introduced into the flame by conventional aspiration.

## Results and Discussion

### Selection of the surfactant

In ISS-SPE, formation of the fine solid particles (sorbent) depends on the interaction between the cationic surfactant and the ion-pairing agent. The alkyl group in the sorbent interacts with the hydrophobic parts in the extracted analyte and acts as an extraction medium. Four cationic surfactants of CTAB, TBAB, DTAB and ADBAC were examined. Experiments were performed using $1.0 \times 10^{-3}$ mol $L^{-1}$ of surfactants and 0.1 mol $L^{-1}$ of $NaPF_6$. Figure 2 shows the effect of surfactant type on the extraction recovery of cadmium. In all cases the sorbent formation occurred and cloudy solutions were observed. But in case of TBAB and DTAB, it was observed that after centrifugation, the solid particles were not sedimented completely and it could thus explain the non-quantitative extraction recoveries. In case of CTAB and ADBAC, the

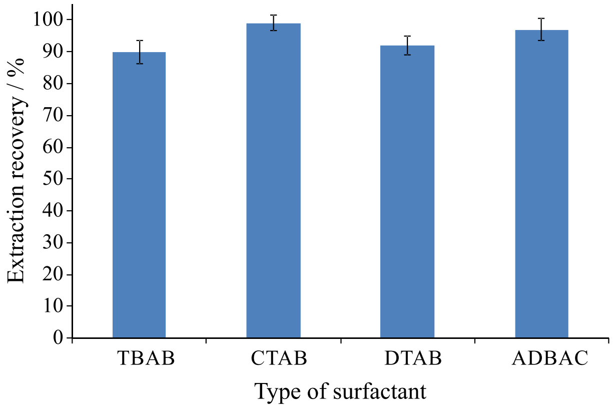

**Figure 2.** Effect of type of surfactant on the extraction of cadmium. Conditions: sample volume, 40 mL; cadmium concentration, 20 µg $L^{-1}$; K-4-BPDC concentration, $2.0 \times 10^{-4}$ mol $L^{-1}$; pH 6.0; surfactants concentration, $1.0 \times 10^{-3}$ mol $L^{-1}$; $NaPF_6$ concentration, 0.1 mol $L^{-1}$.

extraction recoveries were quantitative for both of them, but the repeatability of extraction recovery of cadmium by CTAB (98.5 ± 2.1) was better than ADBAC (97.6 ± 4.1). According to these results, CTAB was chosen as the proper surfactant for subsequent experiments.

### The effect of pH

Separation of metal ions by ISS-SPE involves prior complex formation with sufficient hydrophobicity to be extracted by the fine particles of the sorbent. The pH of the aqueous phase is one of the most important factors in the extraction of metal ions from various media for the formation of metal complex. The influences of the pH on the quantitative recovery values of cadmium at the presented extraction system were investigated at the pH range of 1.0-10.0 using $HNO_3$ and NaOH while other parameters were kept constant. The results are depicted in Figure 3. The extraction efficiency of the complex was increased as the pH of the aqueous solution was increased from 1.0 to 5.0 and is effectively recovered within the pH range of 5.0-10.0. Competition between protons and metal species could thus explain the weak extraction recovery in acid medium. Thus, pH 6.0 was used for extraction of cadmium in the following work. In order to control the pH during the analytical procedure, it was adjusted to 6.0 with acetate/acetic acid buffer solution.

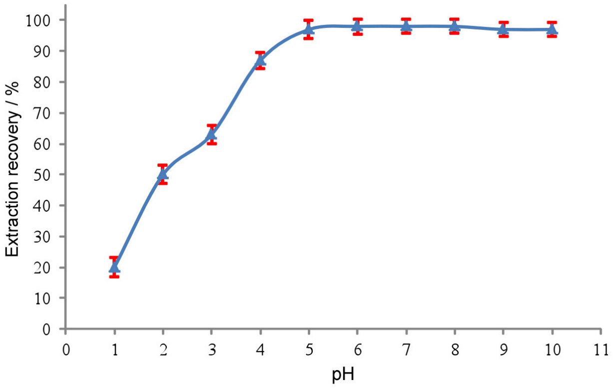

**Figure 3.** Effect of pH on the extraction of cadmium. Conditions: sample volume, 40 mL; cadmium concentration, 20 µg $L^{-1}$; K-4-BPDC concentration, $2.0 \times 10^{-4}$ mol $L^{-1}$; CTAB concentration, $1.0 \times 10^{-3}$ mol $L^{-1}$; $NaPF_6$ concentration, 0.1 mol $L^{-1}$.

