



Determination of illicit drugs in aqueous environmental samples by online solid-phase extraction coupled to liquid chromatography–tandem mass spectrometry



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HIGHLIGHTS

- Online SPE LC–MS/MS method was developed to identify 10 illicit drugs.
- Matrix effects can be reduced by online washing steps.
- Availability of illicit drugs in China has been reported.
- Caffeine, cotinine, and paraxanthine were detected with high concentrations.

ARTICLE INFO

Article history:

Received 8 February 2016

Received in revised form

27 May 2016

Accepted 25 June 2016

Available online 6 July 2016

Handling Editor: Caroline Gaus

Keywords:

Online SPE

Illicit drugs

LC–MS/MS

Matrix effects

ABSTRACT

In this study, a fully automated analytical method, based on online solid phase extraction coupled to liquid chromatography–triple quadrupole tandem mass spectrometry (online SPE–LC–MS/MS), has been developed and optimized for the quantification of 10 illicit drugs and metabolites in environmentally aqueous samples collected from China. The particular attention was devoted to minimize the matrix effects through a washing step, which washed out the interferences effectively and helped to reduce the matrix effect significantly. The key advantages of the method are high sensitivity, selectivity and reliability of results, smaller sample manipulation, full automation, and fairly high throughput. The whole procedure was then successfully applied in the analysis of various surface water and wastewater effluents samples. Pseudoephedrine have been detected at trace levels (several tens ng L⁻¹ or less), while MDA, MDMA, benzoylcegonine and methadone were below the LOQ in all samples. Caffeine, cotinine and paraxanthine, which may be derived from medicines and foods, were detected with the highest frequencies and concentrations.

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1. Introduction

An increasing attention has been focused on the presence of pharmaceutical and personal care products (PPCPs) in the aquatic environments due to their widespread and adverse effects on aquatic ecosystems (Schwarzenbach et al., 2006; Abdelmelek et al., 2011; Boxall et al., 2012). The occurrence, transformation, and

ultimate fate of PPCPs always remain great challenges for environmental scientists because of their ultra-low concentrations (ng L⁻¹ to µg L⁻¹) and the complex matrix interferences in aquatic samples (Yang et al., 2013; Yu et al., 2013; Yan and Song, 2014). Although thousands of PPCPs are currently used, it is reported that only less than 15% of PPCPs are actually identified in the environment due to the lack of suitable analytical methods (Sacher et al., 2001; Ternes et al., 2004). Among PPCPs, illicit drugs are one group of unique compounds, which are highly psychoactive and have unidentified effects on non-target organisms (Binelli et al., 2012; Baker and Kasprzyk-Hordern, 2013; Parolini et al., 2015). It is estimated that there are about 165–315 million illicit-drug users

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distributed all around the world, and thousands tons of illicit drugs are consumed annually (UNODC, 2013). However, only a limited number of studies have reported their occurrence in surface water samples from Spain (Boleda et al., 2009; Mendoza et al., 2014), France (Nefau et al., 2013), Italy (Repice et al., 2013), Belgium (Van Nuijs et al., 2009), and US (Subedi and Kannan, 2014). It's likely due to the lack of easy accessible analytic methods for environmental samples.

Tandem triple quadrupole mass spectrometer coupling with LC (LC-MS/MS) is the most common method for plasma, urine samples. To deal with ultra-low concentrations in the aquatic samples, pre-concentration and cleanup steps have to be considered. Herein solid phase extraction (SPE) is a preferred technique. Various materials, including hydrophilic reversed-phase, cation-exchange, and mixed-mode materials, have been used to adsorb illicit drugs from aquatic samples. For example, Gonzalez-Marino et al. (2012) reported a mixed-mode SPE (Oasis MCX sorbent) method for quantitative determination of 24 illicit drugs and metabolites in urban sewage samples. The selectivity and limit of detection (LOD) for basic drugs are improved through adopting a fractionated elution strategy. Gilart et al. (2014) synthesized two mixed-mode sorbent (strong cation-exchange SPE) to extract a group of pharmaceuticals and illicit drugs selectively from wastewater samples. Several key parameters, such as pH, wash and elution solvents and volumes, were evaluated. Only the sulphonated 2-hydroxyethyl methacrylate/divinylbenzene (50/50) achieved worthy SPE performance with recovery values between 70% and 98%.

