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Article

Ultrasound-Assisted Surfactant-Enhanced Emulsification Microextraction Combined with HPLC for the Determination of Estrogens in Water

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Desenvolveu-se um procedimento de microextração por emulsificação assistida por ultrassom e aperfeiçoada por surfactante (UASEME) combinado com cromatografia líquida de alta eficiência com detector de arranjo de diodos para a determinação de 17β-estradiol (βE2), estrona (E1) e dietilestilbestrol (DES) em água. Ultrassom foi aplicado para auxiliar a emulsificação e Triton X-100 foi usado como dispersor e emulsificante. Tetracloreto de carbono foi usado como solvente extrator. Empregando otimização global, o procedimento foi caracterizado por um intervalo linear aceitável de 10 a 1000 ng mL^{-1} para βE2, E1 e DES ($r > 0,997$), exatidão e precisão validadas (RSD 0,85-1,28% ($n = 5$)) e alta sensibilidade com limites de detecção de 0,200, 0,100 e 0,125 ng mL^{-1} para βE2, E1 e DES, respectivamente. O procedimento foi aplicado para a análise de amostras típicas de água, com fatores de enriquecimento de 85,29, 173,45 e 97,05 para βE2, E1 e DES, respectivamente, e boas recuperações (≥ 89,82%). De maneira geral, o procedimento desenvolvido foi simples e confiável, com potencial de aplicação em larga escala para análises da água.

An ultrasound-assisted surfactant-enhanced emulsification microextraction (UASEME) combined with high performance liquid chromatography-diode array detector procedure was developed for the determination of 17β-estradiol (βE2), estrone (E1) and diethylstilbestrol (DES) in water. Ultrasound was applied to assist emulsification, and Triton X-100 was adopted as the disperser and emulsifier. Carbon tetrachloride was applied as the extraction solvent. Global optimization was used and the developed procedure was characterized by an acceptable linear range of 10 to 1000 ng mL^{-1} for βE2, E1 and DES ($r > 0.997$), a validated accuracy and precision (RSD 0.85-1.28% ($n = 5$)), and high sensitivity with limits of detection of 0.200, 0.100 and 0.125 ng mL^{-1} for βE2, E1 and DES, respectively. Furthermore, we applied this procedure to analyze typical water samples, with enrichment factors of 85.29, 173.45 and 97.05 for βE2, E1 and DES, respectively, and good recoveries (≥ 89.82%). Altogether, the proposed procedure was simple and reliable, with potential application in large-scale water analysis.

Keywords: ultrasound-assisted surfactant-enhanced emulsification microextraction, HPLC, Triton X-100, estrogen, water samples

Introduction

βE2, E1 and DES (shown in Table 1) are three environmental endogenous estrogens which can promote the growth and development of female genitalia. They are generated by ovarian follicles, and enter the environment mainly from the excreta of human, poultry and livestock.[1] Agricultural waste has been recognized as an additional source of estrogens in water.[2] Estrogens have also been used in cosmetics to make the skin more elastic, white and glossy. However, estrogens were banned from cosmetics in the European Union due to their carcinogenicity.[3] The environmental levels of estrogens may be having widespread adverse effects on the reproductive health of humans and wildlife.[4] Therefore, it is important to establish a sensitive and reliable method for the determination of estrogen residues in water.

Currently, many widely used methods for the analysis of estrogens are based on chromatographic techniques such as liquid chromatography (LC),[5-8] gas chromatography (GC)[9] and chemiluminescence's enzyme immunoassay (CLEIA).[10] Besides, the estrogens are derivatized with a

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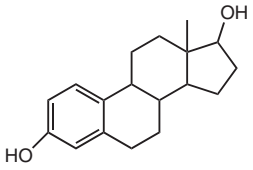
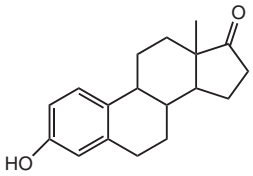
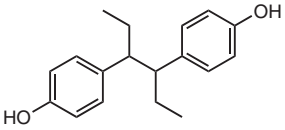
Table 1. Chemical structures of three estrogens

