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ORIGINAL ARTICLE

HPLC-MS/MS multiclass determination of steroid hormones in environmental waters after preconcentration on the carbonaceous sorbent HA-C@silica

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Abstract In this study, a sensitive and multiclass method has been developed for analysis of three families of steroid hormones, i.e. progestins, oestrogens, androgens, by SPE-HPLC-ESI-MS/MS. The extraction efficiency of thermally condensed humic acids onto silica sorbent (HA-C@silica), here for the first time studied for multiclass enrichment of these sex hormones, was tested in different environmental waters (tap and river water, urban wastewater treatment plant effluent) spiked at the nanograms per litre levels (5–1000 ng L^{-1}). Quantitative adsorption was achieved using 200 mg sorbent for preconcentration of 250–1000 mL sample, at the native pH (pH = 6.5–7.7). Elution was performed by two sequential fractions (methanol followed by acetonitrile), obtaining in all the matrices investigated satisfactory recoveries (71% to 124% for river waters and 71–113% for urban wastewater treatment plant effluent) and RSDs below 15% (n = 3). The high enrichment factors (up to 4000) coupled with high-performance liquid chromatography tandem mass spectrometry quantification (MRM mode) provided low limits of detection and quantification (a few ng L^{-1}), that are suitable for environmental monitoring. Most of the analytes were detected in river water and in wastewater effluent samples (in the ng L^{-1} concentration range), attesting their environmental diffusion. The proposed method was extended to a fourth class, Glucocorticoids, achieving good results in river samples, by the same SPE cartridge and chromatographic run.

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1. Introduction

Steroid hormones are active compounds involved in almost all vital physiological functions of the body, such as development of sexual characteristics, salt and water balance and

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metabolism, but also widely employed in medical treatments (Guedes-Alonso et al., 2016). Based on structural differences and affinities, steroid hormones can be divided into four subclasses: oestrogens, androgens, progestogens, corticosteroids (Herrera-Melián et al., 2018). Androgens, the most abundant hormones found in urban wastewater treatment plants (UWWTPs), are used in therapy and growth therapy (Guedes-Alonso et al., 2016; Huysman et al., 2017; Chang et al., 2011); oestrogens and progestins are widely consumed as oral and non-oral contraceptives and in hormone replacement therapy (Guedes-Alonso et al., 2016; Huysman et al., 2017; Chang et al., 2011; Barreiros et al., 2016; Czarny et al., 2017); corticosteroids are used in human medicine for a series of pathologies such as rheumatism, malignant tumours, skin diseases (Huysman et al., 2017; Speltini et al., 2018). Considering steroid hormones' global extensive usage, their chemical properties, including high octanol–water partition coefficients, low water solubility (Barreiros et al., 2016; Czarny et al., 2017; Snow et al., 2013), and partial removal in UWWTPs (Guedes-Alonso et al., 2016; Iparraguirre et al., 2014; Zou et al., 2014), they are frequently detected in effluents, surface waters and tap water at ng L^{-1} levels (Chang et al., 2011; Snow et al., 2013; Zou et al., 2014; Vega-Morales et al., 2010; Rui Zhang et al., 2014). Even at these concentrations, they could act as Endocrine Disrupting Compounds (ECDs), causing adverse effects on human health, wildlife and fisheries by interaction with the endocrine system (Vega-Morales et al., 2010; Chang et al., 2011; Barreiros et al., 2016; Czarny et al., 2017; Pailler et al., 2009; Moreira et al., 2011; Kanso et al., 2013; Wang et al., 2016; Ma et al., 2016; Cavaliere et al., 2016). Laboratory and field studies have shown that oestrogenic exposure can cause reproductive disorders that ultimately could lead to reduction of the fertility and even collapse of wild fish populations (Herrera-Melián et al., 2018; Chang et al., 2011; Snow et al., 2013; Kolodziej et al., 2003; Meijide et al., 2016). Hence, the presence of EDCs in surface waters represents nowadays a topic of high concern for national and international organizations and regulatory agencies committed to public and environmental health. The European directives recommend the monitoring of 45 priority substances and propose a first watch list of substances that may pose a significant risk to or via the aquatic environment (Czarny et al., 2017; Jauković et al., 2017; Sousa et al., 2018). This list includes three oestrogens: estrone (E1), 17β-estradiol (E2) and 17α- ethinylestradiol (EE2) (Huysman et al., 2017; Czarny et al., 2017; Jauković et al., 2017; Decision 495/2015), also cited as contaminants that may require future regulations in Contaminant Candidate List of Environmental Protection Agency (Jauković et al., 2017; United States, 2016). It is evident that the development of fast, reliable and sensitive analytical methods for the determination of steroid hormones in environmental waters is a priority task for the assessment of the concentration levels of these compounds and their related ecological risk. The current analytical methods for determination of steroids essentially rely on liquid chromatography coupled with mass spectrometry which provides a rapid and accurate detection with very low method detection limits (Sousa et al., 2018). The low concentration levels of steroid hormones in surface water and WWTPs, together with the complexity of environmental matrices in which these compounds are dispersed, require a preconcentration step, mainly performed by solid-phase extraction (SPE) using reversed-phase or mixed-mode polymer-based sorbents (Chang et al., 2011; Vega-Morales et al., 2010; Pailler et al., 2009; Jauković et al., 2017; Wang et al., 2016; Ma et al., 2016; Cavaliere et al., 2016; Kolodziej et al., 2003; Kumar et al., 2009; Chang et al., 2009; Zhang and Fent, 2018; Tölgyesi et al., 2010; Kuster et al., 2009). Most methods focused on a single class of hormones, especially oestrogens in view of their evident behaviour as ECDs (Kumar et al., 2009; Alda and Barceló, 2001; LaFleur and Schug, 2011), and only few methods proposed a multiclass analysis (Huysman et al., 2017; Shimko et al., 2019; Chang et al., 2009; Zhang and Fent, 2018; Tölgyesi et al., 2010).

