Passive samplers, as surrogates for biological monitoring, to measure emerging (micro)pollutants in the marine environment

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Introduction

- **Focus:** endocrine disrupting compounds (EDCs) in the marine environment
- **Origin:** industrial, rural and domestic activities
- **Effects:** accumulation and chronic toxicity to aquatic organisms
  - accumulation in the ecosystem
  - loss of habitats and biodiversity

Objectives

- **Challenges:** a broad range of EDCs (18 estrogens, 30 endoergans, 13 gestagens and 8 corticosteroids)
  - ultra-trace contaminant levels (sub ng L⁻¹ to ng L⁻¹)
  - seawater matrix
- **Goals:**
  - developing an analytical U(H)PLC-HRMS/MS method for EDCs
  - developing and optimising a suitable multi-residue extraction method

Materials & methods

Instrumentation

- **U(H)PLC:**
  - Solvents: 0.1% FA in MeOH:H2O:1% FA H2O
  - Pumping system: Gradient elution
  - Column: Hypersil ODS (1.9µm, 100 mm, 2.1 mm)
  - Acute online sampler: 10 µL injection
- **HRMS/MS:**
  - Q-Exactive Benchtop™
  - FAB source, 50-200 Da, 1400 V FABH
  - APCI ionization: Positive and negative mode

Fig. 1. U(H)PLC-HRMS/MS Q-Exactive™ Benchtop.

Pretreatment and extraction

- **Grab samples**
- **Filtration & pH adjustment**
- **Loading & washing**
- **Elution**
- **Evaporate** (Turbosvap)
- **Centrifuging**

Fig. 2. Pretreatment and extraction steps that were optimised.

Results

**U(H)PLC**

- Run time: 12 min
- Flow rate: 0.45 mL min⁻¹
- Column temperature: 45°C
- Best chromatographic separation obtained as depicted in Fig. 3.

Fig. 3. Chromatogram showing androgen separation.

**HRMS/MS**

- Screening mass spectrometric variables by L27 design, depicted in Fig. 4.
- Optimising by D-optimal design (Table 1)

Table 1. The optimised mass spectrometric parameters obtained by a D-optimal design.

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<tbody>
<tr>
<td>Auxiliary gas: 10 a.u.</td>
<td>Vaporizer T: 250°C</td>
<td>Capillary T: 250°C</td>
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<td>S-lens RF: 70</td>
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Fig. 4. Screening of the variables.

**Extraction optimization**

**Screening**

Matrix-matched calibration lines

- 17β-estradiol: \( R^2 = 0.9959 \)
- Metylene testosterone: \( R^2 = 0.9977 \)
- Stanazolol: \( R^2 = 0.9981 \)

Fig. 5. Screening of the extraction variables.

Fig. 6. Surface response modelling of the significant variables: acidification elements and loading volume.

Fig. 7. Matrix-matched calibration lines performed in spiked seawater.

Conclusion & future perspectives

- 55 EDCs were successfully extracted and analysed in seawater
- Method will be validated according to the European guidelines (CD 2002/657/EC)
- Method will be applied for different grab samples from the sea

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