βE2 $C_{18}H_{24}O_2$	
E1 $C_{18}H_{22}O_2$	
DES $C_{18}H_{20}O_2$	

suitable derivatization reagent prior to analysis. However, derivatization reactions are very time-consuming.[11,12]

The low concentration of estrogens in environmental water makes them difficult to be directly determined by chromatographic methods.[13,14] Hence, some sample preconcentration techniques are needed to extract the traces of estrogens from the aqueous medium before analysis. The traditional sample preparation methods include solid phase extraction (SPE)[15] and solid-phase microextraction (SPME).[16] SPE and SPME need a small quantity of solvent and time, but columns are too expensive. Based on liquid-liquid extraction, several new types of preconcentration techniques have been developed. These include hollow-fiber microporous membrane liquid-liquid extraction (HF-MMLLE),[17] stir bar sorptive extraction (SBSE),[18] cloud point extraction (CPE)[19] and dispersive liquid-liquid microextraction solidification of a floating organic drop (DLLME-SFO).[20] DLLME is based on a ternary solvent system. The appropriate mixture of extraction solvent and disperser solvent is quickly added into the target aqueous solution, resulting in the formation of a homogeneous solution which can increase the contact surface between phases and obtain high enrichment factors. Recently, a series of improved DLLME methods have been developed. Ultrasound was used in DLLME to enhance the extraction efficiency of dimethachlon in our previous study.[21] In classical DLLME, organic solvents such as acetone,[22] ethanol,[23] methanol,[24] and acetonitrile[25] are usually used as disperser solvents. However, some surfactants have also been used as disperser solvent in surfactant-assisted dispersive liquid-liquid microextraction (SA-DLLME)[26] and ultrasound-assisted surfactant-enhanced emulsification microextraction (UASEME).[27-29]

Surfactants are amphiphilic molecules. They have hydrophilic and hydrophobic groups.[30] Surfactant could be used as an emulsifier to enhance the dispersion of water-immiscible organic solvent in aqueous phase. Ultrasound radiations could accelerate the formation of fine droplets of extraction solvent, and decrease the extraction time. Then, the two phases could be separated completely by the demulsification of electrolyte and centrifugation. Triton X-100 is a typical nonionic surfactant containing an average of 9.5 oxyethylene units *per* molecule.[31] Triton X-100 has been widely applied in heavy-duty industrial cleaning and as agrochemical.[32] It is also an effective and economic emulsifier, wetting agent, phase dispersant[33] and solubilizer.[34]

The aim of this work was to develop a method of UASEME for the determination of estrogens in water samples. Ultrasound was used to assist emulsification, and Triton X-100 was used as disperser solvent and emulsifier. Parameters affecting the extraction efficiency including the type and volume of dispersant and extraction solvent, ultrasonication time and temperature, sample pH, ionic strength and centrifuging time were optimized.

Experimental

Reagents

βE2, E1 and DES (analytical standards) were all purchased from Sigma. (Sigma, St. Louis, MO, USA) Standard stock solutions of βE2, E1 and DES were prepared in methanol at a concentration of 500 μg mL^{-1}. Working solutions were prepared by dilution of the stock solutions on the day of use. The surfactants including sodium dodecylsulphate (SDS), cetyltrimethyl ammonium bromide (CTAB), Tween 20 and Triton X-100 (Amresco, USA) were prepared in aqueous solutions. Acetonitrile was chromatographic grade (Tedia Company, Fairfield, OH, USA). Methanol, ethanol, acetone, carbon tetrachloride, chloroform, dichloromethane, ethyl acetate and *n*-butanol were analytical grade (Zhiyuan Chemical Reagent Co., Tianjing, China).

