



Matrix effect during the membrane-assisted solvent extraction coupled to liquid chromatography tandem mass spectrometry for the determination of a variety of endocrine disrupting compounds in wastewater



A. Iparraguirre^{a,*}, P. Navarro^a, R. Rodil^b, A. Prieto^a, M. Olivares^a,
N. Etxebarria^a, O. Zuloaga^a

^a Department of Analytical Chemistry, Faculty of Science and Technology, University of the Basque Country (UPV/EHU), P.K. 644, 48080 Bilbao, Spain

^b Department of Analytical Chemistry, University of Santiago de Compostela, Constantino Candieira S/N, 15782 Santiago de Compostela, Spain

ARTICLE INFO

Article history:

Received 17 March 2014
Received in revised form 14 May 2014
Accepted 13 June 2014
Available online 21 June 2014

Keywords:

Endocrine disrupting compounds
Wastewater
Liquid chromatography–triple quadrupole mass spectrometry
Membrane assisted solvent extraction
Solid phase extraction

ABSTRACT

Membrane-assisted solvent extraction (MASE) coupled to liquid chromatography–triple quadrupole mass spectrometry (LC–MS/MS) was studied for the determination of a variety of emerging and priority compounds in wastewater. Among the target analytes studied certain hormones (estrone (E1), 17 β -estradiol (E2), androsterone (ADT), 17 α -ethynyl estradiol (EE2), diethylstilbestrol (DES), equilin (EQ), testosterone (TT), mestranol (MeEE2), 19-norethisterone (NT), progesterone (PG) and equilenin (EQN)), alkylphenols (APs) (4-*tert*-octylphenol (4tOP), nonylphenol technical mixture (NPs) and 4*n*-octylphenol (4nOP)) and BPA were included. The work was primarily focused in the LC–MS/MS detection step, both in terms of variable optimization and with respect to the matrix effect study. Both, electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) were assessed both in the negative and positive mode, including the optimization of MS/MS operating conditions. The best results were obtained, in most of the cases, for ESI using 0.05% ammonium hydroxide as buffer solution in the mobile phase, composed with methanol and water. Under optimum detection conditions, matrix effect during the detection step was thoroughly studied. Dilution, correction with deuterated analogues and clean-up of the extracts were evaluated for matrix effect correction. Clean-up with Florisil together with correction with deuterated analogues provided the most satisfactory results, with apparent recoveries in the 57–136% range and method detection limits in the low ng L⁻¹ level for most of the analytes. For further validation of the method, two separated extraction procedures, the above mentioned MASE, and conventional solid phase extraction (SPE) were compared during the analysis of real samples and comparable results were successfully obtained for E1, E2, EE2, DES, NT, TT, EQ, PG, BPA, ADT, 4nOP, 4tOP, NPs and EQN.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Endocrine disrupting compounds (EDCs) have become a public health concern in modern times because of their detrimental effects on the human endocrine system [1,2]. Although natural and synthetic EDCs can be degraded biologically, they cannot be completely removed in wastewater treatment plants (WWTPs). In fact, they are often detected in WWTP effluents and discharged into surface

waters. Therefore, an elevated concern over the safety and quality of natural or treated water bodies has been generated and the need for water testing by water utilities and regulatory agencies has increased [3–5].

EDCs include natural estrogens, such as estrone (E1) and 17 β -estradiol (E2), natural androgens, such as testosterone (TT), and androsterone (ADT), artificial synthetic estrogens or androgens such as 17 α -ethynylestradiol (EE2), as well as other industrial compounds such as bisphenol A (BPA) and alkylphenols (APs).