### The effect of K-4-BPDC concentration

Concentration of the chelating agent is a critical variable to be optimized in preconcentration methods. Thus, it is highly important to establish the minimal reagent concentration that leads to total complex formation while achieving the highest extraction. In the light of these points, the effects of the amounts of K-4-BPDC on the quantitative recovery of cadmium in ISS-SPE system were examined within the range of $1.0 \times 10^{-6}$-$5.0 \times 10^{-4}$ mol $L^{-1}$. As is shown in Figure 4, the extraction recovery of cadmium was increased by increasing the K-4-BPDC concentration up to $5.0 \times 10^{-5}$ mol $L^{-1}$ and then remained constant. At a low concentration of K-4-BPDC, the complexation was not complete and the extraction efficiency was low; hence, the recovery was decreased. Thus, $20.0 \times 10^{-5}$ mol $L^{-1}$ of K-4-BPDC were chosen as the optimum for the elimination of probable interference effects of some coexisting ions in real sample analysis.

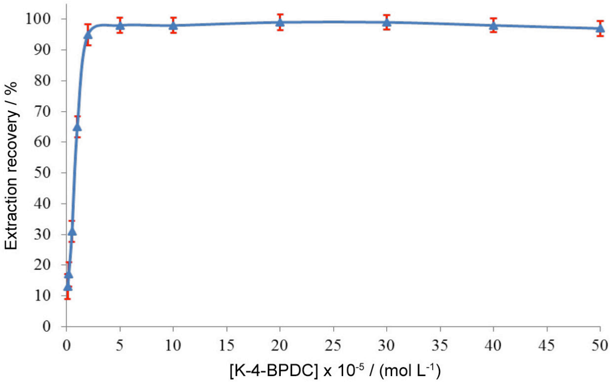

**Figure 4.** Effect of K-4-BPDC concentration on the extraction of cadmium. Conditions: sample volume, 40 mL; cadmium concentration, 20 µg $L^{-1}$; pH 6.0; CTAB concentration, $1.0 \times 10^{-3}$ mol $L^{-1}$; $NaPF_6$ concentration, 0.1 mol $L^{-1}$.

### The effect of CTAB concentration

The amount of sorbent has influence on the extraction efficiency of SPE methods. In ISS-SPE, the amount of sorbent that forms into the sample solution depends on surfactant concentration. In order to investigate the effect of CTAB concentration, several experiments were carried out using different CTAB concentrations. In all experiments, the concentration of $NaPF_6$ was 0.1 mol $L^{-1}$. As is shown in Figure 5, the extraction recovery of cadmium was quantitative when the CTAB concentration was higher than $0.5 \times 10^{-3}$ mol $L^{-1}$. At lower concentrations, the extraction recovery was low probably because of the inadequacy of the sorbent to adsorb the hydrophobic complex quantitatively. Therefore, a concentration of $1.0 \times 10^{-3}$ mol $L^{-1}$ CTAB was chosen for the subsequent experiments.

