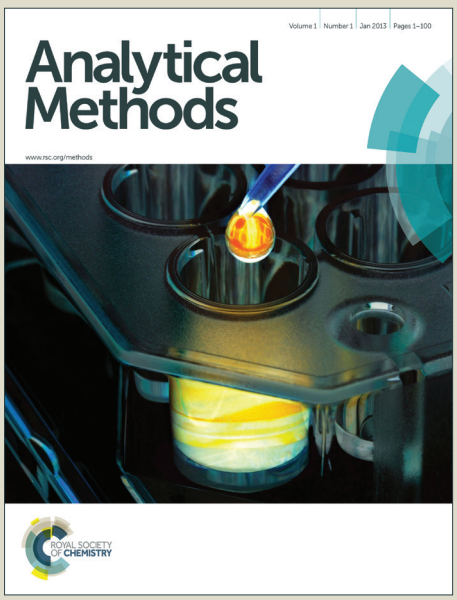
Analytical Methods

Accepted Manuscript



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Simultaneous determination of pharmaceutical and personal care products in wastewater by capillary electrophoresis with head-column field-amplified sample stacking

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Abstract

A sensitive and reliable method using capillary zone electrophoresis with UV-diode array detection (CZE-DAD) has been developed and validated for trace determination of nineteen pharmaceutical and personal care products (PPCPs) in wastewater. Due to the lack of sensitivity of the UV-vis detection, a solid-phase extraction (SPE) method applied for off-line preconcentration and cleanup of water samples, in combination with an on-line preconcentration methodology named head-column field-amplified sample stacking (FASS) have been applied. Several parameters affecting separation and FASS efficiency were investigated in details, including buffer pH and concentration, organic modifier, sample matrix, water plug, and electrokinetic injection voltage and time. Under the optimal FASS-CZE condition, high efficiency was achieved and nineteen PPCPs were baseline separated within 27 min. The accuracy of this assay was assured from the spiking of real samples with standard known concentrations and the intra-day and inter-day relative standard deviations (RSDs) were below 5.6 and 6.3%, respectively. The average recoveries for water samples with the studied PPCPs were greater than 64.7 ± 1.1%. The limits of detection (LODs) were estimated to range from 1.4 to 46.4 ng/L for the studied compounds. This method was successfully applied for the simultaneous determination of PPCPs in wastewater samples from a sewage treatment plant.

Keywords: Capillary electrophoresis; Pharmaceutical and personal care products; Field-amplified sample stacking; Solid phase extraction; Wastewater.

1. Introduction

Pharmaceuticals and personal care products (PPCPs) are a class of potential environmental contaminants that have attracted increasingly more attention [1-3]. In recent years, a number of PPCPs have been detected in many water systems, including rivers, lakes, reservoirs, wastewater and even drinking water [4, 5]. Continuous release and long-term exposure to these substances can present potential risk to ecological environment as well as human health as some are ubiquitous, persistent and biologically active compounds with recognized endocrine disruption functions [6]. Some studies have demonstrated that traces of PPCPs in the aquatic environment may have toxicity effect on organisms and interface with the growth and metabolism [7, 8]. Therefore, it is essential to develop some sensitive, reliable, efficient and rapid methods to detect multi-classes of PPCPs simultaneously in aquatic environment in order to study the occurrence, behavior and fate of PPCPs and then provide references to the further risk research.

Many methods have been developed for identification and quantification of PPCPs in water samples, including gas chromatography-mass spectrometry (GC-MS) [9-11], liquid chromatography-tandem mass spectrometry (LC-MS/MS) [12-14] and capillary electrophoresis (CE) [15-18]. The challenges for GC-MS methods are that chemical derivatization is required before analysis. Different derivatization approaches are needed because the pharmaceuticals have different functional groups, which complicate the development of multi-residue methods. LC-MS/MS methods are well suited to the analysis of PPCPs in water, but ion suppression/enhancement

can be of concern in more complex matrices, potentially compromising accuracy. CE offers an alternative to LC-MS/MS for the analysis of PPCPs. The advantages of CE are the low-cost and flexible selectivity through buffer concentration, pH tuning, and additives, which are crucial for separation of many PPCPs. However, CE is generally not sufficiently sensitive to quantify these compounds without extensive sample pretreatment because the concentrations of PPCPs are as low as nanograms per liter to micrograms per liter in water samples. Therefore, there is an urgent need to improve the detection sensitivity in CE methods to satisfy the microanalysis of PPCPs.

Today, various sample stacking approaches have been shown to provide sensitivity enhancement in CE, including field-amplified sample stacking (FASS) [19-22], dynamic pH junction [23,24], isotachophoretic stacking [25,26] and sweeping [27,28]. Among these techniques, FASS is the simplest and most widely applied one. It is based on the conductivity difference between the sample zone and the running buffer to effect preconcentration. Nowadays, FASS has been shown to provide the greatest sensitivity enhancement and has been applied to determine a lot of compounds, such as monoamines [19], illicit drugs [20], zotepine and its active metabolite [21], phenoxy acid herbicides [22] and so on. But to our knowledge, FASS coupled with CE has not been reported to determine PPCPs in water samples. In this work, we used solid phase extraction (SPE) with Oasis HLB extraction cartridges for sample pretreatment, and then applied head-column FASS technique to develop a sensitive and accurate capillary zone electrophoresis (CZE) method for trace determination of nineteen PPCPs. Application of the proposed method to analyze the

wastewater samples from a sewage treatment plant was evaluated and proved to be satisfactory. The selection of these nineteen PPCPs was based on the occurrence of PPCPs in the sewerage system in our previous study.