Instrumentation

The HPLC equipment consisted of four Agilent 1200 series LC-20AT pumps, a SPD-M20A DAD detector and an automatic injector. The separations were performed on an Agilent TC-C18 column (150 mm × 4.6 mm, i.d, 5 μm). Acetonitrile and water were used as mobile phase with the gradient program as follows: 0-4.5 min, 35:65; 6.0-20 min, 55:45, acetonitrile:water, v/v. The flow rate of

mobile phase was 1.0 mL min^{-1}. The injection volume was 20 μL, and the DAD detector was set at 210 nm, which is the absorption maximum of all analytes. The column temperature was 25 °C. An Agilent chemstation for LC was utilized to control the system, and for the acquisition and analysis of the chromatographic data. An ultrasonic water bath with temperature control (Shanghai Kudos Ultrasound Instrument Co., Ltd., Shanghai, China) was used to emulsify the solutions. A centrifuge with calibrated centrifugal tubes (Shanghai Medical Instruments (Group) Ltd., Corp. Surgical Instruments Factory, Shanghai, China) was used for phase separation.

UASEME procedure

A 10 mL aliquot of the water sample was placed in a screw cap glass centrifuge tube with conical bottom. An amount of 50 μL of CCl_4 as extraction solvent, and 0.3 mL Triton X-100 (0.8×10^{-5} mol L^{-1}) as disperser solvent and emulsifier, were added to the sample solution. The final concentration of Triton X-100 in the sample solution was 2.4×10^{-6} mol L^{-1}. The tube was capped and placed in an ultrasonic water bath for ultrasonication performed at 35 kHz of ultrasound frequency and 25 °C for 5 min. The emulsion was then detached by centrifugation for 5 min at 4000 rpm. After phase separation, the organic phase was deposited at the bottom of the tube and the denser phase was removed to another tube with a conical bottom using a syringe. The denser phase was then dried with nitrogen, dissolved in 0.5 mL acetonitrile, and 20.0 μL was injected into the HPLC for analysis.

Results and Discussion

Optimization of UASEME

In this work, the influence of different experimental parameters, including the type and concentration of disperser solvent, the type and volume of the extraction solvent, ultrasonication time, ionic strength, sample pH and centrifuging time, on the performance of UASEME, were investigated. A quantity of 10.0 mL of deionized water spiked with 100 ng mL^{-1} of each of the three estrogens was used to study the extraction performance under different experimental conditions. All experiments were performed in quintuplicate, and mean values were used for optimization.

Effect of extraction solvent

The extraction solvent not only affects the emulsification, but also the extraction efficiency, and hence, selecting an appropriate extraction solvent is quite important to UASEME. The extraction solvent should have hydrophobicity and good extraction capability for the target analytes, as well as being able to form a stable cloudy system in the presence of Triton X-100 and ultrasound. Based on these aspects, carbon tetrachloride, chloroform, dichloromethane, ethyl acetate and *n*-butanol were tested in this work. Figure 1 shows the effect of the extraction solvent on the extraction efficiency of the target analytes. When ethyl acetate and *n*-butanol were used as extraction solvents, no emulsification was observed in the system. Relatively high extraction efficiency was obtained when carbon tetrachloride was used as extraction solvent. The reason for this might be that the polarity of carbon tetrachloride is more similar to the target estrogens than chloroform and dichloromethane. Therefore, carbon tetrachloride was selected as the optimum extraction solvent.

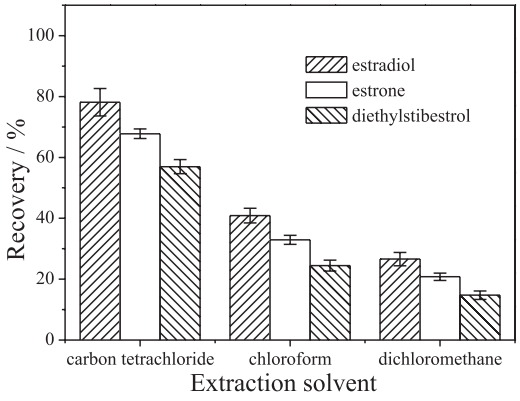


Figure 1. Effect of extraction solvents. Extraction conditions: sample volume, 10.0 mL spiked with 100 ng mL^{-1} of each estrogen; sample pH, 7; the concentration of Triton X-100, 4.0×10^{-7} mol L^{-1}; extraction solvent volume, 50 μL; centrifuging time, 5 min.

