Article

Ultrasound-Assisted Emulsification Solidified Floating Organic Drop Microextraction for the Determination of Trace Cadmium in Water Samples by Flame Atomic Absorption Spectrometry

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Uma técnica de microextração em fase líquida foi desenvolvida para a extração e determinação de quantidades traço de íons cádmio em amostras de água. A emulsificação-microextração assistida por ultrasom através da gota orgânica flutuante solidificada (USAE-SFODME) foi empregada para a extração e a espectrometria de absorção atômica com chama (FAAS) foi empregada para a determinação de Cd. Foram investigados e otimizados os fatores que influenciam na eficiência da técnica de microextração, tais como tipo e volume de solvente, tempo, temperatura, pH, quantidade do agente quelante e efeito da concentração de cloreto de sódio. Usando as condições otimizadas, um fator do enriquecimento de 81,0 foi obtido para um volume de 6,0 mL de amostra de água. A curva analítica de calibração mostrou-se linear no intervalo de 10-450 µg L^{-1} com um limite de detecção (LOD) igual a 0,66 µg L^{-1} de Cd. Os desvios padrão relativos (RSD) para dez replicatas de soluções contendo 20 e 300 µg L^{-1} de Cd foram 3,34% e 2,42%, respectivamente. O método proposto foi avaliado pela determinação de Cd em material de referência certificado de água ou através de experimentos de adição e recuperação.

A liquid-phase microextraction technique was developed using ultrasound-assisted emulsification solidified floating organic drop microextraction (USAE-SFODME) combined with flame atomic absorption spectrometry (FAAS) for the extraction and determination of trace cadmium in water samples. Microextraction efficiency factors, such as extraction solvent type and extraction volume, time, temperature, pH, the amount of the chelating agent, and salt effect, were investigated and optimized. Under optimum conditions, an enrichment factor of 81.0 was obtained for 6.0 mL of water sample. The calibration graph was linear in the range of 10-450 µg L^{-1} with a detection limit of 0.66 µg L^{-1}. The relative standard deviations (RSD) for ten replicate measurements of 20 and 300 µg L^{-1} of Cd were 3.34% and 2.42%, respectively. The accuracy of the proposed method was assessed either by determination of Cd in a certified reference material of water or by addition-recovery experiments.

Keywords: ultrasound-assisted emulsification, solidified floating organic drop microextraction USAE-SFODME, FAAS, preconcentration, cadmium

Introduction

The polluting nature of heavy metals has recently received considerable attention. Harmful health effects, such as high blood pressure, and impairment of the kidney and nervous system, have been imputed to these elements, which accumulate in living organisms and are highly toxic potential.[1] Their intensive technological use (fertilizers, mining and pigments) and their production from burning oil and coal make them extensive contaminants of soil, air and water.[2] Cadmium is recognized as an extremely environmental toxic and carcinogenic metal that can be easily dissolved and transported by water.[3] It is highly toxic to animals, plants, and humans even at low concentrations. Considering this, health organizations have established permissible limits for Cd in human food and drinking water.[4,5] The World Health Organization (WHO) established 3 µg L^{-1} as the maximum permissible amount for this element in drinking water.[4] The limit established by the Environmental Protection Agency (EPA) is 5 µg L^{-1}.[5] Recently, many interests and efforts have been devoted to studies on cadmium determination in water and biological

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matrices, to provide good strategies for environmental and toxicological monitoring.

Modern instrumental methods including spectrometry, inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP-OES), and atomic absorption spectrometry (AAS), among others,[6-8] have been used for determining traces of metal ions in various media. However, direct determination of metal ions at trace levels by flame AAS (FAAS) is limited not only because of insufficient sensitivity, but also by matrix interferences. Under these circumstances, in order to determine trace levels of Cd, a previous separation and enrichment step may be beneficial. Several enrichment procedures have been reported for Cd determination involving different analytical techniques such as solid-phase extraction (SPE),[9] liquid-liquid extraction (LLE),[10] ion-exchange,[11] etc. Despite the good analytical performance obtained from these separation/preconcentration techniques, their use is limited by disadvantages, such as lengthy separation, high reagent consumption, multiple stages, and unsatisfactory enrichment factors.[12]