Based on the present state of the art, aim of this work is to develop a sensitive method for simultaneous extraction and determination of steroid hormones in river water and UWWTPs effluent by SPE using a home-made sorbent based on thermally condensed humic acids (HAs) onto micrometric silica (HA-C@silica), followed by high performance liquid chromatography tandem mass spectrometry with electrospray ionization (HPLC-ESI-MS/MS). The characteristics of HA-C@silica as a mixed-mode carbonaceous sorbent, which guaranteed successful results for preconcentration of glucocorticoids (GCs) from environmental waters (Speltini et al., 2018), prompted us to extend the application of this SPE sorbent to environmental determination of other classes of steroid hormones that can be frequently present in the same sample.

In detail, HA-C@silica was tested for multiclass preconcentration of seven sex hormones belonging to three different classes (Fig. 1) - *viz*. E1, E2, EE2, Testosterone (TST), Progesterone (PROG), 17α-hydroxyprogesterone (H-PROG), medroxyprogesterone acetate (M-PROG) – from tap and river waters, and UWWTP effluents, before and after spiking. After SPE, quantitation was done by HPLC-ESI-MS/MS. The overall performance obtained in terms of recovery, precision, enrichment factor (EF), linearity, matrix effect and sensitivity was discussed. Finally, the analytical procedure has been extended to GCs and it was applied to the environmental monitoring in actual water samples to gain more knowledge on the contamination of natural waters.

2. Experimental

2.1. Chemicals and materials

All chemicals were reagent grade or higher in quality. Silica microparticles (40–63 μm, surface area 550 m^2 g^{-1}, pore volume 0.8 cm^3 g^{-1}), humic acids sodium salt (technical grade), formic acid (FA), ammonium hydroxide solution (NH_4OH), ammonium fluoride (NH_4F), polypropylene tubes and polyethylene frits, high purity steroid hormones standards (E1, E2, EE2, TST, PROG, M-PROG, cortisone (CORT), hydrocortisone (H-CORT), prednisone (PRED), prednisolone (PREDLO), betamethasone (BETA), dexamethasone (DEXA) were supplied by Sigma-Aldrich (Milan, Italy). Analytical grade H-PROG standard was purchased from Steroids (Cologno Monzese, Italy). Analytical grade triamcinolone (TRIAM) and fluocinolone (FLUO) standards were purchased from Farmabios (Groppello Cairoli, Italy). HPLC gradient grade methanol (MeOH), acetonitrile (ACN) and ultrapure water were supplied by VWR (Milan, Italy).

