Optimization of molecularly imprinted solid phase extraction (MISPE) coupled with UHPLC-FD, for the determination of estrogens in wastewaters

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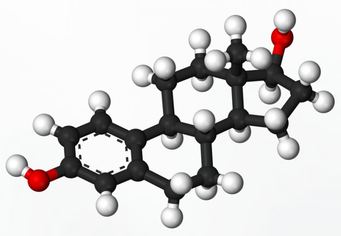
INTRODUCTION:



Female hormones, named estrogens, are considered as endocrine disrupting compounds (EDCs) and they are an important group of contaminants, among emerging pollutants which have attracted the attention of the international community due to their capacity of altering the natural hormonal equilibrium, producing harmful effects in organisms. Some authors have linked the concentrations of estrogens in environmental waters with changes observed in aquatic biota as for example changes in reproduction of fish [1]. The levels of EDCs in the environment are usually in the range of ng·L^{-1} [2] so it is necessary the development of selective extraction methods.

Molecularly Imprinted Solid Phase Extraction (MISPE) is based in the use of a molecularly imprinted polymer as stationary phase of solid phase extraction which allows a selective extraction of a kind of compounds from a matrix.

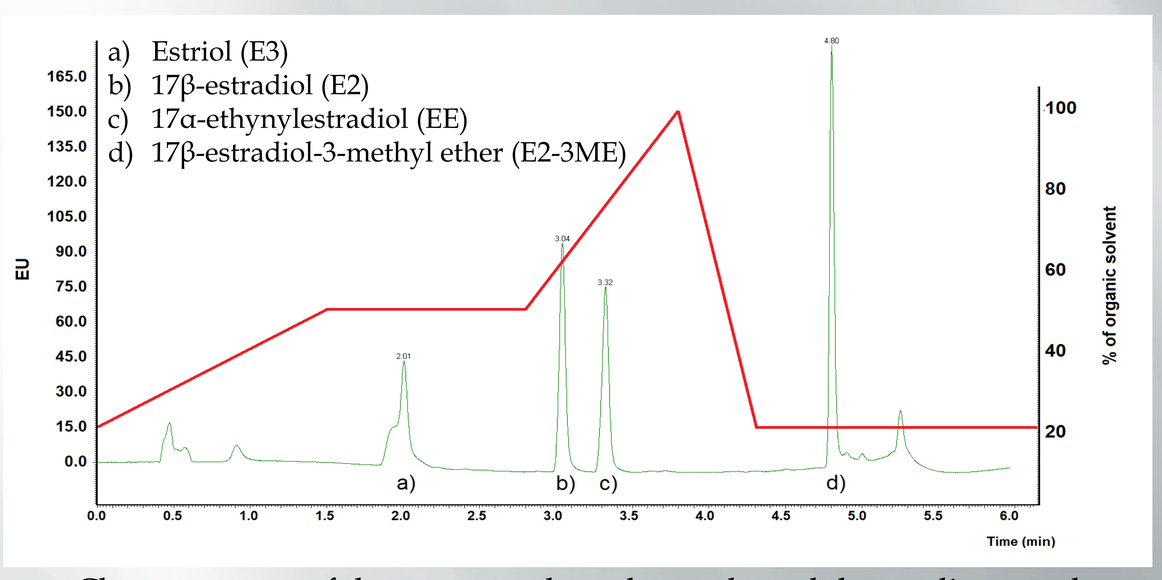
In this study, a molecularly imprinted solid phase extraction (MISPE) coupled to ultra-high performance liquid chromatography with fluorescence detection has been optimized to determine four estrogens (estriol, 17β-estradiol, 17α-ethynylestradiol and 17β-estradiol-3-methyl ether) in wastewater samples.

MATERIALS AND METHODS:

Chromatographic separation:

Mobile phase:
A: Water + 0.1% NH_3
B: Acetonitrile

Chromatographic column:
- ACQUITY BEH C18 column (50 mm × 2.1 mm, 1.7 µm)



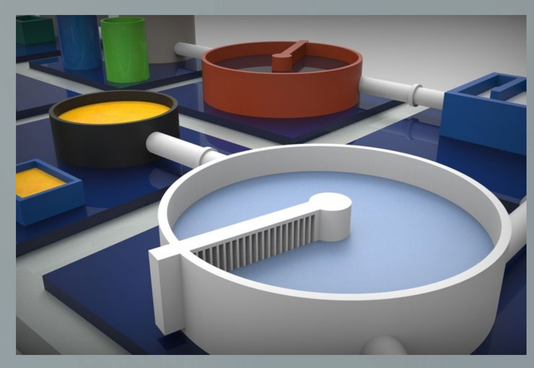
Chromatogram of the compounds under study and the gradient used