Modern trends in analytical chemistry now lean toward the simplification and miniaturization of sample preparation, as well as the minimization of the organic solvents used. In 1996, Jeannot and Cantwell[13] developed a liquid-phase microextraction (LPME) technique based on analyte partitioning between a drop of organic solvent (extraction phase) and a bulk aqueous sample. Different types of LPME[14] have been developed, including single drop microextraction (SDME),[15] hollow fiber LPME,[16] and homogeneous liquid-liquid extraction (HLLE).[17] Microextraction techniques are fast, simple, inexpensive, environmentally friendly, and compatible with many analytical instruments. Nevertheless, drawbacks, such as droplet instability and relatively low precision, are often reported.[18] Subsequently, a novel microextraction technique, dispersive liquid-liquid microextraction (DLLME), which is based on the dispersion of tiny droplets of the extraction liquid within the aqueous solution, was developed.[19] Like HLLE and cloud point extraction (CPE), this technique is also based on a three-component solvent system.[20] The advantages of the DLLME method are speed, low cost, and high enrichment factors. However, the extract solvent is limited by the solvents used; these solvents, such as chlorobenzene, chloroform and tetrachloromethane, have a higher density than water and are toxic and not friendly to the environment.

Not long ago, a new liquid-liquid microextraction method called solidified floating organic drop microextraction (SFODME) was proposed for the extraction and determination of organic analytes. The method is a modified solvent extraction method.[21] Dadfarnia and co-workers[12,22,23] extended its application to inorganic analysis. In SFODME, no specific holders, like the microsyringe needle tip, the hollow fiber or the polychloroprene rubber (PCR) tube, are required for supporting the organic microdrop due to the low density and proper melting point of organic solvent. Moreover, the extractant droplet can be easily collected through low temperature solidification. Most importantly, compared to the traditional DLLME method, it avoided using high-density and toxic solvents.[24] However, the extraction time was lengthy; thus, it cannot satisfy the demand of fast analysis.[25]

On the other hand, ultrasonic radiation is a powerful means for the acceleration of various steps in analytical procedures for both solid and liquid samples.[26] This type of energy greatly helps in the liquid-liquid extraction because it facilitates the emulsification phenomenon and accelerates the mass-transfer process between two immiscible phases.[27] This leads to an increment in the extraction efficiency of the procedure in a minimum time.[28] The most widely accepted mechanism for ultrasound-assisted emulsification is based on the cavitation effect. The implosion bubbles generated by the cavitation phenomenon produce intensive shockwaves in the surrounding liquid and high-velocity liquid jets. These microjets can cause droplet disruption in the vicinity of collapsing bubbles, thus improving emulsification by generating smaller droplet of the dispersed phase right after disruption.[28] Submicron droplet-size results in significant enlargement of the contact surface between both immiscible liquids improving the mass-transfer between the phases.

The application of a miniaturized approach to the ultrasound-assisted emulsification by using a microvolume of extraction solvent provides the advantages of both ultrasonic radiation and SFODME. This new technique is called ultrasound-assisted emulsification solidified floating organic drop microextraction (USAE-SFODME). In USAE-SFODME, a small volume of an organic solvent with a melting point near room temperature is rapidly injected by a syringe into aqueous samples containing analytes and then floated onto the surface of aqueous solution. After sonication, a cloudy solution forms. This cloudy solution is centrifuged to produce fine droplets of the extraction solvent, which are then coalesced and collected at the upper surface of sample solution. The sample is transferred into an ice bath. When the organic solvent solidifies, it is transferred into a new conical vial, and the melted organic solvent is used for analytes determination. Operation simplicity, low cost, rapid, high enrichment factor, and low consumption of the extraction solvent are the advantages of the proposed method. Moreover, the transfer of the solidified phase from aqueous phase can be

carried out easily. Recently, determination of trace amounts of zinc in water samples was successfully performed with this method.[29]

This paper describes the application of USAE-SFODME for trace Cd determination in water samples using FAAS. 1-(2-Pyridylazo)-2-naphthol (PAN), a chelating agent that yields stable complexes with a number of metals and has found numerous applications in trace element separation and preconcentration methods,[30,31] is used to extract Cd into the organic phase. The effects of various experimental parameters on the extraction were investigated and optimized. The proposed method was evaluated by analyzing certified reference material and spiked environmental water samples.

