Electronic Supplementary Material (ESI) for Analytical Methods.

Electronic supplementary information:

Recent advancements in analytical methods for the determination of steroidal estrogen residues in environmental and food matrices.

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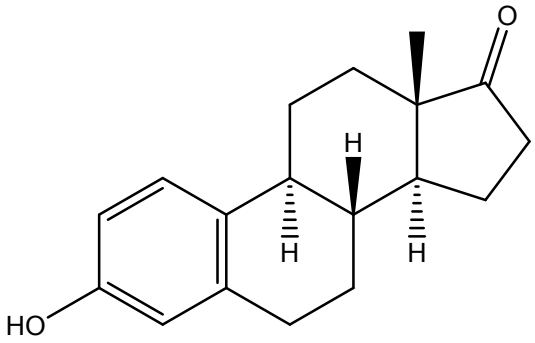
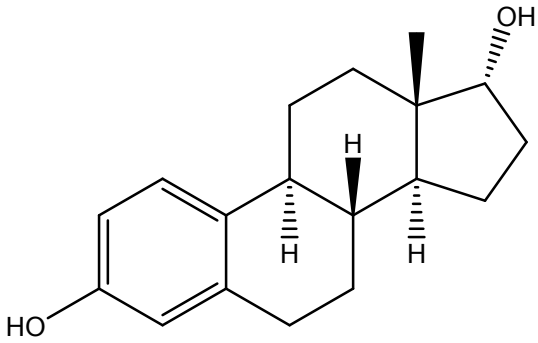
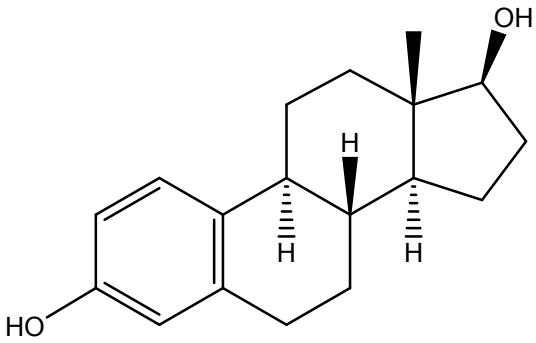
S1: Structures of the analytes of interest



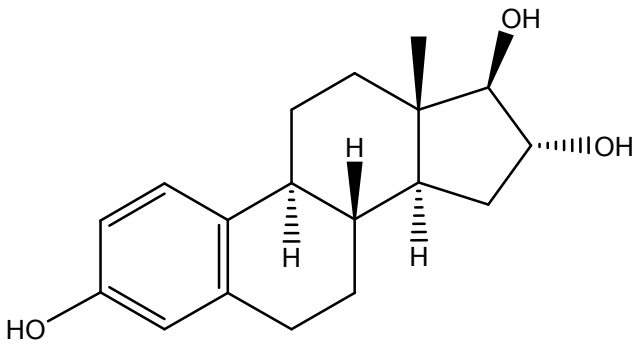
Estrone (E1)



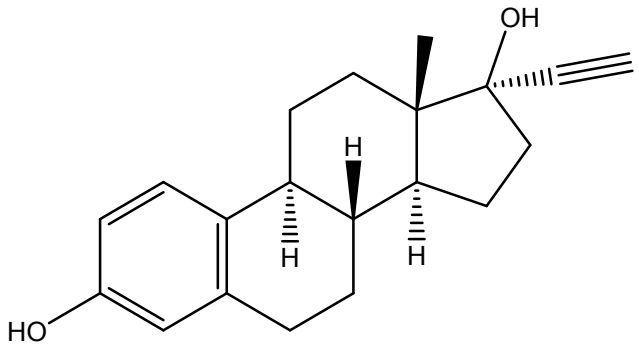
17α-estradiol (αE2)



17β-estradiol (β E2)



Estriol (E3)



Ethinylestradiol (EE2)

S2: Physicochemical properties of the analytes of interest

Estrogen	Formula	CAS	Molecular weight (g/mol)	γ_{sat} (mg/L at 20 °C)	log P_{ow}	pKa	Vapour pressure (mm Hg)	Ref.
βE2	$C_{18}H_{24}O_2$	50-28-2	272.4	12.9	3.94	10.5	2.3×10^{-10}	i-iii
E1	$C_{18}H_{22}O_2$	53-16-7	270.4	12.4	3.43	10.8	2.3×10^{-10}	i, iii
E3	$C_{18}H_{24}O_3$	50-27-1	288.4	13.2	2.81	10.4	6.7×10^{-15}	i-iii
EE2	$C_{20}H_{24}O_2$	57-63-6	296.4	4.8	4.15	10.2	4.5×10^{-11}	iv

References

i. K. M. Lai, K. L. Johnson, M. D. Scrimshaw and J. N. Lester, *Environ. Sci. Technol.*, 2000, 34, 3890-3894.

ii. K. M. Lai, M. D. Scrimshaw and J. N. Lester, *Sci. Total Environ.*, 2002, 289, 159-168.

iii. H. H. Tabak, R. N. Bloomhuff and R. L. Bunch, *Steroid hormones as water pollutants II*, 1981.

iv. Y. J. Kim, *Atmospheric and Biological Environmental Monitoring*, Springer, 2009.