In order to evaluate the removal efficiency of specific estrogenic compounds from water samples, and due to the low concentrations present in real samples, there is a huge need for the development of

* Corresponding author. Tel.: +34 94 601 55 51; fax: +34 94 601 35 00.
E-mail address: arantza.iparraguirre@gmail.com (A. Iparraguirre).

cost-effective and user-friendly multiresidue strategies, as well as highly sensitive and selective methods, for a wide range of emerging pollutants such as EDCs in water samples. The existence of complex interfering components in the aquatic and biological sample matrices requires the development of effective strategies in order to avoid matrix effect.

Nowadays, analytical methods based on liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) offer a tool to identify and quantify compounds of medium to high polarity in different water bodies and in solid matrices [6–9]. However, a serious drawback of LC-MS/MS methods is its susceptibility to matrix effects, i.e. the signal suppression or enhancement by matrix compounds entering the ion source at the same time than the target analytes [10]. It has been reported that atmospheric pressure chemical ionization (APCI) is generally less sensitive to matrix effects than the more commonly used electrospray ionization (ESI). Although LC-MS/MS has been proved to be a more versatile technique applicable to a full range of contaminants, GC-MS is still a more readily available technique in many laboratories. However, when GC-MS is performed, the analysis of underivatized polar compounds is restricted, being necessary a previous derivatization step.

In the last years, microextraction techniques have become popular as sample preparation techniques for water analysis due to the small amounts of solvent (μL range) and sample (mL range) required. Concerning preconcentration and clean-up strategies, the application of sorptive techniques and the use of membranes are becoming promising solvent free methods. Two types of techniques can be distinguished between membrane based liquid-liquid extraction depending on the characteristics of the membrane: (i) supported liquid membrane (SLM) and microporous membrane liquid-liquid extraction (MMLLE), which use porous membranes, and (ii) membrane assisted solvent extraction (MASE) that uses non-porous membranes [11].

MASE is carried out using a non-porous membrane as interface between the sample (donor phase) and the organic solvent (acceptor phase). The organic analytes in the aqueous phase are dissolved in the membrane material and diffuse through the polymer into the acceptor phase [12]. The membrane is not only considered as a barrier for particles and macromolecules, but it can also provide selectivity in terms of permeation and transport through the membrane by choosing appropriate membrane material and organic acceptor phase [13,14]. Thanks to the use of non-porous membranes, miscible and non-miscible water solvents can also be used. Although MASE can be coupled to both LC and GC, due to the common use of non polar solvents as acceptor phases, MASE has been typically combined with GC [15–17]. However, MASE has also been successfully applied to the analysis of moderately polar compounds in combination with LC-MS/MS [18–20].

The aim of the present work was the analysis of certain hormones (E1, E2, ADT, TT, EQ, DES, EE2, MeEE2, NT, PG and EQN), APs and BPA, which are included as priority or emerging pollutants in the European Water Framework Directive (WFD 2000/60/EC). With this purpose, previously optimized MASE extraction [21] was coupled to LC-MS/MS, including some hormones (NT, TT and PG), which had not been studied in the previous work. Different alternatives were studied in order to avoid or minimize matrix effect during the detection in LC-MS/MS, including sample dilution, the use of deuterated analogues and clean-up of sample extract. Developed MASE-LC-MS/MS method was applied to samples from two local WWTPs of Biscay (north of Spain). The results were compared with classical SPE and both extraction techniques followed by LC-MS/MS were applied to samples from two local WWTPs of Biscay (north of Spain).