Experimental

Apparatus

The experiments were performed using a Hitachi Z-5000 atomic absorption spectrometer (Japan) equipped with Zeeman background correction. A Cd hollow cathode lamp was used as the radiation source. The analytical wavelength (228.8 nm), spectral resolution (0.4 nm) and applied lamp current (3 mA) were used as recommended by the manufacturer. All pH measurements were carried out using a pH_3-3C digital pH meter equipped with a combined glass-calomel electrode (Hangzhou Dongxing Instrument Factory, Hangzhou, China). A Model LD5-2A centrifuge (Beijing Jingli Instrument Factory, Beijing, China) was used to accelerate phase separation. A 59 kHz, 200 W ultrasonic bath with temperature control (Shanghai Kudos Ultrasonic Instrument Co, Ltd., Shanghai, China) was used to assist the emulsification process of the microextraction technique.

Reagents and solutions

A stock standard solution of Cd at a concentration of 1000 µg mL^{-1} was purchased from the National Institute of Standards (Beijing, China). Working standard solutions were prepared daily through serial dilutions of the stock solution with deionized water immediately prior to analysis. The chelating agent, 0.2 g L^{-1} PAN solution, was prepared by dissolving the appropriate amount of PAN (Shanghai Chemistry Reagent Company, Shanghai, China) in absolute ethanol. The extraction solvents, 1-bromohexadecane, hexadecane, and 1-dodecanol were obtained from Aladdin Chemistry Reagent Company (Beijing, China).

Nitric acid (0.1 mol L^{-1}) was used to adjust the pH levels 2-3; ammonium acetate buffers (0.2 mol L^{-1}) were prepared by adding an appropriate amount of acetic acid to ammonium acetate solutions to produce pH 4-6 buffers. For pH 7-8, a phosphate (0.2 mol L^{-1}) buffer solution was prepared by adding an appropriate amount of disodium hydrogen phosphate to sodium dihydrogen phosphate. Ammonium chloride buffer solutions (0.2 mol L^{-1}) were prepared by adding an appropriate amount of ammonia to ammonium chloride solutions, resulting in solutions of pH 9-10. Sodium hydroxide (0.1 mol L^{-1}) was used to adjust pH 11.

All reagents used were of analytical reagent grade. Deionized water was used in the preparation of all solutions. The laboratory glassware was kept in 10% v/v nitric acid for at least 24 h and subsequently washed four times with deionized water.

Tap, sea and river water samples from Hebei Province were used for evaluating accuracy. Samples were collected in polytetrafluoroethylene (PTFE) containers, filtered using a 0.45 µm pore size membrane filter to remove suspended particulate matter, and stored in a refrigerator in the dark.

Extraction procedure

In a 10.0 mL conical centrifuge tube, 6.0 mL of standard solutions containing 300 µg L^{-1} Cd, 1.0 mL ammonium chloride buffer, and 1.0 mL PAN solution were mixed. Then, 90 µL of 1-dodecanol were added using a 100 µL syringe. The conical tube was sonicated for 10 min at 40 °C to ensure complete extraction. The mixture was then centrifuged for 2 min at 2000 rpm. After this process, fine droplets of 1-dodecanol coalesced and the organic solvent was collected at the surface. The conical test tube was transferred into an ice bath and the organic solvent solidified after 2 min. The solidified solvent was then transferred into another conical vial where it melted immediately. After this process, the extract was diluted to 500 µL with ethanol and manually injected into the FAAS.