### The effect of $NaPF_6$ concentration

The effect of $NaPF_6$ as an ion-pairing agent was investigated within the range of 0.01-0.2 mol $L^{-1}$ in the presence of $1.0 \times 10^{-3}$ mol $L^{-1}$ of CTAB. The results indicated (Figure 6) that the extraction recovery increased by increasing the $NaPF_6$ concentration up to 0.08 mol $L^{-1}$

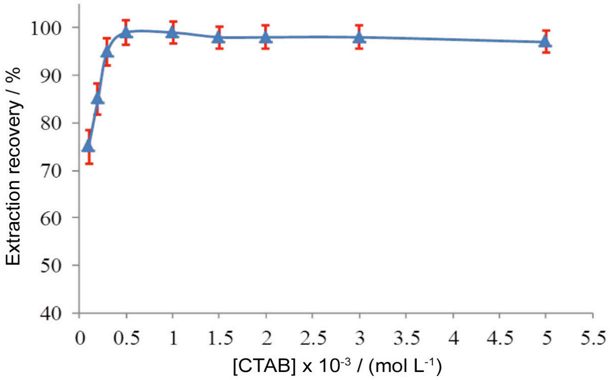

**Figure 5.** Effect of CTAB concentration on the extraction of cadmium. Conditions: sample volume, 40 mL; cadmium concentration, 20 µg $L^{-1}$; K-4-BPDC concentration, $2.0 \times 10^{-4}$ mol $L^{-1}$; pH 6.0; $NaPF_6$ concentration, 0.1 mol $L^{-1}$.

and then remained constant; these results can be interpreted as follows: by increasing the amount of $NaPF_6$, more solid sorbent was formed and, therefore, extraction recovery increased. So, 0.1 mol $L^{-1}$ of $NaPF_6$ was chosen for the subsequent experiments.

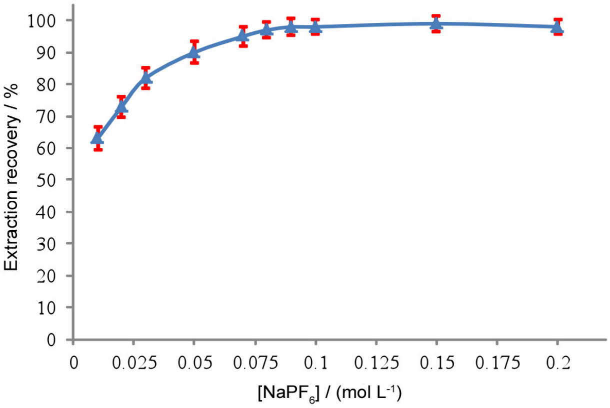

**Figure 6.** Effect of $NaPF_6$ concentration on the extraction of cadmium. Conditions: sample volume, 40 mL; cadmium concentration, 20 µg $L^{-1}$; K-4-BPDC concentration, $2.0 \times 10^{-4}$ mol $L^{-1}$; pH 6.0; CTAB concentration, $1.0 \times 10^{-3}$ mol $L^{-1}$.

### The effect of ionic strength

For investigating the influence of ionic strength on the performance of ISS-SPE, various experiments were performed by adding different amounts of NaCl (0.0-10.0% m/v). Other experimental conditions were kept constant. The results confirmed that the salt addition has no significant effect on the extraction process and the recovery of cadmium was quantitative. The negligible influence of the salt can be ascribed to the rapidity of the cadmium chelate distribution between the involved phases as the likely result of the dispersion process. Thus, no ionic strength buffer was used for subsequent experiments. These observations suggest the possibility of the application of the method for the separation of cadmium from saline solutions such as the seawater.

### The effect of extraction time

In our study, extraction time is defined as the time interval between the injection of the ion-pairing agent ($NaPF_6$) and the start of centrifugation. The effect of extraction time on the extraction recovery of cadmium was studied from 10 s to 20 min. The negligible effect of the extraction time on the extraction recovery of cadmium (98.0 to 101.2%) was observed. This may be due to the fact that the large contact surface area between the fine particles of the sorbent and the aqueous phase results in a very rapid adsorption of the analyte on the surface of the dispersed solid sorbent. Thus, 10 s (a short extraction time) was selected in subsequent experiments.

### The effect of centrifugation rate and time

The effect of centrifugation rate on the extraction recovery was studied in the range of 1000-6000 rpm. The extraction recovery increased from 85 to 98%, when the centrifugation rate increased in the range of 1000-4000 rpm, and then remained approximately constant. Therefore, the rate of 5000 rpm was selected as the optimum point. At the optimum rate, recovery was investigated as a function of centrifugation time. Over 4 min, extraction recovery was quantitative and constant indicating a complete transfer of the solid particles to the bottom of the centrifuge tube and 5 min was selected as the centrifugation time.