Effect of disperser solvent

In DLLME, the disperser solvent must be miscible in both the extraction solvent and water.[32] Several traditional disperser solvents were studied including methanol, ethanol, acetonitrile and acetone. The surfactant can also serve as the disperser solvent and accelerate the emulsification of carbon tetrachloride in water under the energy provided by ultrasound. Different surfactants including SDS, CTAB, Tween 20 and Triton X-100 were investigated. When SDS, CTAB and Tween 20 were used as disperser solvents, the extraction efficiencies were very low. As shown in Figure 2, the highest extraction efficiency was observed when Triton X-100 was used as disperser solvent, and thus, Triton X-100 was selected as the optimum disperser solvent.

Effect of extraction solvent volume

The extraction solvent volume is a crucial factor during the DLLME process.[35] The effect of different volumes of

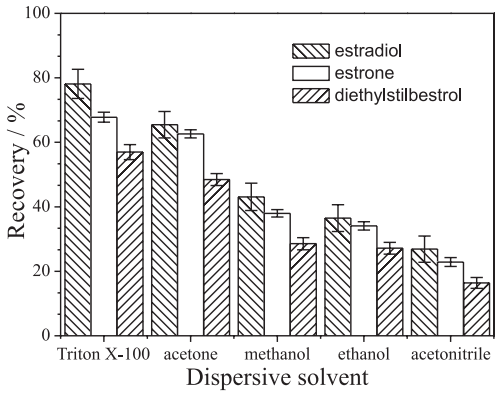


Figure 2. Effect of disperser solvents. Extraction conditions: sample volume, 10.0 mL spiked with 100 ng mL^{-1} of each estrogen; sample pH, 7; disperser solvent volume, 0.5 mL; CCl_4 volume, 50 μL; centrifuging time, 5 min.

carbon tetrachloride between 20 to 150 μL was studied. As Figure 3 shows, the peak recoveries of the three estrogens were increased when the volume of carbon tetrachloride was increased from 20 to 50 μL, and then decreased with further volume increases to 150 μL. The reason for this might be that carbon tetrachloride could not be well emulsified in aqueous solution when its volume was larger than 50 μL. Therefore, 50 μL of carbon tetrachloride was used in further experiments.

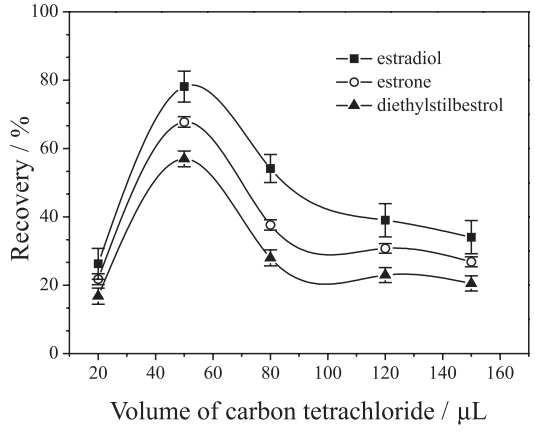


Figure 3. Effect of CCl_4 volume. Extraction conditions: sample volume, 10.0 mL spiked with 100 ng mL^{-1} of each estrogen; sample pH, 7; concentration of Triton X-100, 4.0×10^{-7} mol L^{-1}; centrifuging time, 5 min.

Effect of the concentration of surfactant

The concentration of Triton X-100 can influence the dispersion and sedimentation of carbon tetrachloride. Triton X-100 can also play an important role in the emulsification and mass-transfer process. If the concentration of Triton X-100 is too low, the tiny droplets of carbon tetrachloride might not be formed effectively. Meanwhile, too high concentration of Triton X-100 could prevent the analytes from transferring to the droplets of carbon tetrachloride.[36] Thus, different concentrations of Triton X-100 ranging from 0.8 to 7.2×10^{-7} mol L^{-1} were investigated. Figure 4 indicates that the extraction efficiency increased with increasing concentration of Triton X-100 up to 2.4×10^{-7} mol L^{-1}. The solution would remain cloudy after centrifugation when the concentration of Triton X-100 was higher than 2.4×10^{-7} mol L^{-1}. The reason for this might be that some analytes were incorporated into the micelles, resulting in an increasing solubility in the aqueous solution. Therefore, 2.4×10^{-7} mol L^{-1} Triton X-100 was selected in this experiment.