Results and Discussion

Selection of the extraction solvent type

The organic solvent used as the extracting solvent in this method has to satisfy several criteria: (*i*) it must have low water solubility in order to have good extraction efficiency; (*ii*) it should have low volatility to prevent solvent loss during extraction; (*iii*) it should extract analytes well; (*iv*) its density must be lower than that of water; and (*v*) it must have a melting point (mp) near room temperature (in the range of 10-30 °C). 1-Bromohexadecane (mp 17.3 °C), hexadecane (mp 18 °C) and 1-dodecanol (mp 24 °C) were examined in the extraction of Cd.

The compatibility of these solvents with the USAE-SFODME technique was investigated by adding 90 μL of each to a 6.0 mL aqueous solution containing 300 μg L^{-1} of Cd. In this experiment, the extraction solvents 1-bromohexadecane, hexadecane and 1-dodecanol resulted in preconcentration factors of 40, 63, and 81, respectively. Among these solvents, 1-dodecanol demonstrated the maximum preconcentration factor, making it the most favorable for determination. Furthermore, its stability, low vapor pressure, and low water solubility at extraction conditions make 1-dodecanol the best extraction solvent to be used in this experiment.

Effect of volume of the extraction solvent

To evaluate the effect of the extraction solvent volume, different volumes of 1-dodecanol in the range of 30-120 μL (at 10 μL intervals) were examined in the preconcentration procedure. The results illustrated in Figure 1 show that, by increasing the volume of 1-dodecanol, the analytical signal increases, reaching a maximum value at 60 μL and then remaining constant. In order to ensure complete extraction, 90 μL was selected as the most suitable extraction solvent volume. After the preconcentration procedure, the obtained volume of 1-dodecanol was 90 ± 2 μL.
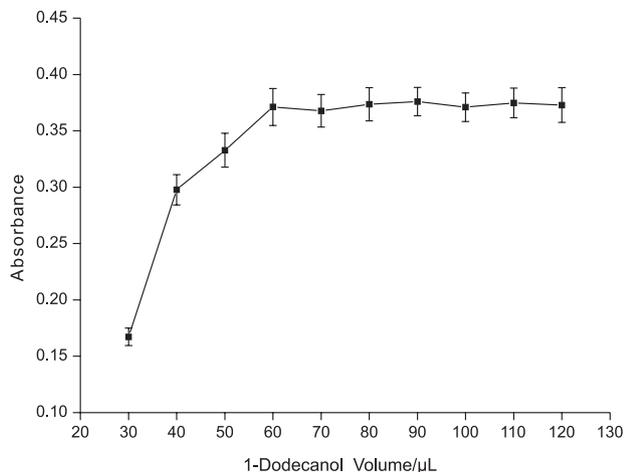

Figure 1. Effect of 1-dodecanol volume on the extraction of Cd using USAE-SFODME method. Extraction conditions: water sample volume: 6.0 mL; PAN volume: 1.0 mL; pH 9.0; Cd concentration: 300 μg L^{-1}; extraction time: 10 min; extraction temperature: 40 °C.

Influence of pH

The separation of metal ions by USAE-SFODME involves prior formation of a complex with sufficient hydrophobicity that allows it to be extracted into the small volume of the floated phase, where the desired preconcentration is obtained. The pH plays a unique role

in metal-chelate formation and subsequent extraction. The effect of pH on the complex formation and extraction of Cd from water samples was studied in the range of 2.0-11.0 by using nitric acid, ammonium acetate, phosphate, ammonium chloride and sodium hydroxide. The results illustrated in Figure 2 show that the analytical signal rose from pH 2.0 to 9.0, was held at pH 9.0-10.0, and then declined at pH greater than 10.0. Thus, the value of pH 9.0 was selected for further experiments.
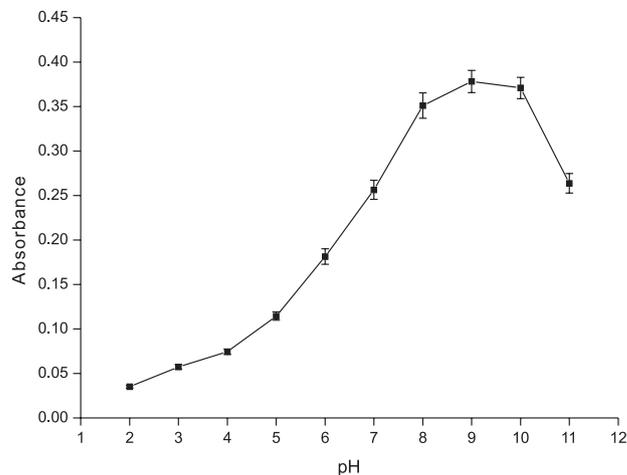