2. Experimental

2.1 Chemicals and materials

Sulfamethazine (SM2), sulfadiazine (SD), sulfamethoxazole (SMZ), sulfamerazine (SM1), sulfadimethoxine (SDM), sulfameter (SMT), enrofloxacin (ENRX), ofloxacin (OF), amoxicillin (AMO), oxacillin sodium salt (OXA), cefalexin hydrate (CEX), cefradin (CED), ibuprofen (IPF), diclofenac (DCF), sulisobenzone (HMBS), triclosan (TCS), bromocresol green (BCG), aspirin (ASP), clofibric acid (CPIB) were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). Oasis HLB solid phase extraction cartridge (200 mg, 6 mL) were obtained from Waters Co. (Milford, MA, USA). HPLC-grade methanol (MeOH) was purchased from TEDIA Co. (Fairfield, OH, USA). Unless otherwise specified, all reagents were of analytical reagent grade. Deoxygenated and deionized water used in the experiment was purified by a Milli-Q system (Millipore, Bedford, MA, USA) for preparation of all solutions. The stock mixture solution of nineteen PPCPs (50 μg/mL, individually) was prepared in methanol and diluted to the desired concentrations before use. H_3BO_3-$Na_2B_4O_7$ buffer was prepared by mixing 0.20 M H_3BO_3 solution with 0.05 M $Na_2B_4O_7$ solution

to the required pH value. H_3PO_4-Na_3PO_4 buffer was prepared by mixing 0.20 M H_3PO_4 solution with 0.20 M Na_3PO_4 solution to the required pH value. The pH values of solutions were measured by a DELTA 320 pH meter (Mettler-Toledo, Shanghai, China).

2.2 Instrumentation

CE experiments were performed on a Beckman P/ACE MDQ CE system (Fullerton, CA, USA) with a photodiode-array detector (DAD). All electrophoretic separations were performed in a bare fused-silica capillary (60 cm, 50 cm to the detector, 75 μm I.D., Yongnian Optic Fiber, Hebei, China). The temperature of the separation was controlled at 25 ^{o}C by immersion of the capillary in a cooling liquid circulating in the cartridge. The sample tray was at room temperature. Detection was carried out by the on column measurement of UV absorption at 200 nm, cathode at the detection side. The Beckman P/ACE MDQ Microsoft system was used for data processing.

2.3 Capillary conditioning

New capillary was preconditioned by successively flush with acetonitrile, water, 1 M HCl, 1 M NaOH for 30 min, respectively. Before each run, the capillary was rinsed with 0.1 M NaOH, H_2O, 0.1 M HCl, and running buffer for 2 min, respectively.

The capillary tip was dipped for 3 s into a vial containing water for cleaning and then a water plug was introduced into the capillary by pressure injection, using 0.5 pounds per square inch (psi) for 10 s. Samples were electrokinetically injected at a negative voltage of 10 kV for 15 s, anode at the detection side. For all the separations the same running buffer was consisted of 50 mM H_3PO_4-Na_3PO_4 (pH 7.4) with 20% methanol, filtered by a 0.22 mm nylon membrane filter and degassed in an ultrasonic for 5 min. The buffer was renewed after every three runs to maintain good reproducibility. Separations were carried out at 20 kV.

2.4 Wastewater sample collection and preparation

Wastewater samples were collected and stored in pre-cleaned brown glass bottles from a sewage treatment plant in Xiamen. The samples were refrigerated in 4 ^{o}C until analyzed within 24 h from collection. Prior to SPE of the PPCPs, stepwise filtration using 0.45 μm nylon membrane filters was performed on each sample to remove the physical particulates. After filtration, one liter of water sample was acidified to pH 3.0 by adding 6.0 M of hydrochloric acid, followed by addition of 0.2 g Na_2EDTA to eliminate the influence of metal ions in wastewater sample. The samples were extracted using Oasis HLB extraction cartridges on the basis of our previous work [29]. Briefly, each cartridge was sequentially preconditioned with 6.0 mL of acetone, 6.0 mL of methanol and 6.0 mL of 5.0 mM ammonium acetate dissolved in 0.1% formic acid solution (v/v). The water samples were then passed through the

pre-conditioned cartridges at a flow rate of approximately 10 mL/min. After that, the cartridge was rinsed with 6.0 mL of 5.0 mM ammonium acetate dissolved in 0.1% formic acid solution (v/v) and dried under nitrogen gas for 20 min. After drying, the cartridge was eluted with 6.0 mL of methanol. Finally, the target fraction was collected in a 10 mL test tube, the volume reduced to almost dryness under a gentle nitrogen stream, and then re-dissolved with 1.0 mL of sample matrix composed of 1.0 mM H_3PO_4-Na_3PO_4 (pH 7.4) by vortex mixing and then 200 μL of the solvent was transferred into a 0.5 mL sample vial that could be placed into the sampler of the CE apparatus for analysis.