2. Experimental

2.1. Reagents and material

The solid reagents 4*n*-octylphenol (4*n*OP, 99%), BPA (99+ %), DES (99.9%), ADT (98.2%), EQ (97.6%), TT (99.9%), NT (99.5%), PG (99.6%), 17 β -estradiol- d_3 ($[\text{H}_3]$ -E2, 98%), nonylphenol- d_4 ($[\text{H}_4]$ -NP, 97%), progesterone- d_9 ($[\text{H}_9]$ -PG, 98%) and equilin- d_4 ($[\text{H}_4]$ -EQ, 98%) were purchased from Sigma Aldrich (Steinheim, Germany), while nonylphenol technical mixture (NPs, 94%), E1 (99.5%), MeEE2 (99.4%), EE2 (99.4%) and E2 (99.7%) were obtained from Riedel-de HaënSeelze (Steinheim, Germany). 4-*Tert*-octylphenol (4*t*OP, 99.4%) and bisphenol A- d_{16} ($[\text{H}_{16}]$ -BPA) were obtained from Supelco. In the case of EQN individual solution at $100 \mu\text{g mL}^{-1}$ in ACN was also purchased from Sigma Aldrich. Individual stock solutions for each target compound, as well as the deuterated analogues, were dissolved to prepare 5000 mg L^{-1} solutions in anhydrous methanol (99.9%, Alfa-Aesar, Karlsruhe, Germany). All the standards and stock solutions were stored at -20°C .

Sodium chloride (NaCl, Merck, Darmstadt, Germany) and HPLC-grade methanol (MeOH) (LabScan, Dublin, Ireland) were used for matrix modification experiments. NaCl was ultrasonically cleaned with methylene chloride (DCM) (HPLC grade, LabScan) and dried at 150°C before use. Ethyl acetate (EtOAc) and isooctane, both HPLC grade, were also purchased from LabScan.

Ultra-pure water was obtained using a Milli-Q water purification system ($<0.05 \mu\text{S/cm}$, Milli-Q model 185, Millipore, Bedford, MA, USA). Acetonitrile (ACN) (Romil-UpS, Waterbeach, Cambridge, UK) and MeOH (Romil-UpS) were used as organic modifiers or mobile phase eluents. Acetic acid (HOAc, Merck), hydrochloric acid (HCl, 36%, Merck), ammonia (25% as NH_4OH , Panreac, Reixac, Barcelona, Spain) and ammonium acetate (NH_4OAc , Sigma Aldrich, Steinheim, Germany) were used for mobile phase modifications.

$125 \mu\text{m}$ (125 mm diameter), $11 \mu\text{m}$ (70 mm diameter) and $0.45 \mu\text{m}$ (90 mm diameter) cellulose filters were purchased from Whatman (Maidstone, UK). Extracts were filtered before analysis with acrodisc syringe (13 mm diameter, $0.2 \mu\text{m}$ pore size) filters (GHP, PTFE, Nylon, PVDF, PES, HT Tuffryn or polysulfone) obtained from Pall Life Sciences (USA).

Home-made low density polyethylene (LDPE) membranes (40 mm length, 6 mm i.d. and 0.02 mm thickness) were cleaned in chloroform (HPLC-grade, Labscan) overnight and kept in clean chloroform until use.

200 mg Bond Elut Plexa cartridges were purchased from Agilent Technologies (USA) and 1 g Florisil cartridges from Supelco (Walton-on-Thames, UK). The SPE step was performed with a Visiprep SPE manifold from Supelco.

2.2. Sampling

Samples were collected at the WWTPs located in Galindo and Gernika (Basque Country, north of Spain).

Samples were collected in pre-washed amber bottles and carried to the laboratory in cooled boxes. Samples were filtered through $0.45 \mu\text{m}$ cellulose filters (influent samples were prefiltered with $125 \mu\text{m}$ and $11 \mu\text{m}$ cellulose filters) and kept in the fridge at 4°C before analysis, which was performed within 48 h.

2.3. Membrane-assisted solvent extraction methodology

The optimization of MASE extraction step for the target analytes is fully described elsewhere [21]. Briefly, 130-mL aliquot of the filtered sample together with 26 g of NaCl was introduced in a 150-mL headspace-vial and membranes were attached to a metal funnel and fixed with Teflon rings (Gerstel, Mülheim an der Ruhr,

Download English Version:

<https://daneshyari.com/en/article/7612917>

Download Persian Version:

<https://daneshyari.com/article/7612917>

[Daneshyari.com](https://daneshyari.com)