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Comparisson between HPLC-DAD/UV and LC-MS/MS to analysis drugs and hormones in surface water samples

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Abstract
The presence of pharmaceuticals and hormones in water bodies has presented more concern due to your continuous use and the waste disposal into freshwaters. The aim of this project was compare the determination of paracetamol, caffeine, estriol, naproxen, ibuprofen, diclofenac, ethinylestradiol, estrone and estradiol using HPLC-DAD/UV and LC-MS/MS method considering detectability and matrix effect at concentrations around ng/L.

Key words:
HPLC-DAD/UV, LC-MS/MS, drugs.

Introduction

Currently, it had an increase in the consumption of drugs which don't need recipe. After it was consumed, these compounds are metabolized and excreted with hormones through wastes which are discarded in domestic sewage.[1] As the majority of the sewage, are treated by biologic methods, that are ineffective in the degradation of these substances, they are released in the hydrosphere, so it can bring several problems.[2] Occurrence of these compounds was reported in Brazil already.[3,4] With more sensitive techniques, it was found substances with concentrations in the range of ng/L and µg/L in natural waters and effluents of sewage treatment station.[5] So, this project aim to compare the analysis of pharmaceuticals and hormones by HPLC-DAD/UV (cheapest) and LC-MS/MS.

Results and Discussion

With the optimized method of HPLC-DAD/UV was acquired a calibration curve for the compounds showed in the Chart 1.

Chart 1. Calibration curve of the compounds analyzed by HPLC-DAD/UV.

Compound	Calibration Curve	LOD (ppb)	LOQ (ppb)	Linearity	Working range (ppb)
Para-cetamol	y = 75,80x – 4280	294	980	0.9333	50 – 1000
Caffeine	y = 15,7x - 578	132	439	0.9870	50 – 1000
Estriol	y = 7,704x - 803,9	258	861	0.9002	250 – 1000
Naproxen	y = 424,7x – 7629	241	805	0.9474	25 – 1000
Ethinyl-estradiol	y = 8,698x – 247,4	265	882	0.9988	100 – 10000

Ad it was found in river's water samples concentration of:

- Paracetamol: 13 ng/L to 17.5 ng/L;
- Caffeine: 21 ng/L to 186 ng/L;
- Estriol: 68 ng/L to 281 ng/L.

For naproxen and ethinylestradiol, the concentrations were below LOD. Furthermore, it was made a calibration curve in the LC-MS/MS with the method to analysis of drugs that ionizes in the negative mode.

Chart 2. Calibration curve of the drugs that ionizes in the negative mode analyzed by LC-MS/MS.

Compound	Calibration Curve	LOD (ppb)	LOQ (ppb)	Linearity	Working range
Naproxen	y = 13,81x - 91,12	17	55	0.9958	10-500
Diclofenac	y = 218,36x + 2009,9	9	29	0.9988	10-500
Ibuprofen	y = 12,98x - 129,15	18	61	0.9949	10-500

So, the same sample analyzed by HPLC-DAD/UV was analyzed in LC-MS/MS, and it was found ibuprofen (33 ng/L) in a sample. Furthermore, it will be made a calibration curve for the hormones (estradiol, estriol, estrone and ethynilestradiol) and for the drugs that ionizes in the positive mode (paracetamol and caffeine), and the same samples will be analyzed.

Conclusions

It can be observed that the number of compounds that can be analyzed simultaneously in HPLC-DAD/UV is smaller than in LC-MS/MS, because of the selectivity, which is smaller in the first one, so, when co-elution of the compounds analyzed by HPLC-DAD/UV happens, the analyze is prejudiced, unlike LC-MS/MS. Furthermore, LOD and LOQ found in the LC-MS/MS method is smaller than the HPLC-DAD/UV method for the drugs that ionizes in the negative mode (naproxen, ibuprofen and diclofenac), so the analysis of this compounds in LC-MS/MS is more appropriate.

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