

Determination of Steroidal Estrogens in Tap Water Samples using Gas Chromatography-Mass Spectrometry

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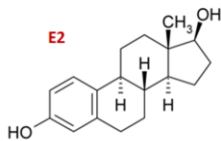


Overview

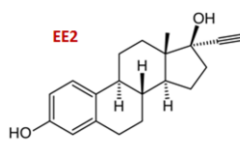
- Why steroidal estrogens?
 - Sources
 - Occurrence
 - Toxicity
- Sample preparation
- Instrumental analysis
- Results



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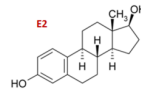
17β-estradiol



17α-ethynylestradiol



3



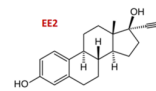
17β-estradiol

LC50 = >2 mg/L
(*Pimephales promelas*)

Seki et al. (2004)



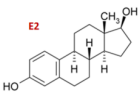
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17α-ethynylestradiol

LC50 = >? mg/L
(*Pimephales promelas*)

Parrott and B. R. Blunt (2005)



17β-estradiol

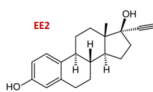
LC50 = >2 mg/L
(*Pimephales promelas*)

LOEC = >30 ng/L

Seki et al. (2004)



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17α-ethynylestradiol

LC50 = >? mg/L
(*Pimephales promelas*)

LOEC = >1 ng/L

Parrott and B. R. Blunt (2005)



Endocrine disrupting properties

- Interfere with endocrine functions of aquatic organisms
 - Induce feminisation
 - Decrease in fertility
 - Hermaphroditism
- Could be of **great concern for humans**



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Sources

- **Wide range of applications** in medicine and veterinary medicine
- Human and animal excretion with subsequent **discharge** into the surface waters **via waste water treatment plants** is considered as **the main source** of these chemicals in aquatic ecosystems

Aim of the study

- Development of efficient analytical methods for reliable determination of the natural estrogen 17 β -estradiol (E2) and the synthetic estrogen 17 α -ethynylestradiol (EE2) in water samples at low ppt levels (\sim 1 ng/L)

Aim of the study



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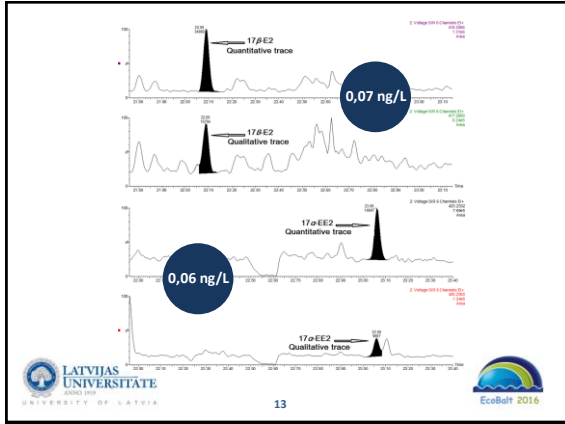


Sample preparation



Instrumental analysis

	TSQ Quantum XLS Ultra GC-MS/MS (Thermo Scientific)			Micromass Autospec Premier GC-HRMS (Waters)	
Ionization	EI ⁺			EI ⁺	
Electron energy	70 eV			36 eV	
Source temperature	250 °C			280 °C	
Mode	Selected reaction monitoring (SRM)			Selected ion recording (SIR)	
Compound	Quant. trace (m/z → m/z)	Qual. trace (m/z → m/z)	CE (eV)	Quant. trace (m/z)	Qual. trace (m/z)
E2	416,3 → 285,3	416,3 → 232,2	15	416,2566	417,2600
EE2	425,2 → 193,2	425,2 → 231,2	20	425,2332	426,2365
E2-d3	419,3 → 288,3	419,3 → 235,2	15	419,2755	420,2789



Validation

<p>GC-MS/MS</p> <p>E2 Recovery - 109,5 % Precision - 7,9 % Linearity - 0,995 Limit of quantification (LOQ) - 0,08 ng/L</p> <p>EE2 Recovery - 107,0 % Precision - 11,1 % Linearity - 0,999 Limit of quantification (LOQ) - 0,08 ng/L</p>	<p>GC-HRMS</p> <p>E2 Recovery - 106,0 % Precision - 4,5 % Linearity - 0,999 Limit of quantification(LOQ) - 0,08 ng/L</p> <p>EE2 Recovery - 108,5 % Precision - 9,9 % Linearity - 0,999 Limit of quantification (LOQ) - 0,08 ng/L</p>
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Sensitivity

LOQ = 0,08 ng/L

LOQ on column (GC-MS/MS) **2 pg**

LOQ on column (GC-HRMS) **0,4 pg**

Results

Sample code	Sampling place	17β-E2 (ng/L)	17α-EE2 (ng/L)
1	Riga	0,06*	0,07*
2	Valmiera	ND	ND
3	Rezekne	ND	ND
4	Daugavpils	ND	ND
5	Aizpute	0,07*	ND
6	Valmiera	0,10	ND
7	Iecava	0,12	ND
8	Preiļi	0,11	ND
9	Jurmala	0,07*	ND
10	Jurmala	0,15	ND
11	Daugavpils	ND	ND
12	Jekabpils	0,09	0,04*
13	Adazi	0,11	ND
14	Valmiera	0,06*	0,06*

Results

- **10 out of 14** samples showed traces of **17β-E2**
- **3 out of 14** samples showed traces of **17α-EE2**

- Highest concentration of 17β-E2 **0,15 ng/L**
- Highest concentration of 17α-EE2 **0,07 ng/L**

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LOEC = >1 ng/L

Conclusions

- **MIP stationary phase** highly selective for estrogens.
- Acceptable performance characteristics were obtained for both **GC-MS/MS** and **GC-HRMS** (however, GC-HRMS provided better results in terms of recovery and precision)

Conclusions

- The **presence of estrogens** in tap water **indicates the uptake potential** of these compounds and is particularly significant because of their high estrogenic potency

Thank you for your attention!

(Questions and discussion)