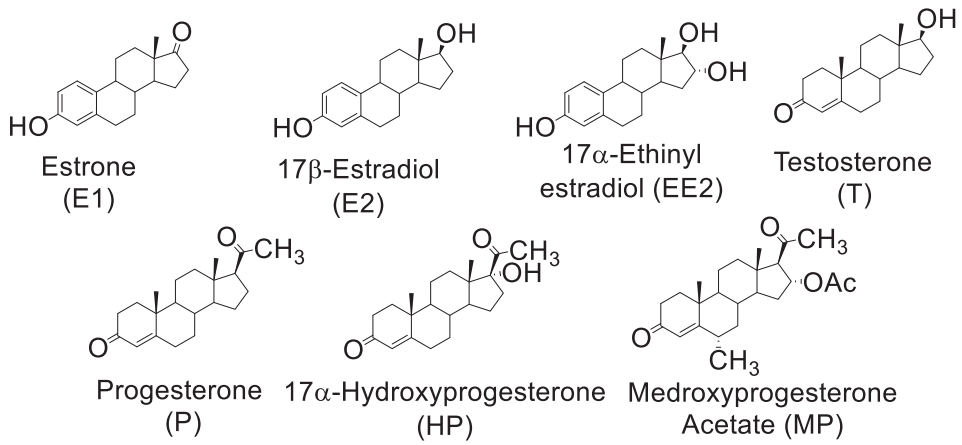

Fig. 1 The seven sex hormones studied in this paper.

Stock solutions of 1000 μg mL^{-1} of each steroid hormone were prepared in MeOH and stored in the dark (4 °C). Steroid hormones working solutions of 0.15–1 μg mL^{-1} were prepared by dilution from a 10 μg mL^{-1} solution, and they were renewed weekly.

2.2. SPE procedure using HA-C@silica

The SPE procedure was carried out placing in a 3 mL SPE cartridge 200 mg HA-C@silica between two polyethylene frits. HA-C@silica is obtained by a thermal treatment of HAs immobilized onto micrometric silica, as reported in previous work (Speltini et al., 2018). Briefly, HAs (100 mg) were dissolved in 50 mL water in a round-bottom flask, and the suspension obtained by adding 1 g silica was magnetically stirred for 2 min. After water evaporation under vacuum, the resulting brownish material was thermally treated at 600 °C for 1 h under N_2 flow into a cylindrical oven (heating ramp 10 °C min^{-1}, cooling ramp 10 °C min^{-1}).

Water samples (500–1000 mL for river water and 250 mL for UWWTP effluent were loaded onto the SPE cartridge at a flow rate of 5 mL min^{-1}, by a multi-channel peristaltic pump (Gilson, Italy) and then the cartridge was dried under vacuum for 5 min. The analytes were eluted (1 mL min^{-1}) with 4 mL MeOH and 4 mL ACN, sequentially. For sample spiking $\leq$ 25 ng L^{-1}, the extracts were evaporated under N_2 flow and reconstituted with 0.25 mL MeOH, prior HPLC-ESI-MS/MS analysis.

2.3. Water samples

Tap water was from the Pavia municipal waterworks. Northern Italy surface waters were collected in Spring and Summer 2018 at 30–50 cm depth, directly in amber glass bottles, from various rivers (Tanaro, Ticino, Staffora), and at the outlet of Pavia UWWTP. Samples were stored in the dark (4 °C) and analyzed within 24 h of collection to check the absence/presence of the target analytes. Staffora river and UWWTP effluent were selected as blank environmental samples due to the absence of all analytes (< MDLs) as verified from recovery tests and quantification by the standard addition method. The physical-chemical parameters of the water samples are reported in Table S1, Electronic Supplementary Material.

2.4. HPLC-ESI-MS/MS analysis

The target analytes were analysed with a HPLC apparatus Agilent 1260 Infinity coupled with an Agilent 6460C MS spectrometer ESI-MS/MS system (Cernusco sul Naviglio, Italy).

