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Simultaneous determination of PPCPs, EDCs, and artificial sweeteners in environmental water samples using a single-step SPE coupled with HPLC–MS/MS and isotope dilution

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ABSTRACT

A high-throughput method for the simultaneous determination of 24 pharmaceuticals and personal care products (PPCPs), endocrine disrupting chemicals (EDCs) and artificial sweeteners (ASs) was developed. The method was based on a single-step solid phase extraction (SPE) coupled with high performance liquid chromatography–tandem mass spectrometry (HPLC–MS/MS) and isotope dilution. In this study, a single-step SPE procedure was optimized for simultaneous extraction of all target analytes. Good recoveries ($\geq 70\%$) were observed for all target analytes when extraction was performed using Chromabond[®] HR-X (500 mg, 6 mL) cartridges under acidic condition (pH 2). HPLC–MS/MS parameters were optimized for the simultaneous analysis of 24 PPCPs, EDCs and ASs in a single injection. Quantification was performed by using 13 isotopically labeled internal standards (ILIS), which allows correcting efficiently the loss of the analytes during SPE procedure, matrix effects during HPLC–MS/MS and fluctuation in MS/MS signal intensity due to instrument. Method quantification limit (MQL) for most of the target analytes was below 10 ng/L in all water samples. The method was successfully applied for the simultaneous determination of PPCPs, EDCs and ASs in raw wastewater, surface water and groundwater samples collected in a local catchment area in Singapore. In conclusion, the developed method provided a valuable tool for investigating the occurrence, behavior, transport, and the fate of PPCPs, EDCs and ASs in the aquatic environment.

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1. Introduction

Recently, pharmaceuticals and personal care products (PPCPs), endocrine disrupting chemicals (EDCs) and artificial sweeteners (ASs) have increasingly gained attention due to their ubiquitous occurrence in the water environment and their potential to cause undesirable ecological effects [1–4]. The main source of PPCPs, EDCs and ASs into the environment is raw wastewater or insufficiently treated wastewater effluents [5,6]. Other important sources include landfill leachate and leaking storage tanks. The widespread occurrence of PPCPs, EDCs and ASs in the aquatic environment such as rivers, lakes and groundwater has been reported over the past decade [4,7–9]. The presence of PPCPs and EDCs in the water environment has been reported to potentially affect aquatic organisms and produce changes that threaten the sustainability of aquatic ecosystem [10–13]. Recently, risk assessment of artificial sweeteners (e.g. sucralose) in the water environment to the aquatic organisms has also gained concerns [14,15]. Although the

toxicity of PPCPs, EDCs and ASs to human health is relatively unknown at trace levels, continuous discharge and chronic exposure to these compounds may pose a risk to human health associated with exposure to very low concentrations of pharmaceuticals in drinking-water over a lifetime [16,17]. Due to the frequent detection and persistence of PPCPs, EDCs and ASs in the aquatic environment, many of these compounds have been proposed as chemical makers of wastewater contamination in surface water and groundwater [3,8,9,18–20]. However, no reports on the occurrence of artificial sweeteners in Asian countries are available in the open literature. Hence, in order to better evaluate the occurrence, fate, and environmental risk of these compounds in the environment to the aquatic ecosystems, development of a robust sensitive analytical method for simultaneous determination and extraction of these chemicals at trace levels in various environmental matrices is critically required.

Currently, several advanced analytical methods, such as gas chromatography–mass spectrometry (GC–MS) [21,22], GC–MS/MS [23] liquid chromatography–mass spectrometry (LC–MS) [24] or LC–MS/MS [25–30] have been reported. However, most of them have some drawbacks, such as a lack of selectivity and sensitivity. Most of the developed methods just focused on determining a

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specific class of compounds [4,23,29,30] with limited method validation data reported. In environmental analysis of trace pollutants, it is challenging to extract the target analytes present in sample at very low concentrations from complex environmental matrices. At present, solid phase extraction (SPE) has been widely used for enriching and purifying a wide range of organic emerging contaminants from the environmental samples [31]. However, it is obvious that besides enriching target analytes, SPE may either enrich some interference or eliminate matrix constituents, which may influence LC separation and tandem MS detection. Thus, SPE extraction and HPLC–MS/MS operating conditions affect directly the sensitivity and accuracy of analytical method.

To improve recoveries of analytes in environmental samples, one of the options is to use different SPE sorbents and perform extraction under various conditions for different classes of target analytes [4,32]. It is obvious that choosing a proper SPE cartridge plays a key role in enhancing recovery of analytes in the environmental water samples. Normally, the selection is frequently based on the physicochemical properties of target analytes and SPE sorbent characteristics. For example, Kasprzyk-Hordern et al. [32] found that Oasis MCX—a strong cation-exchange mixed-mode polymeric sorbent was the best out of the 8 tested SPE sorbent types for extracting basic/neutral pharmaceuticals and illicit drugs in surface water samples. In another study, Scheurer et al. [4] reported that styrene–divinylbenzene (Bakerbond SDB 1) provided notably high recoveries (> 75%) for the artificial sweeteners compared to other SPE cartridges such as Isolute ENV+, C18, Varian Bond Elut PPL, Strata X, Strata X-AW, Oasis HLB, WAX, MAX, and HCX. Although using different SPE cartridges used for enrichment of different classes of analytes may provide a relatively high extraction recovery for analytes compared to a single-step SPE procedure [31], this approach is time-consuming once analyzing with a huge number of target analytes with different physicochemical properties (such as $\log K_{ow}$ and pK_a) and is quite expensive due to SPE cartridge consumption. Most of the published methods did not use isotopically labeled internal standards (ILIS) to correct the matrix effect in analysis of real environmental water samples [4,23,24,33]. This is also one of the drawbacks in applying those methods to quantify the target analytes in different environmental matrices. Because of these reasons, the development of a high-throughput method for the determination of multiple target analytes with different physicochemical properties under different matrices is of importance.