Figure 2. Effect of pH on the extraction of Cd by the USAE-SFODME method. Extraction conditions: water sample volume: 6.0 mL; PAN volume: 1.0 mL; extraction solvent (1-dodecanol) volume: 90 μL; Cd concentration: 300 μg L^{-1}; extraction time: 10 min; extraction temperature: 40 °C.

Effect of amount of PAN

The effect of the amount of PAN (0.2 g L^{-1}) on the absorption was studied, and the results are shown in Figure 3. The absorbance was stable when the PAN volume was higher than 0.6 mL, indicating complete extraction. When the volume of PAN was greater than 1.0 mL, the analytical signal decreased. This effect is probably caused by competition between complexing agent molecules, which are in excess in the solution, and Cd-complex molecules for extraction solvent interaction. Thus, a PAN volume of 1.0 mL was chosen as the optimum amount for Cd determination.

Effect of the extraction time

Extraction time is one of the most important factors in an extraction procedure.[29] In USAE-SFODME, extraction time is defined as the time between injection of extraction solvent and the end of the sonication stage. The effect of extraction time on extraction efficiency was examined in the range of 5-35 min with a constant ultrasonic frequency. The
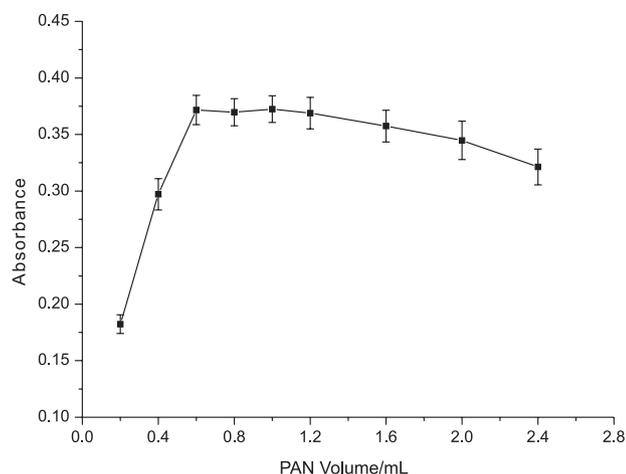
Figure 3. Effect of PAN amount on the extraction of Cd by the USAE-SFODME method. Extraction conditions: water sample volume: 6.0 mL; pH 9.0; extraction solvent (1-dodecanol) volume: 90 μL; Cd concentration: 300 μg L^{-1}; extraction time: 10 min; extraction temperature: 40 °C.

results show that the absorbance signals of Cd increased by increasing the extraction time up to 10 min. After 10 min, the absorbance remained nearly constant. Thus, in the following experiments 10 min was selected as the extraction time.

Effect of extraction temperature

Temperature affects organic solvent solubility in water, as well as the emulsification phenomenon. It also affects the mass-transfer process and the extraction efficiency. To determine the influence of the extraction temperature, the process was investigated by varying the temperature between 25 and 55 °C, as shown in Figure 4. At temperatures lower than 35 °C, it was difficult to obtain a homogeneous emulsion resulting in a prompt phase separation. Here, the mass-transfer process was limited to a short amount of time, leading to poor extraction efficiency and, consequently, low absorbance. In the 35-45 °C temperature range, the emulsification was easily achieved and the highest absorbance was obtained at 40 °C. At a temperature higher than 45 °C, the analytical signal decreased significantly. This may be due to an increase in solubility of the organic phase and the degradation of the complex brought about by high temperatures.[12] Hence, 40 °C is recommended for further studies.