The MS spectrometer was tuned up by direct injection of individual analyte solutions (1 mg L^{-1} in MeOH), and different experimental conditions were investigated to maximize the signal response and increase detection sensitivity. First, the HPLC-ESI-MS/MS conditions proposed in the previous work (Speltini et al., 2018) were applied, but a poor ionization of the target analytes, in particular of oestrogens, was observed. Based on the literature (Shimko et al., 2019; Agilent Application Note), NH_4F was selected as additive for the aqueous phase to increase sensitivity.

The MS operating parameters, optimized by Agilent Mass Hunter Source Optimizer Software (Agilent, USA) were: drying gas (N_2) temperature 350 °C; drying gas flow 12 L min^{-1}; nebulizer 50 psi; sheath gas temperature 400 °C; sheath gas flow 12 L min^{-1}; capillary voltage 4000 V positive, 3000 V negative; nozzle voltage 0 V positive, 1500 V negative; electron multiplier voltage (EMV) 200 V positive, 0 V negative; cell accelerated voltage 4 V positive, 1 V negative.

The quantitative analysis of the target compounds was performed in multiple-reaction monitoring (MRM) mode, using the two most intense transitions of each compound, as reported in Table 1.

The chromatographic separation was achieved on a Zorbax Eclipse Plus C18 column (4.6 × 100 mm, 3.5 μm), maintained at 25 °C (± 0.8 °C), and the injection volume was 5.0 μL. Elution was performed by 1 mM NH_4F in the aqueous mobile phase (A) and ACN (B) according to the following program: 30% B for 0.5 min, linear gradient to 85% B in 12 min, maintenance of 85% B for 5 min, washing step with 100% B for 2.5 min. The initial conditions were re-established by 7-min equilibration time (0.5 mL min^{-1} flow rate, column temperature 25 ± 0.8 °C). A typical MRM chromatogram of a standard solution (150 μg L^{-1}) is reported in Fig. 2.

Table 1 Optimized MRM conditions for the HPLC-HESI-MS/MS analysis of sex hormones.

	Precursor ion* (*m*/*z*)	MRM productions (*m*/*z*)	Dwell time	Fragmentor Energy (V)	Collision energy (V)	Polarity
E1	269	145.1	15	148	44	Negative
		143.1	15	148	60	
E2	271	183.3	100	166	50	Negative
		143.1	100	166	64	
EE2	295	145.1	50	154	44	Negative
		143.1	50	154	68	
PROG	315	109	15	94	24	Positive
		97	15	94	20	
H-PROG	331	109.1	15	118	28	Positive
		97.1	15	118	24	
M-PROG	387	327.4	15	106	8	Positive
		123.1	15	106	24	
TST	289	109	15	76	24	Positive
		97.1	15	76	20	

* $[M-H]^-$ adduct for negative ion and $[M+H]^+$ adduct for positive ion.