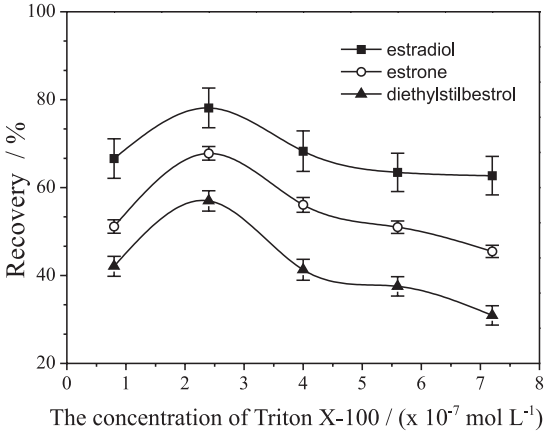


Figure 4. Effect of the concentration of Triton X-100. Extraction conditions: sample volume, 10.0 mL spiked with 100 ng mL^{-1} of each estrogen; sample pH, 7; CCl_4 volume, 50 μL; centrifuging time, 5 min.

Effect of ultrasonication

Ultrasound can improve the interactive rate between the extraction solvent and aqueous phase so that the extraction solvent can be well dispersed in the aqueous solution, and a stable and homogeneous ternary emulsion is formed.[37] Mohammadi *et al.*[38] have used ultrasound to assist with emulsification microextraction of trace amounts of Co and Mn ions in water. The ultrasonication times in the range of 0-15min were evaluated at 25 °C. Figure 5 shows that peak areas increased till 5 min and remained almost constant for longer times. So, 5 min was chosen as ultrasonication time in further experiments. The ultrasonication temperature range from 25 to 55 °C was also investigated. Increasing temperature had no effect on the extraction efficiency. As a result, 25 °C was chosen as the ultrasonication temperature.

Effect of ionic strength

Normally, the solubility of analytes in water could be decreased with the addition of salt due to the salting-out effect.[39] An appropriate ionic strength could prevent the foam formation and accelerate phase separation. However, the viscous solution might prevent the extraction solvent

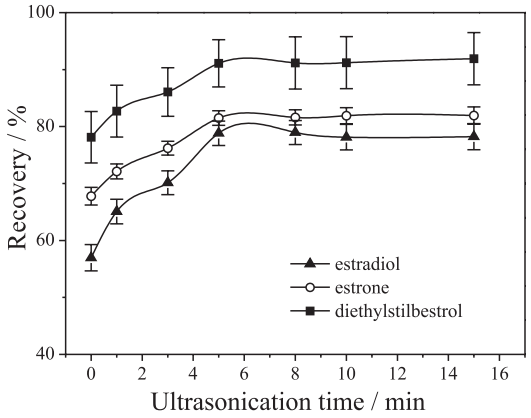


Figure 5. Effect of ultrasonication time. Extraction conditions: sample volume, 10.0 mL spiked with 100 ng mL^{-1} of each estrogen; sample pH, 7; concentration of Triton X-100, 2.4×10^{-7} mol L^{-1}; CCl_4 volume, 50 μL; ultrasonic frequency, 35 kHz; centrifuging time, 5 min.

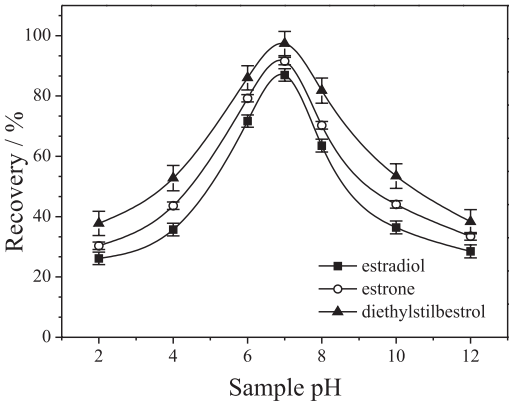


Figure 7. Effect of sample pH. Extraction conditions: sample volume, 10.0 mL spiked with 100 ng mL^{-1} of each estrogens; concentration of Triton X-100, 2.4×10^{-7} mol L^{-1}; CCl_4 volume, 50 μL; addition of NaCl, 0.8 g; ultrasonication time, 5 min; centrifuging time, 5 min.