Effect of salt

To study the influence of ionic strength on the performance of USAE-SFODME, NaCl concentrations were observed in the range of 0-5% m/v while other experimental conditions were kept constant. Increasing the NaCl concentration had
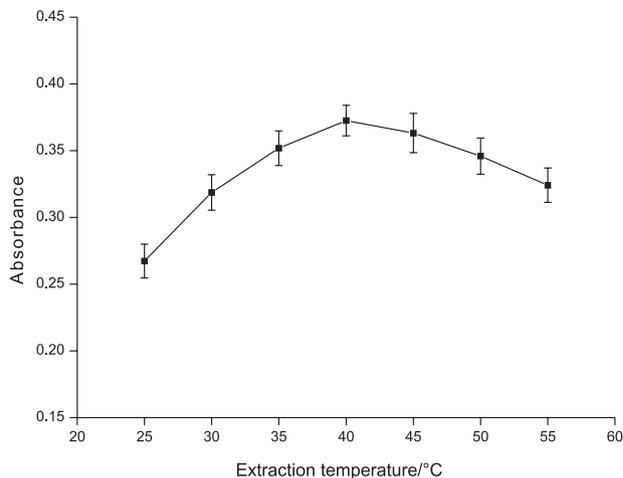

Figure 4. Effect of extraction temperature on the extraction of Cd by the USAE-SFODME. Extraction conditions: water sample volume: 6.0 mL; pH 9.0; PAN volume: 1.0 mL; extraction solvent (1-dodecanol) volume: 90 μL; Cd concentration: 300 μg L^{-1}; extraction time: 10 min.

no significant effect on extraction efficiency or the volume of the floating phase measured before dilution. The enrichment factor is held nearly constant regardless of the amount of salt. Subsequent extraction experiments were therefore carried out without additional salt.

Effect of sonication

The emulsification methods of sonication and vigorous stirring were compared. Vigorously stirring the solution for 30 min gave an analytical signal for Cd that was comparable to that obtained by sonication for 10 min. Sonication also produced smaller droplets of organic solvent in the aqueous bulk; smaller droplets generate larger contact areas between the aqueous phase and the extraction solvent. Therefore, the extraction efficiency of sonication was better than that of vigorous stirring

Effect of coexisting ions

The effects of coexisting ions on the recovery of Cd in real water samples were also studied. In these experiments, 6.0 mL of solutions containing 300 μg L^{-1} Cd and various amounts of interfering ions were treated according to the recommended procedure. If the resulting FAAS signal showed a ± 5% variation, the foreign ion was considered to interfere in Cd determination. The results obtained are presented in Table 1.

Figures of merit

The analytical characteristics of the proposed method, such as linear range, limit of detection, reproducibility,

Table 1. Effect of interfering ions on the recovery of 300 µg L⁻¹ Cd in water samples using USAE-SFODME-FAAS

Interferent	Concentration (µg L⁻¹)	Interferent/ Cd²⁺ ratio	Recovery (%)
Na⁺	3,000,000	10,000	96.5
K⁺	3,000,000	10,000	95.4
Ag⁺	12,000	40	95.3
Ba²⁺	15,000	50	96.5
Mn²⁺	30,000	100	95.8
Co²⁺	6,000	20	97.5
Cu²⁺	6,000	20	98.2
Ni²⁺	6,000	20	100.6
Zn²⁺	7,500	25	95.7
Pb²⁺	15,000	50	96.0
Fe²⁺	12,000	40	97.1
Ca²⁺	30,000	100	97.3
Mg²⁺	30,000	100	95.7
Hg²⁺	6,000	20	96.3
Bi³⁺	9,000	30	95.4
Cr³⁺	6,000	20	98.8
Al³⁺	9,000	30	97.4
Fe³⁺	15,000	50	96.2
As³⁺	6,000	20	95.5
As⁵⁺	15,000	50	95.6
Sn⁴⁺	12,000	40	96.5
Cl⁻	3,000,000	10,000	100.5
NO₃⁻	3,000,000	10,000	95.2
I⁻	300,000	1,000	98.5
CH₃COO⁻	300,000	1,000	97.6
SO₄²⁻	30,000	100	96.4
Cr₂O₇²⁻	30,000	100	97.6
PO₄³⁻	30,000	100	95.8

