

SUPPLEMENTARY MATERIAL TO
**Solid-phase extraction of estrogen hormones onto chemically modified
carbon cryogel**

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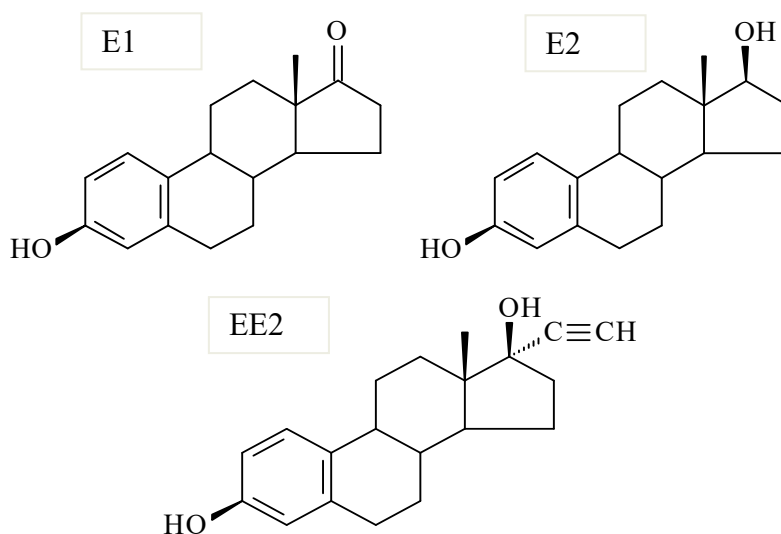


Fig. S-1. Chemical structures of E1, E2 and EE2

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The most abundant ions from each hormone MS spectra were selected as precursor ions: the protonated molecule for E1 (m/z 271.0) and the dehydrated protonated molecules for E2 and EE2 (m/z 255.0 and 279.0, respectively). The most intense product ions resulting from the fragmentation of the selected precursor ions were chosen for quantitative analysis (Table S-I).

TABLE S-I. MS-MS quantification parameters for selected hormones

Hormone	Retention time, min	Precursor ion m/z	Collision energy, %	Fragment ion m/z	Isolation width
E1	6.34	271.0	24	253.0	2
E2	6.10	255.0	27	159.1	2
EE2	5.80	279.0	33	133.2	2

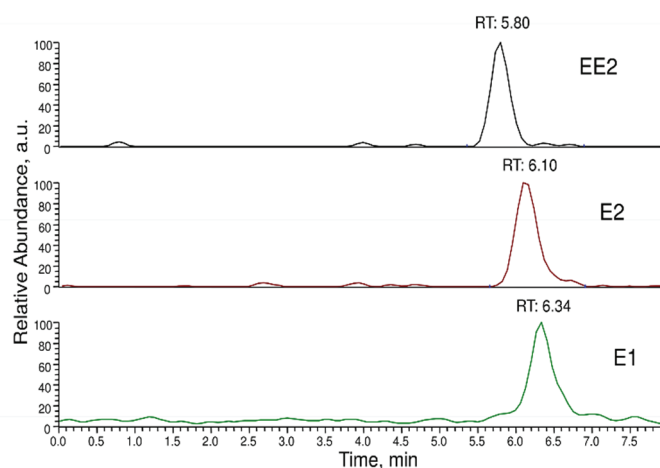


Fig. S-2. SRM chromatograms of selected estrogen hormones from extract of water sample spiked at $0.5 \mu\text{g dm}^{-3}$

METHOD VALIDATION

The linearity of the method was estimated by a calibration curve with six concentrations ranging from 5 to $500 \mu\text{g dm}^{-3}$ (which corresponds to the concentration range of 25 – 2500 ng dm^{-3} in the water sample). The repeatability of the method was estimated by calculating the relative standard deviation ($RSD / \%$) of samples measured in the triplicates ($n = 3$). The limit of detection (LOD) and limit of quantitation (LOQ) were calculated as the minimal quantity of analyte necessary to produce a signal-to-noise ratio of 3 and 10, respectively.^{1,2}

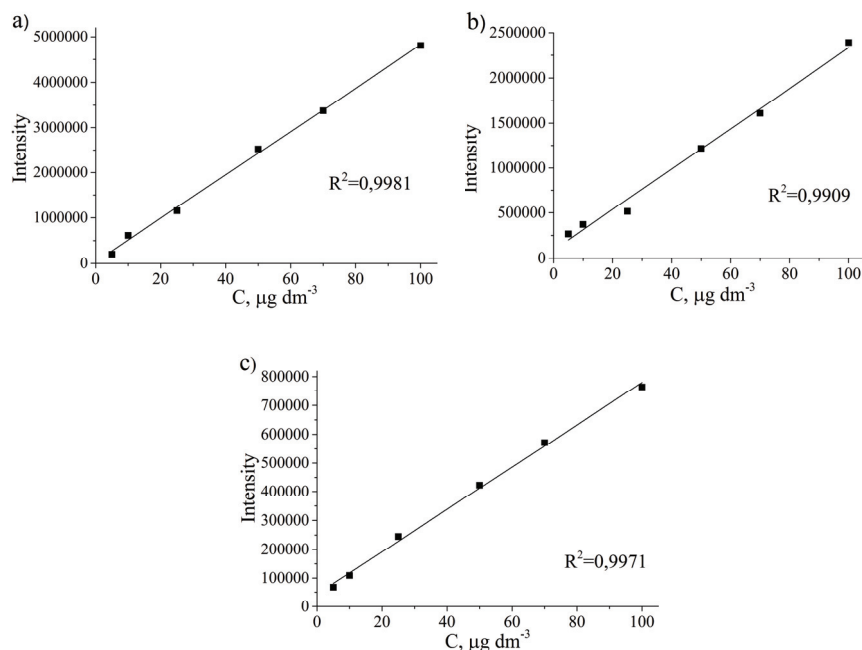


Fig. S-3. Calibration curves of a) E1, b) E2 and c) EE2

In order to estimate the suppression or enhancement of the analyte signal in the matrix solution, spiked and blank extracts of groundwater, surface water, and wastewater samples were prepared and analyzed. The matrix effect (%) was calculated by applying the following equation.³

$$\text{Matrix effect} = \frac{\text{Area}_{\text{matrix}} - \text{Area}_{\text{blank}}}{\text{Area}_{\text{solvent}}} \times 100 \quad (1)$$

where $\text{Area}_{\text{matrix}}$ is the peak area of the analyte in the spiked real water extract, $\text{Area}_{\text{blank}}$ is the peak area of the analyte in the correspondent nonspiked extract, and $\text{Area}_{\text{solvent}}$ is the peak area of the analyte in the appropriate working standard solution in methanol. A matrix effect greater than 100% implies ionization enhancement, while a matrix effect less than 100% indicates ionization suppression.

TABLE S-II. Analytical characteristics of the developed method (n = 3)

Compound	Recovery, % (RSD, %)	Linearity, R ²	LOD, ng dm ⁻³	LOQ, ng dm ⁻³	Matrix effect, %		
					GW	SW	WW
E1	82 (4)	0.9981	6.36	21.19	94	89	91
E2	87 (6)	0.9909	2.63	8.77	117	114	119
EE2	95 (3)	0.9971	5.14	17.12	102	103	110

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