Optimization of fabric phase sorptive extraction for the determination of selected pharmaceuticals in environmental waters

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Abstract
There is a growing public and scientific concern about the possibility of ecosystem and human health effects from pharmaceuticals in environment. Results have shown that several types of environmental waters (drinking water, groundwater, surface water, treated water) were contaminated by the presence of pharmaceutical compounds including psychiatric drugs. For this reason, it is imperative to develop analytical methods of extraction and pre-concentration to allow for subsequent instrumental analysis of these drugs. In this work, fabric phase sorptive extraction (FPSE) is investigated for the extraction of citalopram, clozapine and sertraline (used in the treatment of mental diseases) in water samples with the aid of chemometric tools and high performance liquid chromatography-photodiode array detection (HPLC-UV/DAD). Parameters affecting the efficiency of FPSE were evaluated in depth. The method shows good linearity, with RSD of less than 15%. Relative recoveries higher than 59% were obtained for the studied compounds

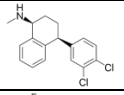
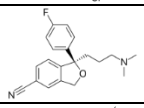
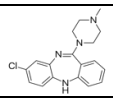
Keywords: Fabric phase sorptive extraction, experimental design, extraction

1. Introduction

Antidepressants are medications that can help relieve symptoms of depression, social anxiety disorder, anxiety disorders, seasonal affective disorder, and dysthymia, or mild chronic depression, as well as other conditions. As with other emerging pollutants, these compounds enter into the aquatic environment mainly through effluents from wastewater treatment plants and hospitals (Hernando et al., 2006). As a result of not being degraded or removed by conventional wastewater treatment plants they are likely to reach the aquatic environment and be detected at very low concentrations (ppt). Recently, a new green sample preparation method namely, fabric phase sorptive extraction has been developed which is highly sensitive and efficient (Kabir and Furton 2014). This technique, developed integrates the advantages of sol-gel technology and rich surface chemistry of cellulose/polyester fabric in an advanced and very effective sorbent material. The FPSE device consists of a flexible and permeable substrate coated with a sorbent, chemically bonded to its surface that allows the incorporation of large amounts of sorbent inside the cellulose/polyester substrate, generating a phenomenal increase in the retention capacity of the analyte.

In this work, a rapid, simple and green method for the analysis of citalopram, clozapine and sertraline (Table 1) that are commonly used in the treatment of mental diseases has been developed using fabric phase sorptive extraction (FPSE) coupled to HPLC–UV/DAD in environmental water samples for the first time. The optimization process was performed through a 2^4 and a 3^2 experimental design. Moreover, the applicability of the new method to the analysis of target analytes in environmental samples was verified on wastewater from a hospital effluent

Table 1. Chemical structures of selected compounds

Compound	Chemical Structure
Sertraline	
Citalopram	
Clozapine	

2. Experimental

2.1. Materials and reagents

Ultra-pure quality water was produced from a Milli-Q-plus ultrapure water system from Millipore Sigma. All solvents used were purchased from Thermofisher Scientific. The analyzed antidepressants were obtained from Sigma-Aldrich and their purities were above 99%. Polyethylene glycol (PEG 300), methyltrimethoxysilane (MTMS), trifluoroacetic acid, sodium hydroxide, and hydrochloric acid were purchased from Sigma-Aldrich.

2.2. Fabric phase sorptive extraction

Several different fabric media were tested. Firstly, to clean and activate the coating of the fabric media, the coated media were immersed in 2 mL of a mixture of methanol and acetonitrile (50/50, v/v) for 5 min and then washed in 2 mL of water for 5 min. To make a prior selection of which fabrics could be efficient for the target compounds, adsorption tests were performed with the fabrics. This test consisted of measuring the concentration of the analytes in the spiked Milli-Q water samples before and after extraction with the fabrics. In a second step, to evaluate the desorption efficiency, the analytes were eluted from the fabrics in 1 mL of methanol for 5 min, and the methanol was measured to check the presence of the analytes. In light of the results obtained in the elution tests, two fabric media were selected (Whatman filter paper and Whatman fiber glass) for later experimental designs. Finally, the extracts were injected in the chromatographic system to evaluate the extraction recoveries.

3. Results and Discussion

3.1. Optimization of the experimental conditions of the selected FPSE

To evaluate the influence of the different variables in the extraction process a 2^4 experimental design was carried out with four variables at two levels to determine the correlation between them followed by a 3^2 experimental design. The optimal final conditions were a sample volume of 1 mL with an ionic strength of 0%, an extraction time of 30 min, and elution with 0.15 mL of methanol for 10 min.

3.2. Analytical parameters

For the calculation of linearity, a standard curve was set up in Milli-Q water with 7 points between 2 μg L^{-1} and 250 g L^{-1} of the mixture of analytes. Linearity was calculated as the ratio between the peak areas and concentration of each compound, and correlation coefficients greater than 0.9944 were obtained in all cases. Intraday repeatability of the method was evaluated using six measurements of each sample whereas inter-day reproducibility was evaluated using a triplicate of each sample during three days. The results were very satisfactory and, in all cases, relative standard deviations were less than 15%. The limits of detection (LOD) and limits of quantification (LOQ) of the method were calculated using the signal-to-noise ratio of each individual peak. Absolute recoveries (Figure 1) in Milli-Q water ranged between 59%–90%.

4. Conclusions

To our knowledge, this is the first attempt to apply the FPSE microextraction technique for extraction and preconcentration of these compounds present in water sample. Based on our results fabric phase sorptive extraction is presented as a fast, sensitive and simple method for the analysis of the target analytes in natural water and wastewater samples.

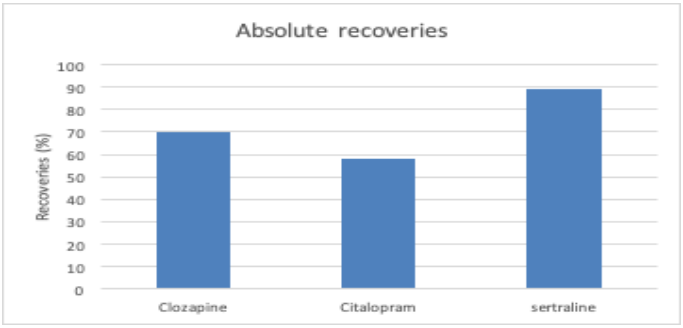


Figure 1. Absolute recoveries obtained from the 3 compounds in Milli-Q water at 10 ppb

References

Hernando, M.D., Mezcua, M., Fernandez-Alba, A.R., Barcelo, D., (2006) Environmental risk assessment of pharmaceutical residues in wastewater effluents, surface waters and sediments. Talanta 69, 334e342

Kabir, A., Furton, K.G., 2014. Fabric phase sorptive extractors (FPSE), US Patent Application: 14,216,121 March 17, 2014

Acknowledgements

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement N. 765860