Toxicity of coastal waters: use of a quick algal bioassay

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Optimization of the SPE step in the analysis of β-blockers and β-agonist-receptors in natural water samples by SPE-GE technique

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Environmental samples, especially sewage and marine-water samples are complex and often contain interfering elements that can mask or interfere with the analysed pharmaceuticals. One of the most suitable techniques for the extraction of SPE (SPE) is the most common sample preparation technique used in environmental areas. Choice of sorbent is a crucial point in SPE because it can control such parameters as selectivity, capacity and matrix effects. This choice depends strongly not only on the target analytes and the interactions of the chosen sorbent through the functional groups of the analytes, but also on the kind of sample matrix and its interactions with both the sorbent and the analytes. This work describes the application of different kinds of SPE sorbents: C18 bonded silica gel (Stratas C18), copolymers (Oasis HLB, Strata X, and Lichelut EN), functionalized copolymers (Isolute ENV+), mixed-mode ion-exchange sorbent (Strata Screen C) for extraction of six β-blockers (acebutolol, atenolol, metoprolol, nadolol, propranolol, pindolol), and two β-agonists (terbutaline, salbutamol) from natural water samples. Parameters such as pH of the loading solutions, the amount and the kind of solvents used in conditioning, washing and eluting steps, were selected and optimized. The obtained extracts were evaporated to dryness, subjected to silylation using BSTFA, and finally analysed by GC-FID technique. The recovery of the analytes form natural water samples in the mentioned above SPE conditions will be discussed.

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Mustard fractionation based on normal phase SPE and reverse phase HPLC (RP-HPLC) for isolation of endocrine disrupting chemicals in environmental extracts

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Directed Extraction (EDA) approach aims to identify adverse pollutants by reducing the complexity of environmental matrices. Single hyperfractionation combined to biosay is powerful to link toxic effects of chemicals to those "classical" pollutants. However, although the emergence of promising chemical tools (e.g. Orbitrap), identification of unknown active chemicals is still time and cost consuming due to the complexity of each active fraction (e.g. mixture effect). Hence, further fractionation steps are often needed. The aim of this study was to develop and to test the use of a first pre-fractionation step on SPE that will be followed by a RP-HPLC fractionation. First the separation of 12 EDCs have been evaluated with several elution conditions. Silicon carbides with 4 step elution - heptane, heptane/dichloromethane (50/50, v/v), ethyl-acetate and methanol/water (50/50, v/v) - allowing the best and reproducible isolation of chemicals, have been chosen for further investigations. For these conditions, recoveries were assessed for the mixture and alone for a blank sample extract spiked with this mixture. Finally, a natural sediment known to exert estrogenic, PXR and AhR activities, was fractionated into fractions. Good mixture recoveries (74-110 %), were obtained. The fractionation F1 contained only the PCBs and the PAHs, while 4-tert-octylphenol, triphenyl phosphate and fenobrate were detected only in F2. Finally, steroids, bisphenol A and clotrimazole were found in F3 while F4 contained more polar chemicals. Fractionation on natural sediment allows isolation of TCDD-like activity in F1 and F2 while PAH like activity was detected in F1, F2 and F3. Then estrogenic compounds were only detected in F2 and F3. Interestingly, the sum of the estrogenic activity found in these 2 fractions is higher than the activity found in the crude extract, which minimizes the occurrence of anti-estrogenic chemicals. Finally, PXR-like activity was mainly detected in F3. This pre-fractionation protocol allows, in the present case study, the isolation of several biological activities. Based on this first isolation directed hyperfractionation has then been undertaken, RP-HPLC (reverse phase HPLC) fractionation (EGC, C18 and a three-function sorbent (Strata Screen C)) and a three-fraction sorbent (Strata Screen C) for extraction of six β-blockers (acebutolol, atenolol, metoprolol, nadolol, propranolol, pindolol), and two β-agonists (terbutaline, salbutamol) from natural water samples. Parameters such as pH of the loading solutions, the amount and the kind of solvents used in conditioning, washing and eluting steps, were selected and optimized. The obtained extracts were evaporated to dryness, subjected to silylation using BSTFA, and finally analysed by GC-FID technique. The recovery of the analytes form natural water samples in the mentioned above SPE conditions will be discussed.