from dispersing in aqueous phase with an increase of ionic strength. Consequently, the effect of emulsification would be dramatically reduced.[40] Figure 6 shows the analytes peak areas *versus* the addition of NaCl in the range from 0 to 2.0 g. The best extraction efficiency was obtained with the addition of 0.8 g of NaCl. Therefore, 0.8 g NaCl was added to all samples in further experiments.

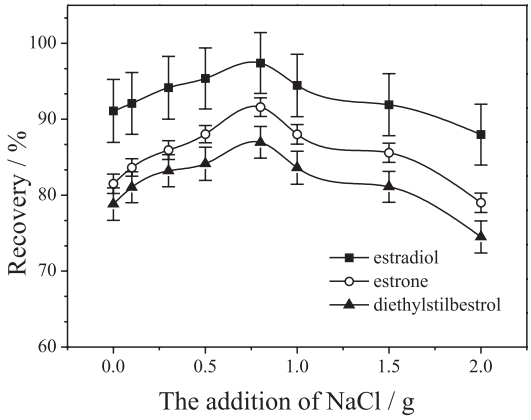


Figure 6. Effect of NaCl. Extraction conditions: sample volume, 10.0 mL spiked with 100 ng mL^{-1} of each estrogens; sample pH, 7; concentration of Triton X-100, 2.4×10^{-7} mol L^{-1}; CCl_4 volume, 50 μL; ultrasonication time, 5 min; centrifuging time, 5 min.

Effect of sample pH

The solubility of target analytes in water and organic phase can be affected by the sample pH.[25] Sample pH was investigated in the range from 2.0 to 12.0, with the best extraction efficiency of the target analytes obtained at pH 7.0 as shown in Figure 7. For this reason, the sample pH was chosen at 7.0 in further experiments.

Effect of centrifuging time

Centrifugation can accelerate the disruption of the emulsion and the sedimentation of carbon tetrachloride. If the centrifuging time is not enough, the carbon tetrachloride would not be completely deposited at the bottom of the tube. The centrifuging time was evaluated in the range between 0 and 20 min at 4000 rpm. As shown in Figure 8, 5 min was the optimum centrifuging time, and therefore chosen as the centrifuging time for further experiments.

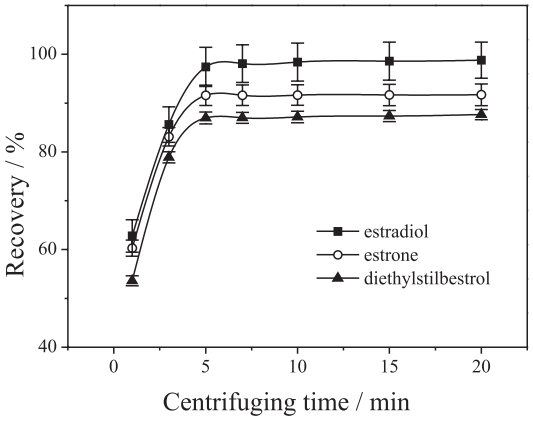


Figure 8. Effect of centrifuging time. Extraction conditions: sample volume, 10.0 mL spiked with 100 ng mL^{-1} of each estrogen; sample pH, 7; concentration of Triton X-100, 2.4×10^{-7} mol L^{-1}; CCl_4 volume, 50 μL; addition of NaCl, 0.8 g; ultrasonication time, 5 min.

