**Multiresidue analysis of a wide variety of organic pollutants in aqueous samples based on polyethersulfone microextraction and solid-phase extraction coupled to liquid chromatography-tandem mass spectrometry analysis**

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The determination of polar organic contaminants in the aqueous media is currently a topic of increasing interest. Compounds such as pharmaceuticals and personal care products can be included in this group. In general, these compounds are not bioaccumulative but highly water soluble, thus, many of them are widely distributed in aqueous environments, as a consequence of human activities and the continuous discharge, e.g. through industrial and municipal wastewater (Lapwoth 2012). Despite the widely use of target or selective methods to screen particular classes of organic microcontaminants, the development of novel and sensitive multiresidue methodologies for water analysis is crucial in order to screen as many compounds as possible in only one run. Such multiresidue approaches are indeed more affordable from the economic and environmental point of view, particularly if they are combined to microextraction techniques.

In this work we have developed a new procedure for the simultaneous determination of multi-class priority and emerging organic pollutants in wastewater and estuary samples using polyethersulfone (PES) polymeric material followed by liquid chromatography-tandem mass spectrometry (LC-MS/MS) analysis**.** The list of target compoundsincludes hormones, phytoestrogens, personal care products and pharmaceuticals, corrosion inhibitors, artificial sweeteners, herbicides, and life-style products.

During method optimization, different variables affecting the chromatographic separation (column type, temperature and flow rate), 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 were studied. The method uses simultaneous positive and negative electrospray ionisation (ESI) for analysis of all compounds in one injection. In the case of PES protocol optimisation ion strength of the water sample (0-30 % NaCl), pH (2, 5 and 8) and the amount of the polymeric material (from 1 to 9 mg of PES) were thoroughly investigated. The performance of the new PES microextraction LC–MS/MS protocol was compared to a standard solid-phase extraction (SPE) procedure using Oasis HLB 200 mg cartridges. Regarding SPE evaluation, the effectiveness of different SPE cartridges (Oasis HLB, Oasis MCX, Envi-Carb and Lichrolut-ENV), sorbent amount (200 mg and 400 mg) and elution profiles using different organic solvents (methanol, acetone and a mixture of them) were studied loading 500 mL of estuary and wastewater samples. Matrix effect was evaluated for both matrices in the extraction and detection steps. Both procedures were validated in terms of recovery (external calibration using isotopically labeled analogues as surrogates, procedural calibration and matrix-matched calibration approaches were tested), method detection limits (MDLs) and precision (as relative standard deviations, RSDs). Finally, the developed methods were applied to the determination of the target analytes in various samples, including wastewater and estuary aqueous real samples from the Basque Country, Spain.