correlation coefficient, and enhancement factor, obtained by processing standard solutions of Cd under the optimum conditions described, are summarized in Table 2. The calibration curves were linear from 10 to 450 µg L⁻¹ for Cd. The calibration equation is $A = 1.52 \times 10^{-3}C + 0.0368$ with a correlation coefficient of 0.9985, where A is the absorbance of Cd, obtained by peak height, in the rich phase at 228.8 nm; and C is its concentration in the sample solution (µg L⁻¹). The limit of detection and quantification defined as $3S_B/m$ and $10S_B/m$ (where S_B is standard deviation of the blank and m is the slope of the calibration graph) were 0.66 and 2.15 µg L⁻¹, respectively. The relative standard deviations (RSD) for ten replicate measurements of 20 and 300 µg L⁻¹ of Cd were 3.34% and 2.42%, respectively. The preconcentration factor, f_c,

is defined as the ratio of Cd concentration in the solidified floating organic drop to that in the initial phase. Equation 1 was used for calculating the preconcentration factor. In this equation, C_S is the Cd concentration (µg L⁻¹) in the floating organic drop after phase separation and C_0 is the initial concentration of Cd (µg L⁻¹).[32] The preconcentration factor was determined to be 81.0 ± 3.0 (n = 3).

$$f_c = \frac{C_S}{C_0} \tag{1}$$

Table 2. Analytical characteristics of USAE-SFODME-FAAS for the determination of Cd

Analytical Parameter	Analytical Data
Linear range (µg L⁻¹)	10 - 450
Slope	1.52×10^{-3}
Correlation coefficient	0.9985
Detection limit (µg L⁻¹)	0.66
RSD (%) (n = 10, 20 µg L⁻¹)	3.34
RSD (%) (n = 10, 300 µg L⁻¹)	2.42
Preconcentration factor[a]	81.0
Preconcentration factor[b]	14.6
Enhancement factor[c]	15.0

[a] The preconcentration factor is the ratio of the Cd concentration in the solidified floating organic drop (90 µL) to that initially in the bulk phase; [b] The preconcentration factor is the ratio of the Cd concentration in 0.5 mL ethanol to that initially in the bulk phase; [c] The enhancement factor is the slope ratio of calibration graph after and before extraction.

For the determination of the absorbance for Cd in the floating organic drop, the extraction solvent was diluted with ethanol to a volume of 0.5 mL; the preconcentration factor for the proposed method is 14.6 ± 0.53.

The enhancement factor,[33,34] defined as the ratio of the slope of the calibration curve for the USAE-SFODME method to that obtained without preconcentration, was 15.0 for Cd.

Analysis of water

The proposed method was used for the determination of Cd in several water samples. The results and the recoveries for spiked samples are given in Table 3. The recoveries for the additions of different Cd concentrations to water samples were in the 94.5-101.5% range. To verify the accuracy of the proposed procedure, the method was used for the determination of Cd in National Standard Reference Material for Environmental Water (GSBZ 50009-88 and GSB 07-1185-2000) after the appropriate dilution. The results of this test are presented in Table 3. Good agreement between the determined and certified values was obtained.