3. Results and discussion

3.1 Optimization of separation conditions

In our preliminary studies, the CZE model was used because of its simplicity and rapidness in practical applications. H_3PO_4-Na_3PO_4 buffer and H_3BO_3-$Na_2B_4O_7$ buffer were tested. The results indicated that H_3PO_4-Na_3PO_4 buffer provided a more promising separation and a more stable electroosmotic flow (EOF) when the electrolytes were at the same concentration and pH value. This is probable because many of the analytes have hydroxyl functional groups, which can complex with boric-based buffers and affect separation of the compounds [30]. So H_3PO_4-Na_3PO_4 buffer was selected as the background electrolyte. In the following optimization

experiments, the stock mixture solution of nineteen PPCPs was diluted by H_3PO_4-Na_3PO_4 buffer to obtain good resolution. After that, the mixture was introduced into the capillary by pressure injection, using 0.5 psi for 10 s.

3.1.1 Effect of buffer pH and concentration

The pH value of running buffer strongly influences the inner surface characteristics of the quartz capillary in CZE and acidic-alkaline equilibrium of the analytes. The effect of buffer pH on the separation was tested at pH values 6.8, 7.0, 7.2, 7.4, 7.6, and 8.0. Several PPCPs overlapped seriously when the pH value was below 7.2 and above 7.6. So the pH value of 7.4 was selected to strike a good compromise for the resolution in the present work. The effect of phosphate concentration on the separation was also investigated. Different concentrations were tested from 20 to 70 mM, with the increasing of phosphate concentration, better resolution was observed. But too high concentration resulted in long migration time, high ionic strength, and Joule heat with negative effects such as band broading. Herein, 50 mM H_3PO_4-Na_3PO_4 buffer showed the most promise and it was chosen for further studies.

3.1.2 Effect of organic modifier

Organic modifier in background electrolyte can improve resolution of the analytes by changing the hydrophobicity of background electrolyte. Effects of organic modifiers on resolution were studied to obtain better resolution of nineteen analytes. A

significant improvement in resolution was obtained in the presence of methanol. The effects of concentration of 10, 15, 20 and 25% (v/v) MeOH added in H_3PO_4-Na_3PO_4 buffer (50 mM, pH 7.4) on resolution were tested as shown in Fig. 1. Resolution was improved and migration time was prolonged with increasing the MeOH concentration from 10 to 20%. Although MeOH concentration below 20% gave short migration time, the peaks of TCS-OF or SD-DCF overlapped (Fig. 1. (A), (B)). The best resolution was obtained at a methanol concentration of 20%.

3.1.3 Influence of separation voltage and capillary temperature

Under the above optimized conditions, the influence of separation voltage (15 - 25 kV) was tested. It was found that nineteen PPCPs were baseline separated in relatively short time when the voltage reached 20 kV. But a further increase in voltage resulted in partial overlap between IPF and SMZ, whereas a decrease prolonged the time of analysis. Optimization of the capillary temperature led to selection of 25 ^{o}C.

According to the factors mentioned above, a simple and rapid separation was obtained with 50 mM H_3PO_4-Na_3PO_4 at pH 7.4 containing 20% methanol and an applied voltage of 20 kV at 25 ^{o}C. Fig. 1. (C) shows the typical electropherogram for the analysis of nineteen PPCPs under the optimized conditions and the baseline separation was fulfilled within 34 min.

3.2 Optimization of FASS conditions

The direct use of CZE-DAD for the analysis of PPCPs would not be appropriate for the monitoring in water due to the poor sensitivity of CE using the DAD detection, because the LODs of CZE-DAD could not reach the desired levels in the range of ng/L. For this reason, off-line SPE procedure and on-line preconcentration methodology (FASS) have been combined in the present work, providing a simple and inexpensive methodology for improving sensitivity. FASS is a simple and efficient technique for sensitivity enhancement by preconcentration samples.

The head-column FASS procedure was as follows: The capillary tip was dipped for 3 s into a vial containing water for cleaning and then a water plug from a different vial was introduced into the capillary by pressure injection. The cleaning procedure of the capillary was necessary to prevent contamination of the sample solution before sample injected. Then the standard solutions or samples were electrokinetically injected at a negative voltage and the separation was performed. In order to achieve the best stacking efficiency, several parameters were optimized, including sample matrix, water plug, and electrokinetic injection voltage and time.

3.2.1 Effect of sample matrix

The effect of the H_3PO_4-Na_3PO_4 buffer added to the sample matrix on the sensitivity was studied. With electrokinetic introduction, the amount of solute injected is proportional to the effective electrophoretic mobility, so the enhancement of the buffer alkalinity lead to the obvious increase of the signal responses because the analytes were negatively charged in alkaline buffers. However, when the pH value

was more than 7.4, two pairs of peaks (IPF-SMZ; CPIB-HMBS) could not be baseline separated. This is probable because these analytes may not be brought into ionization equilibrium in time during the separation procedure. Therefore, the optimal pH value of the H_3PO_4-Na_3PO_4 buffer added to the sample matrix was found to be 7.4. The effect of the H_3PO_4-Na_3PO_4 buffer concentration on the peak height was shown in Fig. 2. The peak height signals increased with the buffer concentration from 0.1 to 1.0 mM due to conductivity modification, and decreased with higher concentration. Accordingly, 1.0 mM H_3PO_4-Na_3PO_4 buffer (pH 7.4) was used as the sample matrix in the following work.