### The effect of coexisting ions

The effect of various ions for the determination of 20 µg $L^{-1}$ cadmium was examined separately as described in the procedure. Given spices were considered to interfere if it resulted in a ± 5% variation of the AAS signal. The results showed that, in excess of 100,000-fold of $Li^+$, $K^+$, $Na^+$, $F^-$, $Cl^-$, $SO_4^{2-}$, $CO_3^{2-}$, 10,000-fold of $Ca^{2+}$, $Mg^{2+}$, $Ba^{2+}$, $Sr^{2+}$, $PO_4^{3-}$, 1,000-fold of $Mn^{2+}$, $Zn^{2+}$, $Cr^{3+}$ and 500-fold of $Ag^+$, $Pb^{2+}$, $Al^{3+}$, $Fe^{2+}$, $Fe^{3+}$, $Ni^{2+}$, $Cu^{2+}$, $Co^{2+}$ ions had no significant interferences in the extraction and determination of cadmium. According to the results, the major ions in the real samples have no obvious influence on cadmium ISS-SPE under the selected conditions.

### Analytical performance

Optimized experimental parameters and analytical performance of method are given in Table 1. Under these experimental conditions, analytical features of proposed method, such as linear range of calibration curve, preconcentration factor, limit of detection (LOD) and limit of quantification (LOQ) were also determined. LOD and LOQ for cadmium were obtained from calibration curve as 0.3 and 0.9 μg L$^{-1}$, respectively. Calculation of LOD and LOQ values was based on three and ten times of the standard deviation of the blank signals, respectively (n = 10). The response of analytical method used linearly changed with the concentration of cadmium in the range of 1 to 50 μg L$^{-1}$ with calibration equation given as: $A = 0.0149\,C + 0.0153$, $R^2 = 0.9992$. In this equation, A is absorbance corresponding to concentration C (μg L$^{-1}$) of cadmium. The preconcentration factor that was calculated by dividing the aqueous phase volume to the final volume of diluted phase was 40. The relative standard deviation (RSD) resulting from the analysis of ten replicates of 40 mL solution containing 20 μg L$^{-1}$ cadmium was 2.2%.

**Table 1.** Analytical performance and optimum conditions of the proposed method for determination of cadmium

| Parameter | Value |
|---|---|
| pH | 6.0 |
| Concentration of K-4-BPDC / (mol L$^{-1}$) | $2.0 \times 10^{-4}$ |
| Concentration of CTAB / (mol L$^{-1}$) | $1.0 \times 10^{-3}$ |
| Concentration of $NaPF_6$ / (mol L$^{-1}$) | 0.1 |
| Extraction time / s | 10 |
| Maximum sample volume / mL | 40 |
| Preconcentration factor | 40 |
| LOD[a] / (μg L$^{-1}$) | 0.3 |
| LOQ[b] / (μg L$^{-1}$) | 0.9 |
| RSD[c] / % ($C_{Cd}$: 20 μg L$^{-1}$, n = 10) | 2.2 |
| Calibration equation (C) / (μg L$^{-1}$) | $A = 0.0149\,C + 0.0153$ |
| Linear range / (μg L$^{-1}$) | 1-50 |
| Correlation coefficient | 0.9992 |

[a]Limit of detection; [b]limit of quantification; [c]relative standard deviation.