The first objective of this study was to develop a fast and reliable method for the detection and quantification of 24 PPCPs, EDCs and ASs in water samples by using a single-step SPE coupled with HPLC–MS/MS and isotope dilution. The second objective was to investigate stability of the target analytes during sample storage and determine an appropriate preservation procedure. Finally, this study aimed to test the applicability of the developed method for the monitoring of PPCPs, EDCs and ASs in wastewater, surface water and groundwater samples.

2. Experimental

2.1. Chemicals and materials

The target analytes studied were 24 PPCPs, EDCs and ASs with different chemical structures and physicochemical properties (i.e. acidic, neutral, hydrophilic, and hydrophobic properties). These compounds were acetaminophen [ACT], caffeine [CF], carbamazepine [CBZ], ibuprofen [IBP], ketoprofen [KEP], fenoprofen [FEP], naproxen [NPX], propyphenazone [PPZ], clofibrac acid [CA], gemfibrozil [GFZ], diclofenac [DCF], indomethacin [IDM], salicylic acid [SA], crotamiton [CTMT], trimethoprim [TMP], and diatrizoic acid

[DTZ], diethyltoluamide [DEET], bisphenol A [BPA], acesulfame [ACE], aspartame [ASP], cyclamate [CYC], saccharin [SAC], sucralose [SUC], and neohesperidin dihydrochalcone [NHDC]. All these PPCPs, EDCs and ASs were purchased from Sigma Aldrich (Sigma Aldrich, Singapore). Their physicochemical properties are summarized in Table A1 (Supplementary Information). Thirteen ^2H -isotope labeled compounds were used as internal/surrogate standards to correct the loss during SPE extraction procedures and ESI–MS/MS. These isotopically labeled internal standards (ILIS) included acesulfame- d_4 [ACE- d_4], acetaminophen- d_4 [ACT- d_4], aspartame- d_5 [ASP- d_5], bisphenol A- d_{16} [BPA- d_{16}], carbamazepine- d_8 [CBZ- d_8], caffeine- d_9 [CF- d_9], cyclamic acid- d_{11} [CYC- d_{11}], diclofenac- d_4 [DCF- d_4], diethyltoluamide- d_{10} [DEET- d_{10}], ketoprofen- d_3 [KEP- d_3], salicylic acid- d_4 [SA- d_4], saccharin- d_4 [SAC- d_4] and sucralose- d_6 [SUC- d_6], which were purchased from Toronto Research Chemicals Ins. (Toronto, Canada). The solvents, HPLC grade methanol and acetonitrile, were provided by Merck (Darmstadt, Germany). The individual stock solutions of each target compounds as well as the ILIS solution were prepared in methanol–water (50/50, v/v) at 2.0 g/L and 0.05 g/L, respectively. The solutions were stored in the dark condition at -18°C . A mixture of all PPCPs, EDCs and ASs was prepared by diluting individual stock solutions with methanol and it was renewed before each analytical run. A separate mixture of ILIS used for internal standard quantification was prepared in methanol–water (75/25, v/v) and further diluted in MeOH/H₂O (75/25, v/v) solution.

2.2. Sample collection and pretreatment

Grab water samples (including raw wastewater, surface water and groundwater) were collected from a local water catchment area in Singapore and were used for development and validation of the method. All water samples were filled in 1 L amber glass bottles immediately carried to the laboratory in ice-packed containers. Once in the laboratory, the samples were filtered using 1.2 μm glass fiber filters (GF/C, Whatman, UK), followed by 0.45 μm membrane filters (PALL corporation, US), subsequently to separate dissolved and particulate phases and stored at 4°C until SPE extraction, which was performed within 24 h in order to avoid any degradation.

2.3. Solid-phase extraction

Due to the wide range of the target analytes with different chemical characteristics, it is challenging to extract all the target analytes in a single-step SPE procedure with good method performance. Therefore, optimization of a single-step SPE procedure is critically required. In this study, the following five cartridges, Chromabond[®] HR-X (500 mg, 6 mL), Chromabond[®] HR-XAW (500 mg, 6 mL), an Bond Elut Plexa (200 mg, 6 mL), and Oasis HLB Plus (225 mg), and SampliQ C18 (500 mg, 6 mL), were used in screening for enrichment purpose. The characteristics of these SPE cartridges are presented in Table A2 (Supplementary Information). The experiment was performed to evaluate extraction efficiency by spiking 200 ng/L of analytes into 500 mL Milli-Q water. The effect of sample pH on recovery of target analytes in Milli-Q water samples was investigated at various pH values ranging from 2 to 10.

For real water samples, prior to SPE extraction, water samples were spiked with the 13 ILIS (including ACE- d_4 , ACT- d_4 , ASP- d_5 , BPA- d_{16} , CBZ- d_8 , CF- d_9 , CYC- d_{11} , DCF- d_4 , DEET- d_{10} , KEP- d_3 , SA- d_4 , SAC- d_4 and SUC- d_6). The SPE cartridges were preconditioned with 6 mL methanol, followed by 6 mL of Milli-Q water at a flow rate of 3 mL/min. After the conditioning step, 250 mL of wastewater samples or 500 mL of groundwater/surface water samples were

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