Analytical performance

The chromatograms of the three estrogens in standard aqueous solution obtained by direct HPLC-DAD (A) and by UASEME-HPLC-DAD (B) are shown in Figure 9. Comparing A and B, the peak heights of βE2, E1 and DES were clearly enhanced in B. In order to investigate the applicability of UASEME for the determination of the estrogens in water samples, several factors including linear range, enrichment factors, regression equations, correlation coefficients and detection limits were

Table 2. Performance characteristics of the developed procedure

Analyte	LR[a] / (ng mL^{-1})	Regression equation	r	LOD / (ng mL^{-1})	RSD / % (n = 5)	Enrichment factor[b]
βE2	10-1000	Y = 225.57x + 159.36	0.9988	0.200	1.27	85.29
E1	10-1000	Y = 262.37x + 135.12	0.9975	0.100	0.85	173.45
DES	10-1000	Y = 325.22x + 183.64	0.9982	0.125	1.28	97.05

[a]linear range; [b](peak area of estrogen after UASEME) / (peak area of estrogen before UASEME).

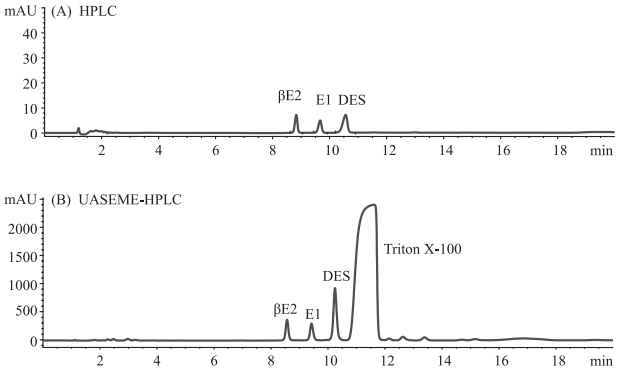


Figure 9. Typical chromatograms of analysis of βE2, E1 and DES in water samples by direct HPLC-DAD (A) and UASEME-HPLC-DAD (B). Concentrations of βE2, E1 and DES were 100 ng mL^{-1}.

evaluated under the optimum conditions. Results are summarized in Table 2.

Analysis of water samples

To demonstrate the capability of the proposed UASEME procedure, it was applied to analyze the levels of the three estrogens in lake, tap and mineral water under the optimized conditions. Results are shown in Figure 10. None of the target estrogens were detected in any of the water samples. In order to validate the accuracy of this method, the extraction recoveries of the three estrogens at three different levels (50.0, 500.0 and 1000.0 ng mL^{-1}) were spiked into actual water samples. Table 3 shows that the recoveries for the analytes were 89.82-104.48% with RSD lower than 6.50%. These excellent results demonstrate that the UASEME-HPLC-DAD procedure is precise and sensitive for trace analysis of βE2, E1 and DES in water samples.

Comparison of UASEME with conventional methods

The extraction efficiency of UASEME was compared with other reported techniques such as SPE, SPME, SBSE, CPE and DLLME-SFO. The LOD, RSD, linearity, and extraction time are listed in Table 4. It is observed that the extraction time of UASEME was greatly shortened. The range of LODs given in Table 4 for SBSE, CPE and DLLME-SFO were higher than with UASEME.

Table 3. Analytical results for estrogens in water samples

Sample	Estrogen	Spiked / (ng mL^{-1})	Found / (ng mL^{-1})	Recovery / %	RSD / % (n = 5)
Tap water	βE2	0	ND[a]		
		50	52	104.48	5.26
		500	502	100.31	1.26
		1000	1003	100.31	1.54
	E1	0	ND[a]		
		50	45	90.56	1.72
		500	500	100.09	1.45
		1000	936	93.63	1.44
	DES	0	ND[a]		
		50	47	94.66	4.69
		500	502	100.48	1.49
		1000	1030	103.05	3.27
Water of Dianchi Lake	βE2	0	ND[a]		
		50	48	96.41	2.74
		500	505	101.08	1.64
		1000	974	97.42	1.43
	E1	0	ND[a]		
		50	49	98.18	3.34
		500	498	99.62	1.08
		1000	965	96.52	2.48
	DES	0	ND[a]		
		0.05	49	97.33	6.26
		0.5	506	101.14	1.50
		1	1023	102.31	2.09
Mineral water	βE2	0	ND[a]		
		50	47	93.75	4.51
		500	449	89.82	1.24
		1000	952	95.24	2.71
	E1	0	ND[a]		
		50	51	101.99	3.34
		500	491	98.12	1.36
		1000	953	95.26	2.06
	DES	0	ND[a]		
		50	49	97.74	6.50
		500	505	101.04	1.21
		1000	1013	101.27	1.40

[a]not detected.