S3: Summary of MIP methods discussed

Analyte	Sample matrix	Initial Sampl Volume/ mL	Functional monomer	Cross Linker	Initiator	Recovery %	LOD (ng/L)	Special Remarks	Ref
βE2	Waste Sea water effluent	3	MAA	EGDMA	Benzophenone	96.1-101.4	0.07	Portable and reusable bio sensor	23
E1,βE2,E3	Lake and River water	15	MAA	EGDMA		62.8–98.0	1000–5000	Duel template stir bar sportive extraction is used	25
βE2	Lake, River and Effluent water	30	Gelatine			88.3-99.1	40	Use of gelatin as functional monomer	16
E1,βE2,E3	Tap, Lake and River water	500	3-isocyanatopropyl triethoxysilane			85-95	86-430	Use of mesoporous silica	22
E1,βE2,EE2	Tap and River water		MAA	EGDMA	ADVN	90.4-98.0	100-260	Use of hollow spheres	20
βE2	Milk	10	MAA	EGDMA	ADVN	94.8-97.0	4600	Use of core shell type hollow spheres	24
E1,βE2,E3	Milk Powder	2g	AA	EGDMA		77.3-96.6	1.5-5.5 ng/g	MMIPs as fiber coating	18
E1,βE2,EE2	Milk	0.2	MAA	EGDMA		81-110	600000-1700000	For the first time MECK-UV used for the analysis of steroids in milk	21

S4: Summary of SPE methods discussed

Analyte	Matrix	Sample Volume/ mL	Cartridge type	Conditioning	Eluent	Derivatization	Detection Method	LOD (ng/L)	Recovery %	Special Remark	Ref:
E1,E23, αE2,βE2	Milk	10	Carbograph-4	5 mL Methanol 20 mL of 10mmol/L HCL 10 mL of Milli-Q water	10 mL of DCM/ Methanol (80:20, v/v)		UPLC-MS/MS	3.0- 30	86-109	Use of GCB base SPE, conjugate determination without deconjugation	43
βE2,EE2	River water	1000	C18	Hexane Acetone Methanol Water	4 mL Acetone		YES			YES for estrogen determination	52
EE2	WWTP effluent water	200 and 500	Oasis HLB	6 mL of ACN 6 mL of Water	8 mL of ACN		LC-MS/MS	1300-5900	87-98	Wrong way round ionization, determination of all analytes in one run	42
βE2,EE2	WWTP influents and effluents	500	Oasis HLB	5 mL Methanol 5 mL Water	5 mL Methanol		UPLC-MS/MS	0.02-0.06	45.7-82.1	Comparatively low LODs	40
E1,αE2,βE2 EE2,E3	WWTP influents and effluents	500	Oasis HLB	5 mL Methanol 5 mL Water	10 mL of Methanol	BSTFA+ 1%TMCS	GC×GC-qMS	1.4-8.6	87-96	Less initial cost due to the novel method GC-GC-qMS	39
βE2	Seawater	100	C 18 silica beads	20 mg/ml in 80 vol% Methanol	200 µL Methanol (50%V/V)		ELISA	100	101-103	Fully automated, portable method	54
EE2	WWTP effluent and surface water	1000	Oasis HLB		10 mL Methylene Chloride		ELISA	0.5			55
E1,βE2,EE2,E3	Sediment, Sludge,Soils	100	Oasis HLB Strata C18-E (as a cleanup)	3 mL Ethyl Acetate 3 mL Methanol 3 mL Distilled water	6 mL of Methanol	50 µL BSTFA+TMCS in 50 µL Pyridine	GC-MS	300-570	80-120	As a further cleanup after MAE	37
E1,βE2,EE2,E3	Drinking and Waste water	1000	variety of C18 ,SPE cartridges	ACN Methanol Water	ACN		HPLC-MS/MS HPLC-UV HPLC-Fluorescence	0.091-0.32	22-100	Comparison of the various EDC detection methods.	30
E1,βE2,EE2,E3	Tap, mineral, underground and river water	250	Empore C18 disk	1 mL Methanol	Methanol		LC-UV	3.0-13	85-126	Multivariate analysis for improved selectivity and sensitivity	29