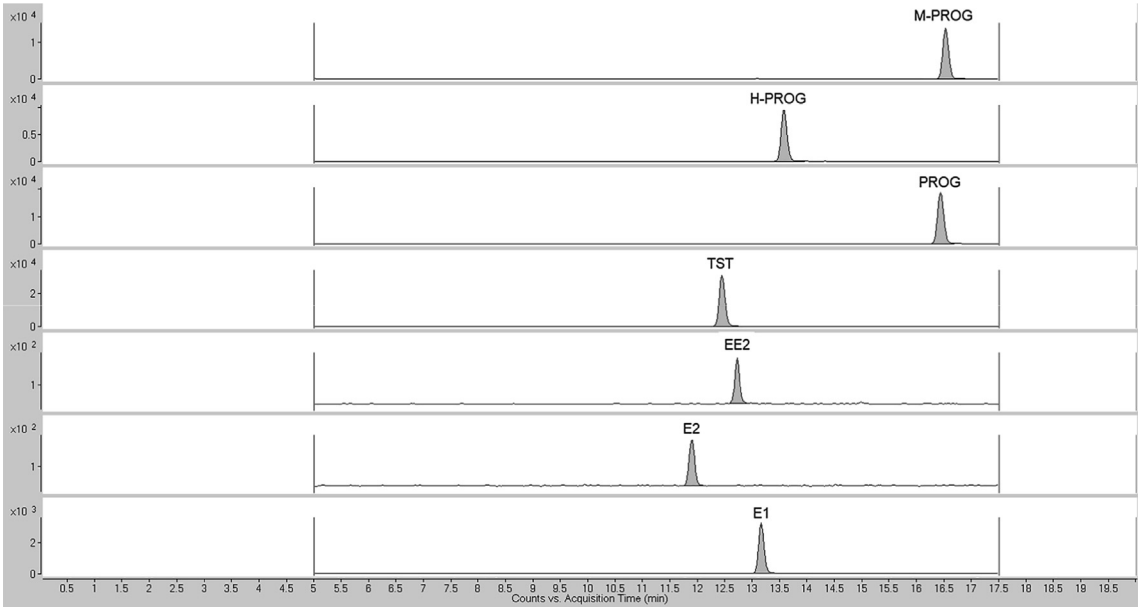

Fig. 2 A typical MRM chromatogram of a standard solution of sex hormones (150 μg L^{-1}).

2.5. Analytical evaluation of the SPE/HPLC-ESI-MS/MS procedure

In term of a consistent application of the proposed procedure to multiclass enrichment of steroid hormones from real-world water samples, the entire analytical procedure was within-laboratory evaluated based on the main figures of merit (Speltini et al., 2018; Rui Zhang et al., 2014; Tölgyesi et al., 2010), *viz*. trueness, precision, linearity, detection and quantification limits.

2.5.1. Trueness and precision

In the absence of certified reference materials, trueness and precision of the method were investigated through recovery tests (Speltini et al., 2018; Dorival-García et al., 2013) performed in tap, river and UWWTP effluent matrices, spiked with each steroid in the range 5–1000 ng L^{-1} for tap and river waters, and in the range 25–1000-ng L^{-1} for UWWTP effluent (n = 3). Within-laboratory precision was evaluated by calculating the relative standard deviation (RSD%).

2.5.2. Calibration curves, linearity and matrix effect

The standard addition method on the SPE eluate was chosen for matrix-matched quantification (Speltini et al., 2018; Speltini et al., 2019), in the linear range 10–150 μg L^{-1}. As previously described (Speltini et al., 2018; Speltini et al., 2019); different -small- volumes of a concentrated standard solution were directly added on each SPE eluate by the HPLC autosampler. This approach matches good precision and compensation of matrix effects that are due to those constituents of the matrix retained on the HA-C@silica and eluted with the analytes causing ion suppression or improvement at the electrospray interface, with consequent errors and inaccurate

results. To evaluate this matrix effect, the responses obtained in pure methanol were compared with those observed in the SPE eluate (Speltini et al., 2018).

2.5.3. Detection and quantification limits

Instrumental detection limits (IDLs) have been calculated from the matrix-matched calibration curves obtained from a blank pre-concentrated matrix (1000 mL river water and 250 mL UWWTP effluent). In detail, for each analyte IDL was calculated as three times the ratio between the baseline noise away from the peak tail and the regression line slope (Sheehan and Yost, 2015); instrumental quantification limits (IQLs) were calculated as 3.3 times IDLs. Estimated MDLs and MQLs were obtained from IDLs and IQLs, respectively, taking into consideration the EFs (Guedes-Alonso et al., 2016; Barreiros et al., 2016; Speltini et al., 2018; Speltini et al., 2019).

3. Results and discussion

3.1. Solid-phase extraction on HA-C@silica

As described in Section 2.2, this work focuses on multiclass enrichment of three classes of steroid hormones, using HA-C@silica, a *mixed-mode* sorbent material recently successfully applied by this research group for preconcentration of GCs (Speltini et al., 2018) and benzotriazoles and benzothiazoles (Speltini et al., 2019) from environmental waters. Due to its peculiar characteristics – *viz*. the presence of sp^2 hybridized carbon and polar groups- HA-C@silica was here tested for the extraction of oestrogens, progestins and androgens. It was investigated firstly in tap water samples (500 mL) enriched with 1 μg L^{-1} of each compound. Based on literature data about the commercial SPE cartridges (Pailler et al., 2009; Moreira et al., 2011; Jauković et al., 2017; Kumar et al., 2009; Kuster et al., 2009; Chen et al., 2012), the extraction was carried out at the sample native pH and under acidic conditions (pH 3). Generally (data shown in Table S2, Supplementary material), the pH influence was not so pronounced considering the RSDs, although higher extraction efficiencies were achieved for all analytes at native pH values. Therefore, the extraction was done with no pH adjustment.

