Multi-residue analysis of pharmaceuticals by on-line preconcentration LC-MS/MS in water samples

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Introduction

The impact of pharmaceuticals towards aquatic and ground ecosystems is still poorly known. A necessary step for a better understanding of the behavior and impact of pharmaceuticals consists in a characterization of pharmaceutical contamination of water bodies. This requires powerful analytical method able to quantify compounds at very low concentration (few ng/L).

Multi-residue analytical methods for determination of pharmaceuticals in environmental matrix have been reported in literature. Most of reported methods use a time consuming off-line Solid-Phase Extraction but few publications deal with on-line methods for sample preparation [1, 2].

In our work, a multi-residue chromatographic method has been developed and validated for multi-class pharmaceuticals and metabolites in drinking and surface waters. The extraction step has been performed on-line (EUqan system developed by Thermo Fisher Scientific) in two runs (negative and positive electrospray ionisation). Advantages of this method are commonly the short sample preparation time, the productivity and the use of a small sampling volume.

Experimental

Sample preparation:
Filtration pH between 6 and 8
Internal standards: d4-carbamazepine, d4-diclofenac, d4-ketoprofen, d4-sulfamethoxazole

Experimental conditions:
Analytical column: Hypersil Gold C18 (150mm x 2.1 mm, 3µm)
Extraction column: Strata-X (20mm x 2.0mm, 25µm)
Mobile phase A: Acetonitrile
Mobile phase B: Acetonitrile + 0.05% HCOOH
Flow rate: 300µL/min (gradient)
Volume injection: 1mL

Detection:
ESI+ TSQ Vantage (Thermo Fisher Scientific)
SRM mode (2 transitions if available)

ESI-

Results

Impact of pH in on-line extraction step

Chromatograms of bezafibrate (5ng/L), chloramphenicol (10ng/L) and gemfibrozil (5ng/L) in surface water

Chromatograms of 4-chlorobenzoic acid (60 ng/L) in drinking water (ESI+)

Limit of quantification

 Limits of quantification (LOQ) are between 5.0 and 20 ng/L except 2-hydroxyibuprofen (40 ng/L)

Linearity and recovery

Recoveries are between 70 and 110% except ibuprofen (128%) and clarithromycin (40%)

Conclusion

• Development of a reproducible, cost-effective and rapid multi-residue method in aqueous samples (tap, ground and surface waters)
• Reasonable LOQ (ranging from 5 to 40 ng/L) with a volume injection of 1 mL (tests with 2 and 5 mL are provided)

Perspective

• In 2011, a survey is scheduled for one year to determine the impact of pharmaceuticals in Dordogne’s region (France)

References