SPE cartridges:

Molecularly imprinted cartridges:
- Affinimip® SPE Estrogens
  3 mL, 100 mg. of sorbent

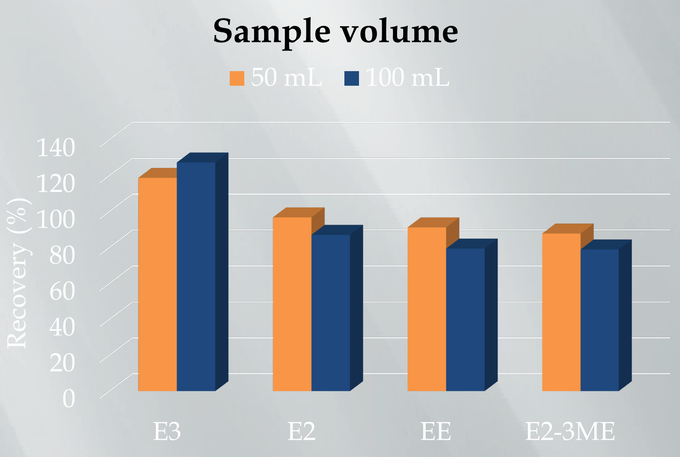
Sample collection:

Influent and effluent of a WWTP and effluent of a veterinary hospital in Gran Canaria (Spain)



RESULTS:

Optimized variables:



MISPE procedure:

Equilibration
- 3 mL acetonitrile
- 3 mL ultrapure water

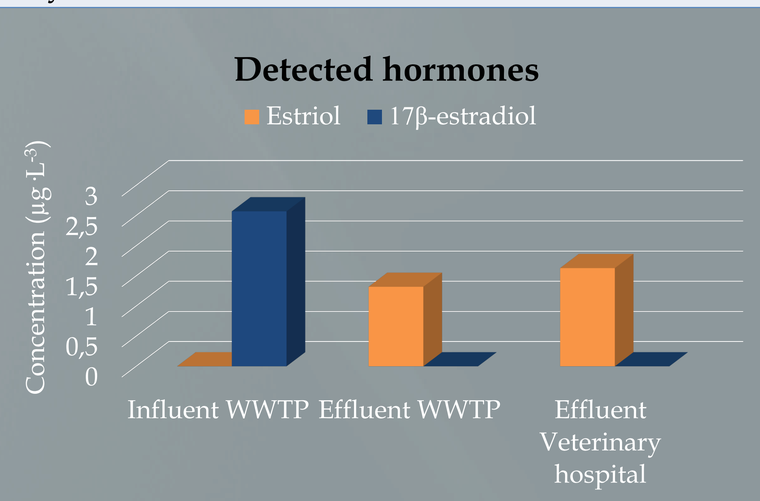
Loading
- 50 mL of water

Wash step
- 3 mL ultrapure water

Elution
- 1.5 mL methanol

Application to real samples:

Recoveries (%)			
	Influent WWTP	Effluent WWTP	Effluent veterinary hospital
Estriol	40.0 ± 1.8	94.3 ± 4.1	87.0 ± 5.0
17β-estradiol	80.7 ± 0.6	62.4 ± 9.7	105.8 ± 5.4
17α-ethynyl-estradiol	75.8 ± 2.5	60.0 ± 7.1	90.8 ± 3.3
17β-estradiol 3 methyl ether	86.1 ± 4.3	66.0 ± 1.7	98.8 ± 3.5



CONCLUSIONS

In accordance with the obtained results, the MISPE-UHPLC-FL procedure is easy, cheap, selective and sensitive, with low detection limits and good recoveries. The application in real sewage samples was satisfactory.

REFERENCES

[1] J.R. Colman, D. Baldwin, L.L. Johnson, N.L. Scholz, Aquat. Toxicol. 91 (2009) 346–354.
[2] R. Guedes-Alonso, Z. Sosa-Ferrera, J.J. Santana-Rodriguez, J. Anal. Methods Chem. 2013 (2013) e210653.