### Analysis of real samples

Food samples (spinach, lettuce, black tea and fish) and real water samples (tap water, mineral water, river water and sea water) were subjected to the proposed method to evaluate the concentration of cadmium. The obtained results are given in Table 2 and Table 3. Recovery studies were also carried out after it was spiked to samples of known concentrations of cadmium. The recovery values calculated for the added standards ranged from 96.0 to 104.0%, thus confirming the accuracy of the procedure and its independence from the matrix effects. These results confirm the validity of the proposed preconcentration method. Furthermore, the accuracy of the developed method was evaluated by applying the recovery experiments for the determination of cadmium in water certified reference materials (CRMs). The following standard reference materials were used to verify the accuracy of the proposed method: NIST SRM-1643e and SRM-1640a. The results listed in Table 4 reveal that there is a good agreement between obtained results with certified values and

**Table 2.** Determination of cadmium in water samples

| Sample | Cadmium concentration / (μg L$^{-1}$) Added | Cadmium concentration / (μg L$^{-1}$) Found[a] | Recovery / % |
|---|---|---|---|
| Tap water (Drinking water system of Behshahr, Iran) | 0.0 | 2.3 ± 0.2 | – |
| | 10.0 | 12.2 ± 0.5 | 99.0 |
| | 20.0 | 22.4 ± 0.5 | 100.5 |
| Mineral water (Damavand mineral water, Iran) | 0.0 | n.d.[b] | – |
| | 10.0 | 9.8 ± 0.7 | 98.0 |
| | 20.0 | 19.7 ± 0.6 | 98.5 |
| River water (Tajan river, Sari, Iran) | 0.0 | 3.6 ± 0.2 | – |
| | 10.0 | 13.4 ± 0.6 | 98.0 |
| | 20.0 | 23.5 ± 0.7 | 99.5 |
| Sea water (Caspian sea water, Sari, Iran) | 0.0 | 5.1 ± 0.3 | – |
| | 10.0 | 14.7 ± 0.4 | 96.0 |
| | 20.0 | 24.6 ± 0.7 | 97.5 |

[a]Mean value ± standard deviation based on three replicate measurements; [b]not detected.

**Table 3.** Determination of cadmium in food samples

| Sample | Cadmium amount / (μg g$^{-1}$) Added | Cadmium amount / (μg g$^{-1}$) Found[a] | Recovery / % |
|---|---|---|---|
| Fish (carp) | – | n.d.[b] | – |
| | 2.00 | 2.08 ± 0.09 | 104.0 |
| Spinach (leaves) | – | n.d. | – |
| | 2.00 | 1.95 ± 0.11 | 97.5 |
| Lettuce | – | 0.22 ± 0.03 | – |
| | 2.00 | 2.28 ± 0.05 | 103.0 |
| Black tea | – | n.d. | – |
| | 2.00 | 2.05 ± 0.10 | 102.5 |

[a]Mean value ± standard deviation based on three replicate measurements; [b]not detected.

**Table 4.** Determination of cadmium in standard reference materials using the ISS-SPE

| Certified reference material | Certified / (μg L$^{-1}$) | Found[a] / (μg L$^{-1}$) | Recovery / % |
|---|---|---|---|
| SRM 1643e | 6.41 ± 0.07 | 6.32 ± 0.22 | 98.6 |
| SRM 1640a | 3.96 ± 0.07 | 4.02 ± 0.13 | 101.5 |

[a]Mean value ± standard deviation based on three replicate measurements.

**Table 5.** Comparison of ISS-SPE with other reported methods for the determination of cadmium

| Method | LR / (μg $L^{-1}$) | LOD / (μg $L^{-1}$) | RSD / % | EF | Ref. |
|---|---|---|---|---|---|
| SPE-ionic liquid-modified silica | 1-800 | 0.60 | 3.7 | 75 | 30 |
| Cloud point extraction | 3-300 | 1 | 1.3 | 55.6 | 42 |
| Flow injection wetting-film extraction | 1.5-45.0 | 0.7 | 3.9 | 35 | 43 |
| SPE-polyurethane foam | 10-1000 | 0.8 | 3.1 | 37 | 44 |
| SPE-functionalized resin | 2.0-20.0 | 1.1 | 4.0 | 33 | 45 |
| Ultrasound-assisted emulsification microextraction | 10-600 | 0.91 | 2.56, 1.62 | 13.4 | 46 |
| Cloud point extraction | 2.0-200 | 0.90 | 4.2 | 13.5 | 47 |
| ISS-SPE | 1-50 | 0.3 | 2.2 | 40 | Present work |

LR: linear range; LOD: limit of detection; RSD: relative standard deviation; EF: enrichment factor; SPE: solid-phase extraction; ISS-SPE: *in situ* surfactant-based solid-phase extraction.

indicate that the proposed procedure was helpful for the determination of cadmium in real samples with complicated matrices.

