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Sample as solid support in MSPD: A new possibility for determination of pharmaceuticals, personal care and degradation products in sewage sludge

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HIGHLIGHTS

- The use of the sample as a solid support in MSPD was proposed.
- Different solid supports were evaluated.
- The method was successfully applied in real sludge samples.
- PPCPs were detected in concentrations between 2.5 and 5400 ng g^{-1}.

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ABSTRACT

A method based on matrix-solid phase dispersion (MSPD), focused on the principles of green analytical chemistry, aimed at the use of alternative solid supports and less toxic solvents, was developed for the simultaneous determination of 19 pharmaceuticals, 4 personal care products (PPCPs) and 4 degradation products in sewage sludge samples. Higher recoveries were achieved when 2 g sample was macerated for 5 min in a glass mortar, transferred to a centrifuge tube, and 1 min vortex agitation with 5 mL methanol. The performance of the method was evaluated through linearity, recovery, precision (intra-day), method detection and quantification limits (MDL and MQL) and matrix effect. The calibration curves prepared in methanol and in the matrix extract showed a correlation coefficient ranging from 0.98 to 0.99. MQL values ranged from 1.25 to 1250 ng g^{-1}. Recoveries between 50 and 120% were reached with RSDs lower than 20% for most compounds. The method presented low and medium matrix effects for most analytes. This method was successfully applied to real samples and of the 27 compounds determined, amitriptyline, carbamazepine, diclofenac, haloperidol, ketoconazole, miconazole, albendazole, mebendazole, thiabendazole, triclosan and triclocarban were detected in concentrations between 2.5 and 5400 ng g^{-1}.

1. Introduction

Pharmaceuticals and personal care products (PPCPs) are a class of emerging contaminants that are used to improve the quality of daily life and/or to prevent or treat human and animal disease (Boxall et al., 2012). PPCPs constitute an important class of compounds which includes antibiotics, hormones, analgesics, anti-inflammatory drugs, blood lipid regulators, β-blockers, preservatives, bactericides/disinfectants, insect repellents, fragrances, and sunscreen ultraviolet filters (Yang et al., 2017).

PPCPs have been extensively and increasingly used. More than 600 pharmaceutical substances have been shown to be present in the environment worldwide (Küster and Adler, 2014). PPCPs can be released to the environment from multiple sources, including domestic wastewater, hospital discharges, improper manufacturer disposal, sewage treatment plants and water treatment plants (Yang et al., 2017).

Some studies indicated that the effluent from wastewater treatment plants are one of the major pathways of PPCPs to the receiving soil, water bodies and sediments (Li et al., 2016; Yang et al., 2017). Besides, according to their physicochemical characteristics, PPCPs can have greater affinity for the organic phase,

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being more likely to be adhered to the sediment or particles present in the water column. In addition, they can be adhered to the sludge during wastewater treatment (Jørgensen and Halling-Sørensen, 2000; Vazquez-Roig et al., 2013; Křesinová et al., 2016; Wang et al., 2018).

For the extraction of PPCPs from sludge samples, techniques such as ultrasonic assisted extraction (UAE) (Yu et al., 2011; Albero et al., 2015; Ekpeghere et al., 2017; Luque-Muñoz et al., 2017), microwave-assisted extraction (MAE) (Dorival-García et al., 2013; Petrie et al., 2016) pressurized liquid extraction (PLE) (Pamreddy et al., 2013; Salvia et al., 2015; Ekpeghere et al., 2017) and QuEChERS (Peysson and Vulliet, 2013; Cerqueira et al., 2014a, 2014b; Rossini et al., 2016; Ponce-Robles et al., 2017) have been used. However, with the increasing concern about the importance of follow the green analytical chemistry principles, techniques that minimize the use of energy, sample size and the number of steps and allow the use of reagents obtained from renewable sources should be preferred (Gałuszka et al., 2013). The matrix solid phase dispersion (MSPD) have gaining attention for the extraction of PPCPs from sludge samples (Albero et al., 2013; Casado et al., 2015; Li et al., 2016; Soares et al., 2017).

MSPD was proposed by Barker in 1989 for the extraction of drugs in biological tissues, and its advantages includes simplicity (it does not require any instrumentation or specific instrument), flexibility, ruggedness and mild extraction conditions (Capriotti et al., 2015).

Since its proposal, some modifications aimed at making the method simpler and easier to execute have been proposed, such as the modification called vortex-assisted extraction (VA-MSPD) where the elution step that is usually carried out in a cartridge was changed to a vortex agitation (Sebastià et al., 2010; Caldas et al., 2013). Other interesting and green advances includes the use of alternative solid supports obtained from renewable sources, aimed at reducing costs and generating less aggressive residues to the environment have been made. In the literature, the use of diatomaceous earth during the extraction of sunscreens (Casado et al., 2013) and triclosan from sewage sludge (González-Mariño et al., 2010), sand in the analysis of essential oils in herbs (Dawidowicz et al., 2011), golden mussel shell for the extraction of pesticides and PPCPs in golden mussel tissues (Rombaldi et al., 2015), booster biocides in fish tissue (Vieira et al., 2018), chitin for the extraction of pesticides in DWTS sludge (Soares et al., 2017) and reused C18 for the extraction of pesticides in onion (Rodrigues et al., 2010) have been reported.

