Journal of Chromatography A, 1283 (2013) 53–61

Contents lists available at SciVerse ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Fully-automated on-line solid phase extraction coupled to high-performance liquid chromatography–tandem mass spectrometric analysis at sub-ng/L levels of selected estrogens in surface water and wastewater

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ARTICLE INFO

Article history:
Received 29 October 2012
Received in revised form 8 January 2013
Accepted 22 January 2013
Available online 28 January 2013

Keywords:
On-line SPE
HPLC–MS/MS
Estrogens
Surface water
Wastewater

ABSTRACT

A fully-automated on-line solid phase extraction liquid chromatographic/electrospray ionization tandem mass spectrometric method for the analysis of estrone (E1), 17-β-estradiol (β-E2), 17-α-ethinylestradiol (EE2), 17-α-estradiol (α-E2) and estriol (E3) in surface water and wastewater was developed. The method showed a very good linearity from 250 ng/L down to compound specific quantification limits, which were included between 0.25 and 2.00 ng/L. These limits were obtained with 2.5 mL aliquots of injected sample and the total analysis time per sample was slightly less than 10 min. Under these conditions, detection limits were 0.15 ng/L for E1, 0.31 ng/L for β-E2, 0.52 ng/L for EE2, 0.59 ng/L for α-E2 and 0.95 ng/L for E3. The method reliability was tested on different kinds of real samples spiked with the estrogens, obtaining recoveries approximately included between 71 and 95%. The application to samples collected in rivers, lakes and wastewater treatment plants evidenced the presence of the investigated compounds at sub-ng/L or low ng/L concentration levels.

1. Introduction

Endocrine disrupting chemicals (EDCs) are exogenous substances that cause adverse health effects in an intact organism, or its progeny in relation to reproduction and sexual character development [1]. A wide range of organic compounds, such as some pesticides, polycyclic aromatic hydrocarbons, steroid estrogens, bisphenols, nonylphenols and phthalates, are suspected of having these adverse effects [1].

Within the various substances with reported endocrine-disrupting properties, the steroidal-estrogenic hormones and the synthetic steroids are considered to be the most potent estrogenic compounds [2]. Steroidal estrogens, such as 17-α-estradiol, 17-β-estradiol, estrone and estriol are naturally present in females and to a much lesser extent in males [3]. Estradiol and the synthetic estrogen 17-α-ethinylestradiol are active ingredients in a number of drugs widely used as contraceptives, in physiological hormonal replacement therapies, treatment of prostate and breast cancer [2], and hair lotions for contrasting alopecia [4]. Estrogens are therefore constantly excreted by humans and animals and are not removed completely in wastewater treatment plants, being finally discharged into surface water where they have been found at concentrations ranging from sub-ng/L levels to tens of ng/L [7–11]. These apparently low concentrations are actually of concern in environmental terms, since it has been demonstrated that estrogens exert a significant endocrine-disrupting activity and are capable of inducing an estrogenic response in fish at concentration levels as low as 0.1–1.0 ng/L [5,6].

Some analytical methods have been developed in the last ten years for analysing estrogens in freshwater and wastewater at these concentration levels, most of them based on solid-phase extraction (SPE) and high-performance liquid chromatographic/tandem mass spectrometric determination (HPLC–MS/MS) [8,10,12–18]. SPE is usually conducted on 250–1000 mL of sample volume, which entails a time-consuming extraction procedure. In addition, some experimental approaches involving a derivatization step of estrogens are sometimes adopted; in this case an additional clean-up procedure is necessary, thus increasing the total analysis time. Vuillet et al. [12] using a sample volume of 1000 mL and a C-18 cartridge, achieved limits of detection (LODs) of the method in the range of 0.01–0.20 ng/L without any derivatization procedure. Similar LODs (0.038–0.110 ng/L) were achieved by Matejicek and Kuban [13] with a very complex method involving a SPE step with a styrene-N-vinylpyrrolidone co-polymer cartridge, followed by a clean-up with a Florisil-based sorbent and a derivatization procedure with a specifically synthesized reagent. A procedure as complex as the

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http://dx.doi.org/10.1016/j.chroma.2013.01.084