3.2.2 Effect of water plug, electrokinetic injection voltage and time

The water plug was optimized for the highest detection signal of the analytes. The results showed that little improvement was achieved by prolonging water plug injection time at 0.5 psi. After the sample injection time was optimized under a constant injection voltage for each water plug length, the 10 s of water plug injection time provided the highest signal. Moreover, application of higher voltage and a longer injection time period should result in more solute injected in principle. So the highest injection voltage (10 kV) of the Beckman P/ACE MDQ CE system was used and the effect of electrokinetic injection time was presented in Fig. 3. It was apparent that the maximum and constant peak heights were obtained with 15-20 s so that 15 s was chosen as the optimal time.

In summary, the optimized head-column FASS conditions were as follows: 1.0

mM H_3PO_4-Na_3PO_4 buffer (pH 7.4) in sample matrix was used to prepare the sample, a water plug was pressure injected using 0.5 psi for 10 s and samples were electrokinetically injected at a negative voltage of 10 kV for 15 s. A typical head-column FASS electropherogram was shown in Fig. 4 for nineteen PPCPs standard solution. The nineteen PPCPs were successfully separated within 27 min, the shortening of the sepatation time may be caused by the presence of sample matrix and water plug. More importantly, it could be seen clearly that the response of the analytes had been improved and a more smooth baseline was obtained. These improvements would have positive help to enhance the detection sensitivity in CE.

3.3 Validation of the method

Quantification of the target analytes was based on external calibration curves, which were established with the peak area as ordinate versus the concentration of each analyte in μg/mL as abscissa. Four different concentrations of multi-component standards were electrokinetically injected under optimal FASS and separation conditions. The analytical results are listed in Table 1. Good linearities were obtained with correlation coefficients larger than 0.9917. The precision of the proposed method for spiked samples was studied. The results showed that the intra- and inter-day relative standard deviations (RSDs) were below 5.6 and 6.3%, respectively. Recoveries of the PPCPs in wastewater sample were determined at two different concentration levels (200 and 500 ng/L) in triplicate and calculated as the percentages

of the measured concentrations relative to the spiked concentrations. The limits of detections (LODs) of sample were calculated on the basis of the baseline noise, which was defined as the sample concentration generating a peak of height three times the level of the baseline noise (signal-to-noise ratio of 3). After preconcentration by a factor of approximately 2,500 for OF to 35,000 for IPF using SPE and FASS, the LODs were in the range from 1.4 ng/L to 46.4 ng/L, which were better than the detection limits obtained via other CE methods for simultaneous detection of PPCPs (Table 2).

3.4 Wastewater analysis

Two wastewater samples were collected from a sewage treatment plant in Xiamen within one week from each other. A representative electrophoretogram of PPCPs analysis of the wastewater sample is presented in Fig. 5. (A). The peak was identified by comparing the migration time and by spiking the sample with standard under exactly the same conditions. Fig. 5. (B) is the electrophoretogram of the sample spiked with standard PPCPs solution. It can be seen that six compounds, IPF, SMZ, CPIB, HMBS, ASP and BCG can be detected in the wastewater sample (Fig. 5(A)). The results of the analyses were summarized in Table 3.

4. Conclusions

A head-column FASS technique coupled with CZE for the improvement of detection sensitivity of the PPCPs in wastewater sample has been developed in this work. The validation of the method for quantitation of PPCPs in wastewater showed that this method has high sensitivity and accuracy and it is also readily adaptable to other kinds of water samples. This method offers a good alternative to GC-MS and LC-MS/MS for PPCPs determination in the event of unavailability, failure or disaster recovery.

Acknowledgment

This study was supported by the Technology Innovation Project of Chinese Academy of Sciences for the function of instrumental development (No. YG2012123), and the Knowledge Innovation Program of Chinese Academy of Sciences (No. IUEQN201301).

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Figure captions:

Fig. 1. Effect of concentration of MeOH added in background electrolyte on separation each at 10 μg/mL. Electropherograms: (A) 10%; (B) 15%; (C) 20%, (D) 25%. Peaks: 1, TCS; 2, OF; 3, ENRX; 4, SM2; 5, CED; 6, AMO; 7, CEX; 8, OXA; 9, SM1; 10, SMT; 11, SDM; 12, SD; 13, DCF; 14, IPF; 15, SMZ; 16, CPIB; 17, HMBS; 18, ASP; 19, BCG. Symbol ★: overlapped peaks, (A) SD-DCF; (B) TCS-OF; (D) IPF-SMZ and CPIB-HMBS. Running buffer: 50 mM H_3PO_4-Na_3PO_4 buffer (pH 7.4) with (10-25%) MeOH. Separation voltage: 20 kV. Injection: 0.5 psi for 10 s.

Fig. 2. Effect of the H_3PO_4-Na_3PO_4 buffer concentration added to the sample matrix on the peak height each at 1.0 μg/mL. Running buffer: 50 mM H_3PO_4-Na_3PO_4 buffer (pH 7.4) with 20% MeOH. Separation voltage: 20 kV. Injection: 10 kV for 15 s, negative voltage.

