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-endorphin in natural water samples by SPE-GE technique

MF Cabanu, A Michalik, M Ciewarzek, N Mgwoswa, M Kwiatkowski, P Stepnowski, J Kimiska

University of Gdańsk, GDANSK, Poland

Environmental samples, especially sewage and marine-water samples are complex and often contain interfering elements that can mask or interfere with the analysed pharmaceuticals. The choice of sorbent is crucial in SPE because it can control such parameters as selectivity, affinity, and capacity. 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. The work describes the application of different kinds of SPE sorbents: C18 bonded silica gel (Strata C18), copolymers (Osiris HLB, Strata X, and Lichisorb ENH), functionalised copolymers (Isolute ENV+), mixed-modifier bonded silica gel (Phenyl MCX C8) and a functional sorbent (SPE Screen C8) for extraction of six β-blockers (atenolol, atenolol-mod, metoprolol, nadolol, propranolol, pindolol), and two β-endorphin (terbutaline, salbutamol) from natural water samples. Parameters such as pH of the loading samples, 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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TU 082

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

N Crescut1, JM Porcher1, H Budzinski2, S Aït-Aïssa1

INERIS, VERNEUIL EN HALATTE, France

ISMP, LPTC, TALENCE, France

Directed Extraction (EDA) approach aims to identify adverse pollutants by reducing the complexity of environmental matrices. Single hyperfractionation combined to biosays is useful to link direct adverse chemicals and to direct chemical analyses to these “classical” pollutants. However, although the emergence of promising chemical tools (e.g. Orbi-trap), 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. Silica cartridges with 4 step elution - heptane, heptane/dichloromethane (50/50, v/v), ethyl-acetate and methanol/water (50/50, v/v) - backflushed had been chosen for further investigations. For these conditions, recoveries were assessed for the mixture along and for a blank sample extract spiked with this mixture. Finally, a natural sediment known to exert estrogenic, PXR-like and AhR-like activity was subjected to these conditions. Good mixture recoveries (74-110 %), were obtained. The fractionation F1 contained only the PCBs and the PAHs, while 4-tetra-octylphenol, triphenyl phosphate and fenofibrate 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 that of the crude extract, which may indicate 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 undergone, RP-HPLC hyperfractionation of blastic MCX and a three-function sorbent (EPS Screen C8) for extraction of six β-blockers [atenolol, atenolol-mod, metoprolol, nadolol, propranolol, pindolol] and two β-endorphin (terbutaline, salbutamol) from natural water samples. Parameters such as pH of the loading samples, 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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Towards a common mass spectra database for the identification of unknown environmental samples

Z Schülke1, I Schymanski1, S Neumann3, C Hug2, C Gallampoli3, M Krause1, J Słobodnik1, W Brack2

1UFZ Helmholtz Centre for Environmental Research, LEIPZIG, Germany
2Leibniz Institute for Plant Biochemistry, HALLE, Germany
3Ludwig University-Centre for Experimental Medicine, LINKÖPING, Sweden

“Environmental Institute, KOŠ, Slovak Republic

The identification of unknown compounds in environmental samples isolated during non-targeted screening or effect-directed analysis (EDA) is often a challenge on the way to the successful outcome of such-type studies. The effectiveness of mass spectrometric techniques highly depends on the occurrence of anti-estrogenic chemicals. Finally, PXR-like activity was mainly detected in F3.

the highest endocellular concentration (30.8 µg/L) of [d-Asp3] microcystin-RR was measured in a Planktothrix rubescens algal bloom in 2009 sample. In the same sample the extracellular concentration was never above the WHO limits for drinking waters (1 µg/L).