In these preliminary tests, elution was performed with MeOH (4 mL), which provided quantitative recovery for all analytes except for PROG (50%). Hence, further tests were done in the same experimental conditions (500 mL tap water spiked with 1 μg L^{-1} of each hormone) to assess the performance of other eluents: MeOH + 2% v/v NH_4OH (alkaline solvent), MeOH + 0.2% v/v FA (acidic solvent) and ACN (aprotic solvent). Alkaline and acidic MeOH did not lead to improvements in the elution of PROG, while the aprotic solvent provided quantitative recovery for this compound, which indeed does not present —OH groups in the skeleton. On the other hand, ACN provided lower recovery than ones obtained with MeOH for the other compounds, as reported in Table S3, Supplementary material. By these evidences, it seemed clear that the SPE procedure has to be performed with elution in two sequential steps, using 4 mL MeOH followed by 4 mL ACN.

HA-C@silica was then tested first in a river water sample not containing the analytes (blank sample from Staffora river) and on the same sample after spiking (500 mL enriched at 25–600 ng L^{-1}) to verify the recovery. As it is shown in Table 2, good performance was obtained at the different concentrations, with recovery slightly lower for PROG. The highest EF (4000) was achieved by preconcentrating 1 L of river water enriched with 5 ng L^{-1}, obtaining satisfying recoveries also at the lowest concentration level for at least three consecutive extractions (71–124%).

The SPE procedure was then evaluated on a more complex aqueous matrix, that is UWWTP effluent (physical-chemical parameters are reported in Table S1, Electronic Supplementary Material). In this matrix, accurate recoveries were achieved processing a sample volume of 250 mL at the three concentration levels investigated (25, 300 and 1000 ng L^{-1}), for all contaminants (see Table 2).

These results collected on different water matrices demonstrate the real applicability of HA-C@silica for preconcentration of different classes of sex hormones in environmental waters at low nanograms per litre levels, with results comparable to those reported in the most recent literature (Zhang and Fent, 2018).

3.2. HA-C@silica SPE followed by HPLC-ESI-MS/MS: Figures of merit

3.2.1. Trueness and precision

Trueness, investigated by recovery tests as the percentage of analyte extracted in relation to the spiking level, was satisfactory. As reported in Table 2, the mean recoveries (%) obtained

Table 2 Mean recovery (%) in different aqueous matrices, for each concentration level.

	Mean recovery (%)						
	River water (500 mL)				UWWTP effluent (250 mL)		
Spike (ng L^{-1})	600	300	25	5[b]	1000	300	25
E1	120	79	81	101	76	95	95
E2	124	91	109	120	89	87	90
EE2	105	86	106	104	71	89	75
PROG	74	72	75	71	79	106	109
H-PROG	115	103	117	105	91	107	113
M-PROG	79	81	84	91	93	103	112
TST	120	83	115	111	83	85	92

RSDs < 15%, $n = 3$.
[b] 1 L sample.

in raw river water (500–1000 mL) at environmentally significant concentrations ranged from 71% to 124% for the target analytes. Quantitative extraction for all the analytes (71–113%) was also obtained in UWWTP matrix (250 mL).

Intra- and inter-day precision showed RSDs below 15% in all matrices.

3.2.2. Calibration curves and linearity

The matrix effect showed an average signal suppression of about 20% for all compounds with respect to the response given by the standard solution in pure MeOH (data not shown). A quite good compensation was achieved by the standard addition method operated by the instrument directly on the SPE eluate. Matrix-matched standard calibration showed good linearity in the range of 10–150 μg L^{-1} for all steroid hormones for river water and UWWTP effluent with correlation coefficients (R^2) higher than 0.9937.

