

Determination of tricyclic antidepressants in water, fish and mussel tissue by liquid chromatography tandem mass spectrometry

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Over the last decades, many pharmaceuticals and personal-care products have been released to the environment but, so far, some of these emerging contaminants have been overlooked. Among them, tricyclic antidepressants (TCAs) are extensively used, and once they enter the aquatic environment, mainly through human excretion, they are distributed in different compartments, such as surface water or biota. Due to the lack of analytical methods available, specially for their determination in biota, the aim of the present work was to develop a method for the accurate and precise determination of four tricyclic antidepressants, including amitriptyline, nortriptyline, imipramine and clomipramine in different environmental matrices, such as water (estuary, seawater and wastewater treatment plant effluent) and biota (fish homogenate, fish liver and mussels) in order to be applied in further studies dealing with their environmental distribution and accumulation patterns.

The analysis step performed by liquid-chromatography tandem mass spectrometry (LC-MS/MS) was fully optimised after the assessment of variables affecting the chromatographic separation (column type and mobile phase), the electrospray ionization (capillary voltage, nebulizer pressure, drying gas temperature and drying gas flow) and mass spectrometric detection (fragmentor voltage and collision energy) of the target analytes. The extraction of solid samples was accomplished using focused ultrasonic solid-liquid extraction, which under optimum conditions required a low amount of sample (0.5 g), solvent (7 mL acetonitrile:H₂O, 95:5 v/v) and short extraction time (30 seconds). Furthermore, different clean-up strategies were optimized and evaluated by means of solid-phase extraction (SPE) using reverse phase sorbent (Plexa) and mix-mode strong cation exchanger (CX). Mixed mode SPE rendered clean extracts and the best results in terms of extraction efficiency and matrix effect. The same SPE mode was also used for the preconcentration of target compounds from environmental water matrices. The use of CX-SPE allowed the minimisation of matrix effect, which was negligible also in the detection step regardless of the evaluated matrix. Under optimised conditions, the method was validated for each matrix in terms of recovery with external calibration as quantification approach, and using isotopically labeled compounds as surrogates. Apparent recovery values were in the 74-118 % range, regardless of the matrix, and method detection limits (MDLs) were in ng/g level for biota and low ng/L level for water samples, what meets the reported environmental concentration levels. Finally the developed method was applied to the analysis of real samples from the Biscay Coast.

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