### Comparison of ISS-SPE with other reported methods for the determination of cadmium

LR, LOD, RSD and enrichment factor (EF) obtained by ISS-SPE were compared with other reported methods in order to know the potentiality of the present method for the determination of cadmium. The results are summarized in Table 5**.** The characteristics of the presented method are comparable or even better than those mentions in the table. All these results indicate that ISS-SPE is a reproducible and efficient technique that can be used for the preconcentration of metal ions like cadmium from water samples.

## Conclusions

The *in situ* surfactant-based solid-phase extraction (ISS-SPE) methodology was successfully used for the preconcentration of trace amount of cadmium in food and natural water samples. This method is found to be simple, sensitive and low cost method for the determination of cadmium. The relative standard deviation, detection limit and the duration time of this procedure are also satisfactory. The method significantly improved the performance of the FAAS detection for cadmium. It is believed that the proposed procedure can be also useful for analysis and monitoring of cadmium level in other food products, environmental and biological samples.

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## References

1. Wangersky, P. J.; *Marine Chemistry*; Springer-Verlag: Berlin, 2001.
2. Garrido, M. L.; Olivas, R. M.; Camara, C.; *J. Anal. At. Spectrom.* **1998**, *13*, 295.
3. FAO/WHO Joint Expert Committee on Food Additives. *WHO Tech. Rep. Senal No. 505*, p. 32; 1972.
4. World Health Organization (WHO); *Guidelines for Drinking-Water Quality, Vol. 1, 3rd edition*; WHO Press: Geneva, 2008.
5. Oehme, I.; Wolfbeis, O. S.; *Microchim. Acta* **1997**, *126*, 177.
6. Pesavento, M.; Alberti, G.; Biesuz, R.; *Anal. Chim. Acta* **2009**, *631*, 129.
7. Sitko, R.; Zawisza, B.; Malicka, E.; *TrAC, Trends Anal. Chem.* **2012**, *37*, 22.
8. Li, X. G.; Feng, H.; Huang, M. R.; Gu, G. L.; *Anal. Chem.* **2012**, *84*, 134.
9. Huang, M. R.; Ding, Y. B.; Li, X. G.; *Analyst* **2013**, *138*, 3820.
10. Huang, M. R.; Rao, X. W.; Li, X. G.; Ding, Y. B.; *Talanta* **2011**, *85*, 1575.
11. Li, X. G.; Ma, X. L.; Huang, M. R.; *Talanta* **2009**, *78*, 498.
12. Buchet, A. J.; Witzenbacher, M.; *J. Chromatogr. A* **1996**, *737*, 67.
13. Fritz, J. S.; *Analytical Solid Phase Extraction*, 1st ed.; Wiley-VCH: New York, 1999.
14. Atanassova, D.; Stefenova, V.; Russeva, E.; *Talanta* **2001**, *51*, 889.
15. Ghaedi, M.; Shokrollahi, A.; Niknam, K.; Niknam, E.; Najibi, A.; *J. Hazard. Mater.* **2009**, *168*, 1022.
16. Ghaedi, M.; Shokrollahi, A.; Kianfar, A. H.; Mirsadeghi, A. S.; Pourfarokhi, A.; Soylak, M.; *J. Hazard. Mater.* **2008**, *154*, 128.
17. Ghaedi, M.; Fathi, M. R.; Marahel, F.; Ahmadi, F.; *Fresenius Environ. Bull.* **2005**, *14*, 1158.
18. Chen, H.; Jin, J.; Wang, Y.; *Anal. Chim. Acta* **1997**, *353*, 181.
19. Prasad, K.; Gopikrishna, P.; Kala, R.; Rao, T. P.; Naidu, G. R. K.; *Talanta* **2006**, *69*, 938.
20. Amorim, F. A. C.; Ferreira, S. L. C.; *Talanta* **2005**, *65*, 960.