3.2.3. Detection and quantification limits

The calculated MDLs are in the range 0.02–0.9 ng L^{-1} for river water and 0.5–4.1 ng L^{-1} for UWWTPs effluent. The calculated MQLs are in the range 0.5–3.0 ng L^{-1} for river water and 1.8–13.7 ng L^{-1} for UWWTPs effluent. These results highlight that method sensitivity is suitable for environmental monitoring, as proved by ultra-trace determination of hormones in actual samples, described in the following.

3.3. Determination of steroid hormones in real-world samples

Based on the good results obtained by recovery tests, the proposed analytical method was applied to enrichment of real-world surface waters (Tanaro and Ticino rivers) collected in high-density populated areas of Northern Italy, and of UWWTP effluent sampled at the Pavia WWTP upstream the UV treatment. As expected and as reported in Table 3 and Fig. S1, steroid hormones were detected at few nanograms per litre, attesting their environmental diffusion in surface waters. In particular, high levels of oestrogens were found, probably due to their extensive usage and poor metabolization (Huysman et al., 2017; Barreiros et al., 2016). The results highlight the applicability of the proposed SPE coupled to HPLC-ESI-MS/MS method for environmental monitoring of steroid hormones at the low nanograms per litre levels. However, deeper monitoring investigations are required to be more aware about the actual contamination levels of these xenobiotic compounds in the water ecosystems considered.

Table 3 Steroid hormones concentrations (ng L^{-1}) detected in real-world waters after pre-concentration on HA-C@silica.

	Concentration (ng L^{-1})		
	Tanaro River[a]	Ticino River[a]	UWWTP effluent[b]
E1	76	14	39
E2	9	34	< MQL
EE2	3	6	15
PROG	4	6	10
H-PROG	6	< MDL	< MDL
M-PROG	6	< MDL	< MDL
TST	6	7	2

[a] River water (1 L).
[b] UWWTP effluent at the Pavia WWTP collected upstream the UV treatment (250 mL).

Table 4 Mean recovery (%) obtained in blank river water for the fifteen steroids (1 L, 5 ng L^{-1}).

	Mean recovery (%)[a]
Spike (ng L^{-1})	5
E1	107
E2	118
EE2	109
PROG	84
H-PROG	106
M-PROG	96
TST	109
CORT	84
H-CORT	87
PRED	84
PREDLO	101
BETA	105
DEXA	102
TRIAM	106
FLUO	89

[a] RSDs < 15%, $n = 3$.

3.4. Application of method extended to GCs in river water

The good preconcentration results obtained on HA-C@silica in this work and in the previous one for GCs (Speltini et al., 2018) prompted us to verify the applicability of the HPLC-ESI-MS/MS method for the simultaneous and quantitative determination of the four classes of steroid hormones (oestrogens, progestins, androgens and GCs). For this reason, eight GCs (Speltini et al., 2018) were separated and fragmented in the new chromatographic conditions, proposed in this work (see Electronic Table S4, Supplementary Material).

Recovery tests were then performed in triplicate on the blank river water matrix (1 L) enriched with 5 ng L^{-1} of the fifteen analytes, obtaining quantitative recoveries (see Table 4).

At the same time, an aliquot of Ticino river sample was analysed; oestrogens, progestins, androgens were confirmed (see Table 3) and among GCs, CORT, H-CORT and DEXA were quantified at concentrations of 2–3 ng L^{-1}, (see Fig. S2, Supplementary Material).

These findings show that all compounds are quantitatively pre-concentrated on the same cartridge and quantified in a single chromatographic run, further widening the method applicability compared to the most recent methods proposed in the literature (Zhang and Fent, 2018).

4. Conclusions

The present paper proposes a sensitive and straightforward method for multi-analyte determination of four classes of steroid hormones in environmental waters. The extraction was performed on HA-C@silica, a homemade mixed-mode carbonaceous sorbent here applied for the first time for multiclass SPE of sex hormones. The developed SPE procedure coupled with HPLC-ESI-MS/MS method provided good recovery

and high enrichment factors in raw river water and UWWTP effluent, also at low nanograms per litre levels, and MDLs and MQLs suitable for identification and quantification of the target analytes in real-world samples.

Moreover, this work gives new evidences of the versatility of HA-C@silica, therefore further work is ongoing to widen HA-C@silica application in the sample treatment field, for both extraction and clean-up of trace analytes in complex matrices.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.arabjc.2019.10.009.

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