Table 3. Determination of Cd in the dissolved fraction in certified reference materials and spiked natural water samples using the USAE-SFODME-FAAS method (n = 3)

Sample	Certified	Added	Found[a]	Recovery (%)
GSBZ 50009-88 ($\mu g\ L^{-1}$)	150.0 ± 6.0	–	147.60 ± 6.68	98.4
GSB 07-1185-2000 ($\mu g\ L^{-1}$)	81.3 ± 6.0	–	80.64 ± 5.20	99.2
Tap water[b] ($\mu g\ L^{-1}$)		0.0	< LOD	–
		15.0	14.18 ± 0.58	94.5
		20.0	19.66 ± 0.90	98.3
Sea water[c] ($\mu g\ L^{-1}$)		0.0	8.62 ± 0.50	–
		10.0	18.36 ± 0.88	97.4
		15.0	23.85 ± 1.24	101.5
River water[d] ($\mu g\ L^{-1}$)		0.0	< LOD	–
		15.0	14.28 ± 0.66	95.2
		20.0	19.70 ± 1.30	98.5
River water[e] ($\mu g\ L^{-1}$)		0.0	5.20 ± 0.35	-
		10.0	15.02 ± 0.86	98.2
		15.0	20.25 ± 1.14	100.3

[a] Mean of three experiments ± standard deviation; [b] From the drinking water system of Baoding, China; [c] Beidaihe Sea water, Qinhuangdao, China. [d] Yongding River water, Baoding, China; [e] Tang River water, Baoding, China.

Table 4. Characteristic performance data obtained by using USAE-SFODME-FAAS and other techniques for Cd determination

Method	LOD ($\mu g\ L^{-1}$)	RSD (%)	Preconcentration factor	Sample consumption (mL)	Calibration range ($\mu g\ L^{-1}$)	References
CPE-FAAS	0.9	4	—	11	3-400	35
CPE-FAAS	1.0	0.8-3.0	55.6[a]	10	3-300	32
IL-based USA-DLLME-ETAAS	0.0074	3.3	63[b]	10	0.02-0.15	36
HFRLM-FAAS	1.3	5.5	120[b]	20	2-30	16
SFODME-FI-FAAS	0.0079	0.54	640[a]	160	0.08-30	23
USAEME-FAAS	0.91	2.56	95[a]	8	10-600	37
USAE-SFODME	0.66	2.42	81[a]	8	10-450	Proposed method

[a] Preconcentration factor, as the ratio of the concentration of analyte after preconcentration to that without preconcentration given the same analytical response; [b] The enhancement factor is the slope ratio of calibration graph after and before extraction; CPE-FAAS: cloud point extraction-flame atomic absorption spectrometry; IL-based USA-DLLME-ETAAS: ionic liquid-based ultrasound-assisted dispersive liquid-liquid microextraction–electrothermal atomic absorption spectrometry; HFRLM-FAAS: hollow fiber renewal liquid membrane extraction-flame atomic absorption spectrometry; SFODME-FI-FAAS: solidification of floating organic drop microextraction-flow injection flame atomic absorption spectrometry; USAEME-FAAS: ultrasound-assisted emulsification microextraction-flame atomic absorption spectrometry.

Comparison to other methods

A comparison of the proposed method with other reported preconcentration methods is given in Table 4. Generally, the preconcentration factor and the LOD obtained using the proposed method are comparable to or better than those reported methods. IL-based USA-DLLME-ETAAS showed a lower LOD than the USAE-SFODME method, but had a higher RSD.[36] A lower enrichment factor and higher LOD than SFODME-FI-FAAS may have been the result of the

determination system and the fact that this method used a larger sample volume.[23]

Conclusion

USAE-SFODME, combined with FAAS, was evaluated for the preconcentration and the determination of the trace amounts of Cd (at $\mu g\ L^{-1}$ level) from various water samples. The application of ultrasonic radiation is an efficient tool to improve the extraction efficiency of the microextraction procedure with minimal time. 1-Dodecanol was chosen as

the extraction solvent for the method because of its proper melting point and lower density compared to water. In this work, an enrichment factor of about 81 times was attained with only 6.0 mL water sample. The method was successfully applied to environmental water samples. Satisfactory recoveries and reproducibility were obtained. The USAE-SFODME method has numerous advantages including rapidness, simplicity, low cost, low toxicity, high efficiency and low organic solvent consumption. Although the results obtained in this research were primarily focused on Cd determination, the system may be readily applied for the determination of other metals with the help of various chelating agents and organic solvents.

Acknowledgments

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