Most of traditional SPE methods for trace contaminant analysis require relative large sample volumes along with multiple cleaning processes. They can be labor intensive and time consuming. They also generate large amounts of hazardous chemical waste as well as expose laboratory personnel to dangerous chemicals and fumes. There are also considerable costs due to materials and time needed to prepare, extract, and analyze each sample. As requirement of more sustainable and environmentally friendly methods, laboratories have moved towards "greener" alternative methods for the analysis of environmental samples. The online SPE strategy is an ideal choice to improve method sensitivity, shorten pretreatment and analysis times, and increase the number of the samples analyzed in the same time frame. Like offline SPE mentioned above, there are also many sorbents available for online SPE. Ion exchange resins and hypercross linked polymer resin are available from numerous manufacturers, and widely used to capture a broader range of analytes within a single extraction. Fontanals et al. (2011) published a fully automated, online SPE-LC-MS/MS method using HILIC for illicit drugs and other polar drugs in environmental waters. Using this method, up to 10 mL of environmental waters could be analyzed at low ng L⁻¹ level. However, only a few analytical methods for analyzing illicit drugs based on popular reverse phase (Postigo et al., 2008; Heuett et al., 2015).

The primary aim of this study is to develop a simple and easy accessible analytic method to determine trace amount of 10 selected illicit drugs and metabolites in the environmental aquatic samples. Furthermore the occurrence of these selected illicit drugs and metabolites in Chinese WWTP effluents and surface waters has also been examined.

2. Materials and methods

2.1. Chemicals and reagents

Cotinine (CTN), caffeine (CFI), ¹³C₃-CFI, (±)-amphetamine-D₁₁ (AMP-D₁₁), paraxanthine (PXT), (R, R) (-)-pseudoephedrine (PS-EPH), (±)-3, 4-methylenedioxyamphetamine (MDA), (±)-3, 4-methylenedioxymethamphetamine (MDMA), benzoylecgonine

(BEG), BEG-D₈, (±)-methadone (MET), MET-D₃, (±)-2-ethyl-1, 5-dimethyl-3, 3-diphenylpyrrolinium (EDDP), (-)-11-nor-9-carboxy-Δ⁹-tetrahydrocannabinol (THC-COOH) and THC-COOH-D₃ were purchased from Cerilliant (Round Rock, TX, USA) as 1.0 or 0.1 mg mL⁻¹ solutions in acetonitrile (ACN) or methanol (MeOH). The purity of all standards was ≥98.2%. The mixed stock solution (containing all the analytes) was prepared in MeOH at 100 μg L⁻¹. Mixed isotope internal standards (containing all the deuterated analytes) were also prepared in MeOH at 100 μg L⁻¹. All standard solutions were stored in the dark at -20 °C. Working standard mixtures and calibration solutions were prepared at different concentrations by appropriate dilution of the stock solution with ultrapure water.

LC-grade ACN and MeOH were supplied by J. T. Baker (Center Valley, PA). Deionized water (DI) was obtained by purifying demineralized water in a Milli-Q system (Millipore, Bedford, MA). MS grade formic acid (98.2%) and acetic acid (99.7%) for mobile phase modification was obtained from Sigma-Aldrich (St. Louis, MO). Online PLRP-S cartridges (2.1 × 12.5 mm) were purchased from Agilent (Sunnyvale, CA, US).

2.2. Sample collections

Twenty-two surface water samples were collected along the Huangpu River in Shanghai during the summer of 2014. Four wastewater effluents were collected in June of 2014 from sewage treatment plants (Shanghai, Guangzhou, Hefei and Jiangsu) around China. Wastewater treatments in all studied WWTPs are based at least on a preliminary clarification step followed by a biological treatment, which in most cases consists of conventional activated sludge process. Grab samples were collected using amber glass bottles (previously cleaned). Upon arrival to the laboratory, samples filtered using a 0.8 μm cellulose filters were purchased from Jinteng (Shanghai, China), and stored at 1 °C until analysis.

2.3. Online SPE

An Agilent 1290 infinity flexible cube was employed to achieve On-line SPE. It includes one 2-position/10-port quick change valve with two trapping columns, as well as a piston pump and solvent selection valve that can draw up to three solvents. The two cartridges with Agilent PLRP-S material alternate in use, each cartridge can deliver more than 300 enrichment and elution cycles.

The method followed four steps: loading sample, cleanup, elution and online SPE column regeneration (Table 1). In the first step (loading sample), 5.0 mL sample was drawn by syringe from a 6 mL vial and pumped into a 5.0 mL loop using the UHPLC auto-sampler, and then delivered to one of online SPE columns with 15.0 mL H₂O by the piston pump. After sampling, the cleanup step was immediately initialized. The mobile phase of piston pump was changed to 10% ACN and kept for 4.0 min to remove part of organic impurities concentrated on the SPE column along with analytes. After cleanup, the 2-position/10-port valve changed valve position that coupled the online SPE column with the chromatographic column, in which the analytes were eluted from the online SPE column to the analytical column by UHPLC mobile phase in back-flush mode. Simultaneously, the regenerated step of another trapping column initialized. The SPE column was rinsed with 9 mL of ACN followed by 12 mL of H₂O, which ensured the removal of any residual contamination from the last elution. Two trapping columns were alternatively used during the online SPE circle. To avoid the subtle differences between these two trapping columns, each sample should be measured at least once using two trapping columns.

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