Table 4. Comparison of the developed propcedure with other sample preparation techniques for the determination of estrogens in water

Procedure	LR[a] / (ng mL^{-1})	LOD / (ng mL^{-1})	RSD / %	Extraction time	Reference
SPE-LC/MS/MS	0.015-1.5	0.001-0.03	< 17	-	15
SPME-GC/MS/MS	0.005-0.5	0.0002-0.003	< 12	> 2 h	16
SBSE-HPLC/DAD	0.5-300	0.04-0.11	< 9.5	= 43 min	18
CPE-HPLC/UV	1-192	0.23-5.0	< 12	= 65 min	19
DLLME-SFO-HPLC/UV	5-1000	0.8-3.1	< 14	> 30 min	20
UASEME-LC/DAD	10-1000	0.1-0.2	< 1.28	< 15 min	This work

[a] linear range.

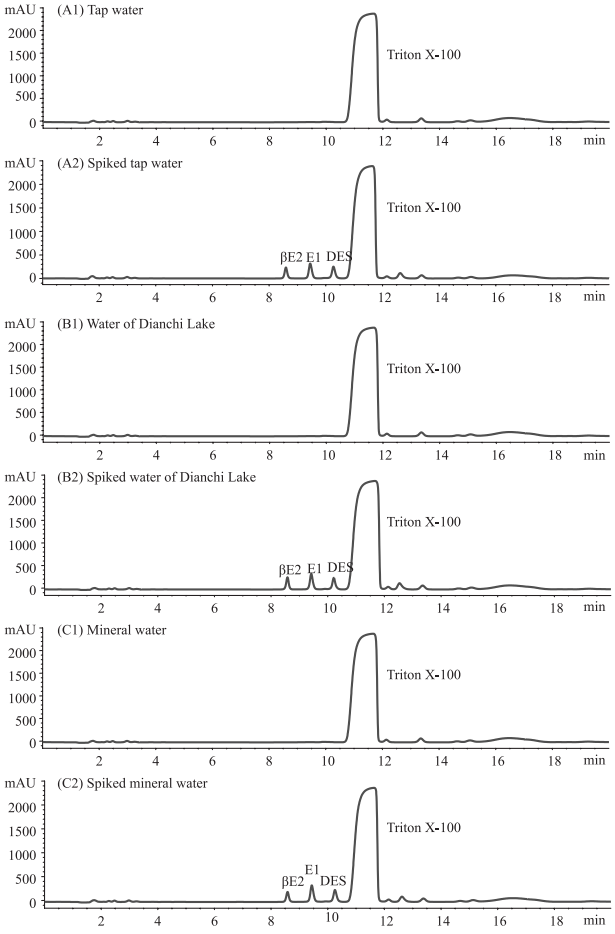


Figure 10. Typical chromatograms of analysis of βE2, E1 and DES in three real water samples by UASEME-HPLC-DAD. Chromatograms A1, B1 and C1 were of tap, Dianchi Lake and mineral water samples. Chromatograms A2, B2, and C2 were of tap, Dianchi lake and mineral water samples spiked with βE2, E1 and DES at concentrations of 50 ng mL^{-1} of each one.

Conclusions

In this work, ultrasound was applied to assist emulsification, and Triton X-100 was adopted as disperser solvent and emulsifier in ultrasound-assisted surfactant-enhanced emulsification microextraction (UASEME). The developed procedure presented quantitative recoveries and enrichment factors, good repeatability, short extraction time and good linearity. Therefore, the UASEME-HPLC-DAD procedure is a simple and reliable microextraction method which can be successfully applied for the determination of estrogen residues in water.

Acknowledgments

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