Fig. 3. Effect of the electrokinetic injection time on the peak height each at 1.0 μg/mL. Running buffer: 50 mM H_3PO_4-Na_3PO_4 buffer (pH 7.4) with 20% MeOH. Separation voltage: 20 kV. Injection voltage: 10 kV, negative voltage.

Fig. 4. Typical electropherogram of a standard PPCPs solution each at 1.0 μg/mL. Peaks: 1, TCS; 2, OF; 3, ENRX; 4, SM2; 5, CED; 6, AMO; 7, CEX; 8, OXA; 9, SM1; 10, SMT; 11, SDM; 12, SD; 13, DCF; 14, IPF; 15, SMZ; 16, CPIB; 17, HMBS; 18, ASP; 19, BCG. Running buffer: 50 mM H_3PO_4-Na_3PO_4 buffer (pH 7.4) with 20% MeOH. Separation: 20 kV. Injection: 10 kV for 15 s, negative voltage.

Fig. 5. Representative electropherograms illustrate method application. (A) wastewater sample, (B) wastewater sample spiked with 200 ng/L of standard PPCPs. Other conditions and peak identifications are as described in Fig. 4.

Table 1 Linear range, regression equation, correlation coefficient, RSDs, sample recovery and sample LOD.

Compound	Linear range (μg/mL)	Regression equation[a)]	r	RSD (%, n = 5)		Sample recovery (%) [b)]	Sample recovery (%) [c)]	Sample LOD (ng/L)
				intra-day	inter-day			
TCS	0.1-1.0	$y = 4.561 \times 10^3 x + 52.72$	0.9995	3.7	4.2	73.2 ± 2.6	78.5 ± 1.6	30.6
OF	0.1-1.0	$y = 2.622 \times 10^3 x + 6.19$	0.9998	4.6	5.1	64.7 ± 1.1	71.2 ± 0.5	46.4
ENRX	0.1-1.0	$y = 5.774 \times 10^3 x + 33.91$	0.9997	2.9	2.5	79.3 ± 3.8	78.9 ± 2.7	27.5
SM2	0.05-1.0	$y = 1.899 \times 10^4 x - 463.85$	0.9990	5.2	3.8	82.6 ± 0.9	85.3 ± 2.1	7.2
CED	0.05-1.0	$y = 1.281 \times 10^4 x + 295.29$	0.9917	2.4	3.7	64.8 ± 1.2	69.3 ± 1.3	17.6
AMO	0.05-1.0	$y = 2.707 \times 10^4 x + 96.46$	0.9985	1.3	4.1	89.6 ± 2.3	90.5 ± 0.9	6.6
CEX	0.05-1.0	$y = 5.401 \times 10^4 x + 568.54$	0.9988	5.6	6.3	85.3 ± 1.6	85.7 ± 0.8	3.2
OXA	0.05-1.0	$y = 6.163 \times 10^4 x + 479.46$	0.9989	0.6	2.7	74.3 ± 2.4	78.8 ± 1.7	3.7
SM1	0.05-1.0	$y = 7.315 \times 10^4 x + 946.29$	0.9986	1.8	5.5	90.1 ± 0.7	87.4 ± 2.6	2.5
SMT	0.05-1.0	$y = 7.187 \times 10^4 x + 1435.21$	0.9972	3.6	3.9	92.5 ± 1.9	93.1 ± 0.9	2.5
SDM	0.05-1.0	$y = 9.003 \times 10^4 x + 437.79$	0.9995	0.9	2.7	85.7 ± 1.5	87.9 ± 1.5	2.1
SD	0.05-1.0	$y = 8.892 \times 10^4 x + 507.69$	0.9995	3.4	5.9	79.2 ± 1.0	81.2 ± 2.4	2.8
DCF	0.05-1.0	$y = 1.041 \times 10^5 x + 5663.89$	0.9940	2.1	4.7	75.4 ± 2.6	73.4 ± 1.8	2.5
IPF	0.05-1.0	$y = 1.770 \times 10^5 x - 1426.69$	0.9998	1.3	2.8	73.2 ± 4.5	79.3 ± 2.7	1.4
SMZ	0.05-1.0	$y = 1.259 \times 10^5 x + 530.48$	0.9994	3.5	6.0	87.5 ± 1.0	89.0 ± 1.1	1.9
CPIB	0.05-1.0	$y = 1.650 \times 10^5 x - 1054.15$	0.9997	2.4	2.2	76.9 ± 0.7	81.3 ± 2.6	2.0
HMBS	0.05-1.0	$y = 1.346 \times 10^5 x - 514.61$	0.9993	4.4	5.1	83.6 ± 1.1	89.7 ± 1.9	2.0
ASP	0.05-1.0	$y = 1.583 \times 10^5 x - 915.13$	0.9997	0.9	2.5	87.3 ± 3.9	90.6 ± 2.0	2.3
BCG	0.05-1.0	$y = 2.021 \times 10^5 x - 2777.79$	0.9999	3.8	4.9	72.2 ± 2.3	77.6 ± 1.5	2.4

[a)] x, concentration of PPCPs (μg/mL) and y, peak area. [b)] sample spiked with analytes at 200 ng/L. [c)] sample spiked with analytes at 500 ng/L.