21. Anthemidis, A. N.; Zachariadis, G. A.; Farastelis, C. G.; Stratis, J. A.; *Talanta* **2004**, *62*, 437.
22. Carasek, E.; Tonjes, J. W.; Scharf, M.; *Quim. Nova* **2002**, *25*, 748.
23. Coelho, L. M.; Arruda, M. A. Z.; *Spectrochim. Acta, Part B* **2005**, *60*, 743.
24. Rezende, H. C.; Nascentes, C. C.; Coelho, N. M. M.; *Microchem. J.* **2011**, *97*, 118.
25. Lemos, V. A.; Baliza, P. X.; *Talanta* **2005**, *67*, 564.
26. Xie, Z. H.; Xie, F. Z.; Guo, L. Q.; Lin, X. C.; Chen, G. N.; *J. Sep. Sci.* **2005**, *28*, 462.
27. Narin, I.; Soylak, M.; Elci, L.; Dogan, M.; *Talanta* **2000**, *52*, 1041.
28. Tuzen, M.; Parlar, K.; Soylak, M.; *J. Hazard. Mater.* **2005**, *121*, 79.
29. Ciftci, H., *Desalination* **2010**, *263*, 18.
30. Liang, P.; Peng, L.; *Talanta* **2010**, *81*, 673.
31. Zhou, Q. X.; Zhao, X. N.; Xiao, J. P.; *Talanta* **2009**, *77*, 1774.
32. Jahromi, E. Z.; Bidari, A.; Assadi, Y.; Milani Hosseini, M. R.; Jamali, M. R.; *Anal. Chim. Acta* **2007**, *585*, 305.
33. Li, R.; He, Q.; Hu, Z.; Zhang, S.; Zhang, L.; Chang, X.; *Anal. Chim. Acta* **2012**, *713*, 136.
34. Bagheri, A.; Taghizadeh, M.; Behbahani, M.; Asgharinezhad, A.; Salarian, M.; Dehghani, A.; Ebrahimzadeh, H.; Amini, M. M.; *Talanta* **2012**, *99*, 132.
35. Fritz, J. S.; Macka, M.; *J. Chromatogr. A* **2000**, *902*, 137.
36. Yousefi, S. R.; Shemirani, F.; *Microchim. Acta* **2011**, *173*, 415.
37. Yasini, P.; Shemirani, F.; Khani, R.; *Food Anal. Methods* **2012**, *5*, 1303.
38. Andac, M.; Asan, A.; Isildak, I.; Cesur, H.; *Anal. Chim. Acta* **2001**, *434*, 143.
39. Cesur, H.; Bati, B.; *Turk. J. Chem.* **2002**, *26*, 599.
40. Jamali, M. R.; Gholinezhad, M.; Balarostaghi, S.; Rahnama, R.; Rahimi, S. H. A.; *E-J. Chem.* **2013**, *2013*, 615175.
41. Jamali, M. R.; Assadi, Y.; Shemirani, F.; *Sep. Sci. Technol.* **2007**, *42*, 3503.
42. Afkhami, A.; Madrakian, T.; Siampour, H.; *J. Hazard. Mater.* **2006**, *138*, 269.
43. Adam, I. S. I.; Anthemidis, A. N.; *Talanta* **2009**, *77*, 1160.
44. Gama, E. M.; Silva Lima, A.; Lemos, V. A.; *J. Hazard. Mater.* **2006**, *136*, 757.
45. Lemos, V. A.; Novaes, C. G.; Silva Lima, A.; Vieira, D. R.; *J. Hazard. Mater.* **2008**, *155*, 128.
46. Ma, J. J.; Du, X.; Zhang, J. W.; Li, J. C.; Wang, L. Z.; *Talanta* **2009**, *80*, 980.
47. Xiang, G.; Wen, Sh.; Wu, X.; Jiang, X.; He, L.; Liu, Y.; *Food Chem.* **2012**, *132*, 532.

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