The dispersants could be inert materials that have a simple abrasive role to ensure complete matrix disruption, or some selective materials that can enhance the technique selectivity and perform the clean-up together with the extraction step (Capriotti et al., 2015). In an interesting way, some samples could have in their composition, substances that can make it abrasive or selective, and thus, not needing the use of a dispersant. This aspect have been few investigated and it appears as a good option since it reduces the consumption of reagent and generate less amount of residues.

Polar compounds such as PPCPS have been traditionally determined using reverse-phase liquid chromatography (RP-LC). However, hydrophilic interaction liquid chromatography (HILIC), which is characterized by the use of a hydrophilic stationary phase and an aqueous-polar/organic solvent mobile phase (Dejaegher and Vander Heyden, 2010; Lanças, 2010; da Silva et al., 2016) is gaining interest nowadays, especially for the analysis of polar compounds (Dejaegher and Vander Heyden, 2010; Yuan et al., 2013; Kahsay et al., 2014). More hydrophilic compounds elute near the solvent front in RP-LC columns, often together with matrix interferences. The use of HILIC allow a better separation and retention of such compounds (Dejaegher and Vander Heyden, 2010).

Thus, this study aimed to assess a fast and low cost method based on the principles of green analytical chemistry for the simultaneous extraction of 19 pharmaceuticals, 4 personal care products (PCPs) and 4 degradation products in sewage sludge samples, using MSPD with determination by hydrophilic interaction chromatography–tandem mass spectrometry. Also, the presence of these compounds was investigated in samples obtained from a Wastewater Treatment Plant (WWTP).

2. Material and methods

2.1. Reagents and standards

Amitriptyline, ketoconazole, diclofenac, mebendazole and propranolol were supplied by the United States Pharmacopeia (USA). Albendazole, carbamazepine, diltiazem, gemfibrozil, glibenclamide, flurazepam, haloperidol, lidocaine, miconazole, nifedipine and nimesulide were provided by Fiocruz (Fundação Oswaldo Cruz, Brazil). Methylparaben, propylparaben, methylchloroparaben, 2-hydroxybenzophenone, 2,2-dihydroxybenzophenone and 4-hydroxy-ibuprofen were obtained from Sigma Aldrich (Brazil). Clofibric acid, triclocarban, triclosan and ibuprofen were purchased from Dr. Ehrenstofer GmbH (Augsburg, Germany). Some physicochemical properties of the compounds are listed in Table S1 (CHEMSPIDER; DRUGBANK). Individual compound stock solutions containing 1000 mg L^{-1} of the target compounds and a mixture of analytes were prepared in methanol and stored at −18 °C.

Methanol (MeOH), ethanol and acetonitrile (MeCN) both LC-grade were purchased from J.T.Baker (Phillipsburg, NJ, USA). Water was purified by a Direct-Q UV3® (resistivity 18.2 MΩ cm, Millipore, USA).

C18 Bondesil was purchased from Varian (USA). Beach sand was collected at Bojuru beach, located in the south of the Rio Grande do Sul state, Brazil.

2.2. Sewage sludge sample and sample preparation

Sewage sludge samples were collected in the drying beds of the CORSAN, the Wastewater Treatment Plant (WWTP) in Rio Grande city, Rio Grande do Sul state, Brazil. This WWTP treats an average of 400,000 m^3 wastewater/month through the process of employing activated sludge, and serves about 3500 residences. Samples were collected, frozen and freeze-dried (Freeze drier L108, Liobras, Brazil) prior to analysis.

Different sorbents and solvents were tested for optimization of the VA-MSPD extraction. Under the final conditions, samples (2.0 g) were macerated in a glass mortar for 5 min. Samples were then transferred to a polypropylene tube (15-mL capacity), to which 5 mL of methanol was added. The resulting mixture was vortexed for 1 min and centrifuged for 5 min at 11,011 × g. Finally, 10 μL was injected into the LC system, according to Fig. 1.

2.3. HILIC-MS/MS analyses

HILIC-MS/MS analyses were performed by a Waters Alliance 2695 Separations Module fitted to an autosampler, a membrane degasser and a quaternary pump. Mass spectrometry was performed by a Micromass Quattro Micro API with an ESI interface. The LC separation was carried out by an Atlantis HILIC analytical column (50 × 4.6 mm I.D., 3 μm) (Waters, USA). Analytical instrument control, data acquisition and treatment were performed by the software Masslynx version 4.1, 2005 (Waters, USA). A 10 μL sample was injected by an autosampler. Ionization of the compounds was