Table 2 Simultaneous detection of PPCPs in water samples by CE technique.

Sample Matrix	Number of PPCPs	Pretreatment	Technique	LODs	Ref.
wastewater	8	SPE	CE-UV	1.6-68.7 μg/L	[15]
water	13	-	CE-C^4D [a)]	61-1676 μg/L	[16]
ground water	9	SPE	LVSS-CZE-UV	2.59-22.95 μg/L	[17]
wastewater	19	SPE	FASS-CZE-DAD	1.4-46.4 ng/L	This article

[a)] C^4D, capacitively coupled contactless conductivity detection.

Table 3 Analytical results of nineteen PPCPs in wastewater samples (n = 3).

	Concentrations of PPCPs (ng/L)																	
	TCS	OF	ENRX	SM2	CED	AMO	CEX	OXA	SM1	SMT	SDM	SD	DCF	IPF	SMZ	CPIB	HMBS	ASP	BCG
Sample 1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	7.02	UC	UC	75.5	467.8	851.7
Sample 2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	5.11	UC	UC	63.1	408.3	614.9

[a)] ND-not detected, UC-unquantified concentration.

Figure 1

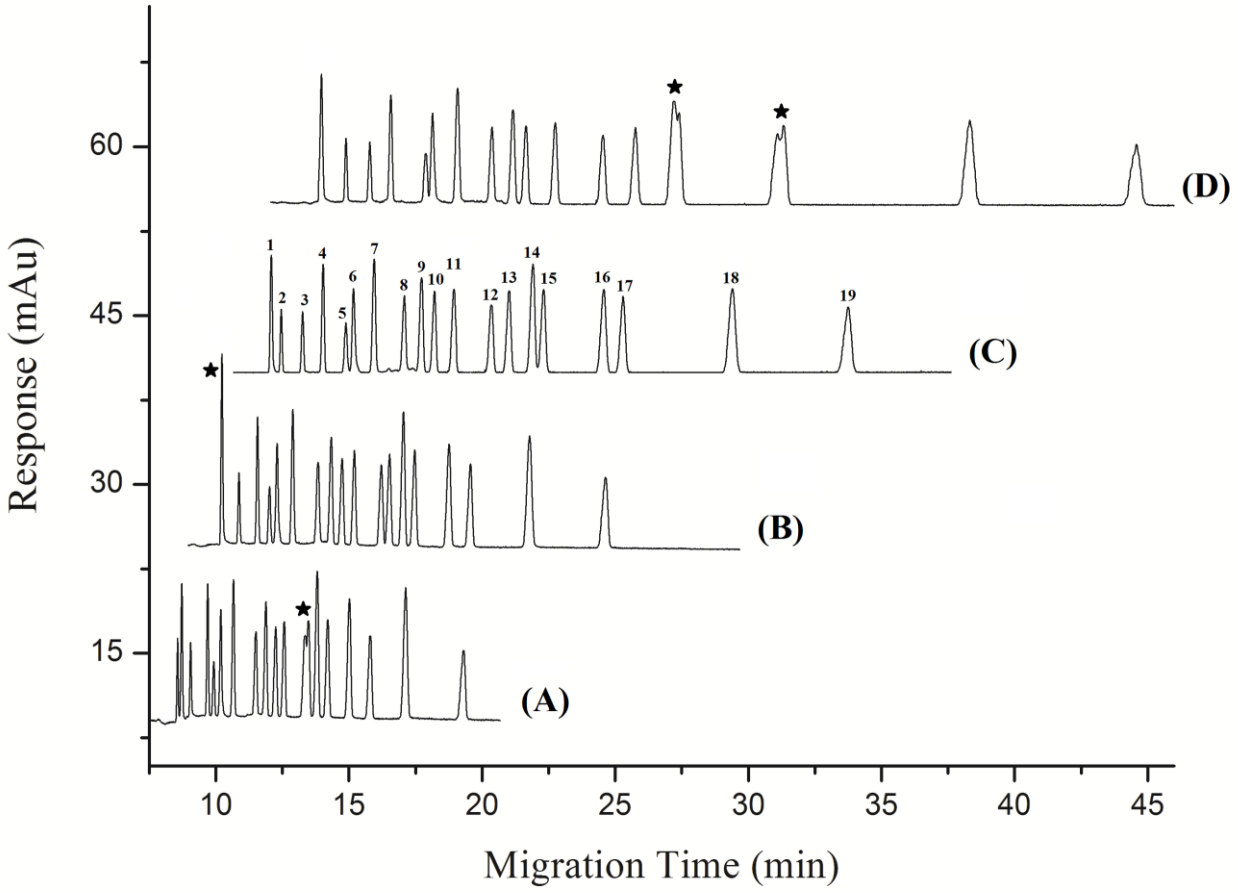

Figure 2

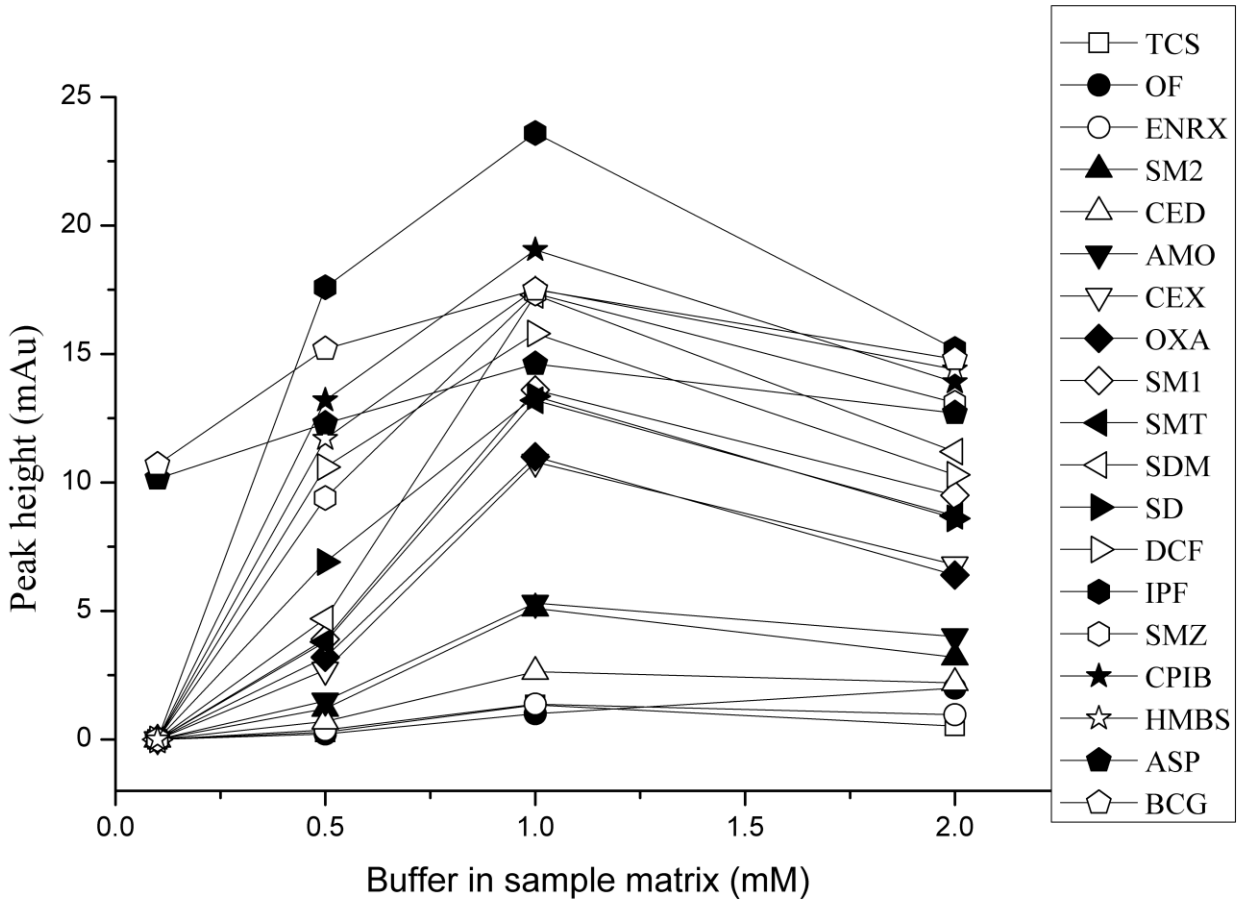

Figure 3

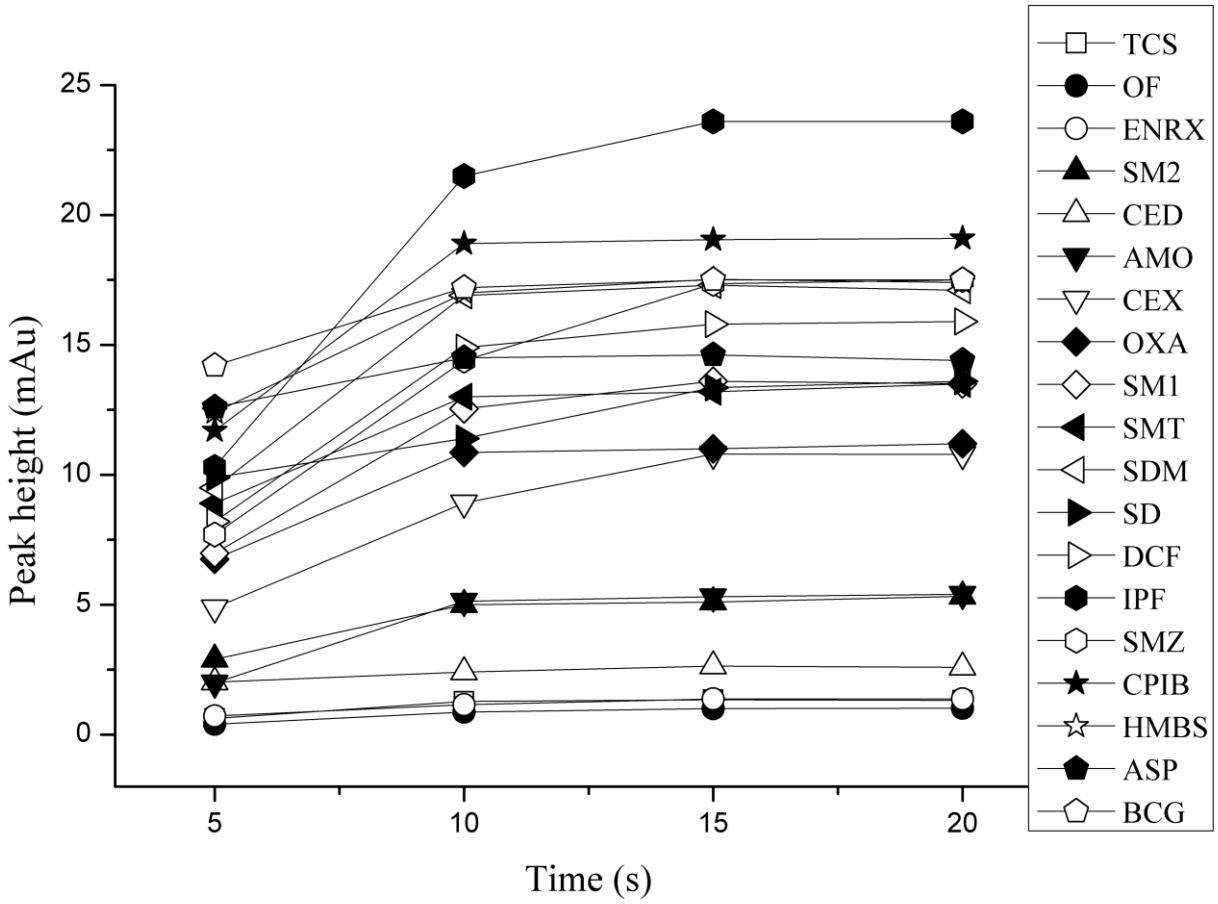

Figure 4

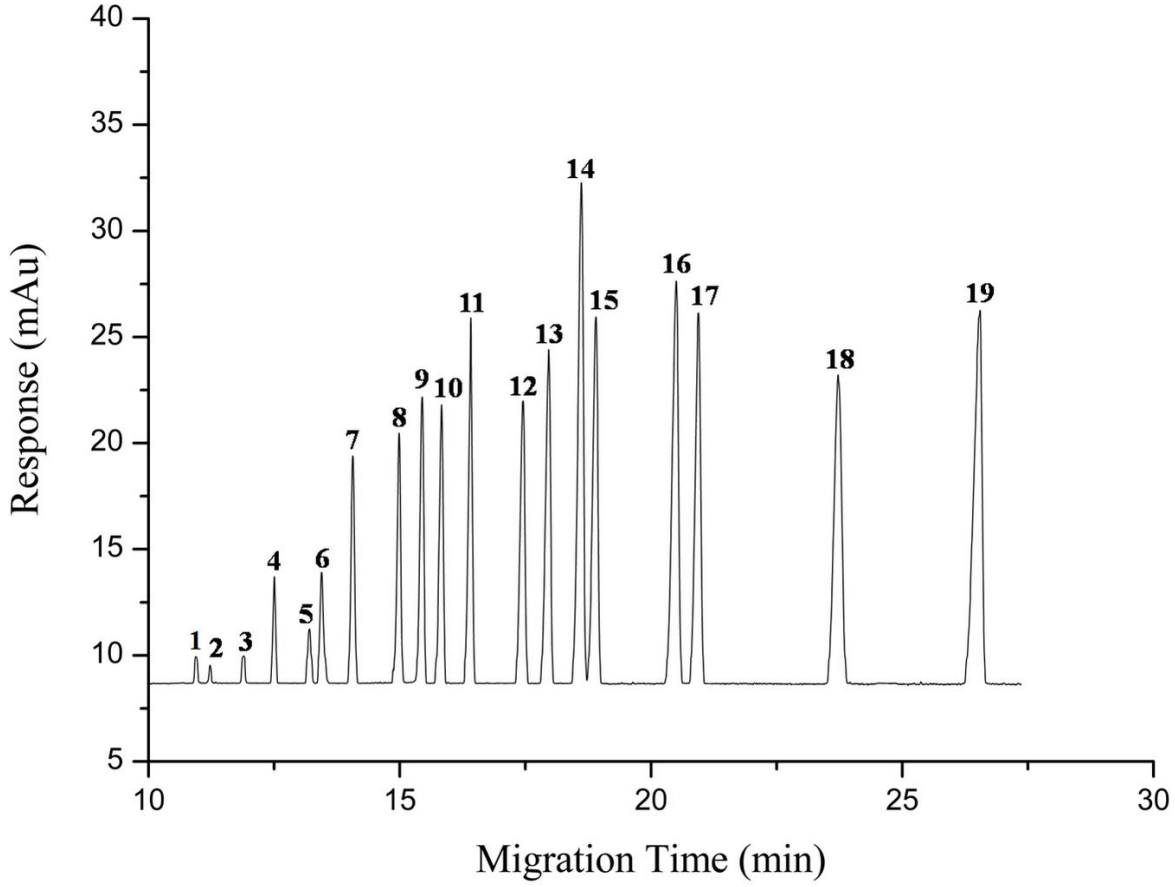

Figure 5