A Rapid LCMS Method for Evaluating PPCPs Contaminants Found in Drinking Water

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Novel Aspects

A rapid six and a half minute method to analyze and quantify multiple pharmaceutical and personal care products in environmental water by LC-MS/MS.

Introduction

Pharmaceutical and personal care products (PPCPs) encompass a family of compounds used by individuals for health and cosmetic purposes, as well as compounds used by the agricultural industry to maintain health of livestock. The number of individuals who are using these products is increasing which has caused an increase in environmental detection. The effect on humans and the environment is still unknown causing the need for more research on the topic. These contaminates are introduced into local waterways via sewage plants and natural disposal (ie; animal excrement and landfill waste). This poster demonstrates a method for evaluating a combination of PPCPs listed in EPA 1694, 6810 and 4167 at parts per billion levels using liquid chromatography tandem mass spectrometry (LC-MS/MS).

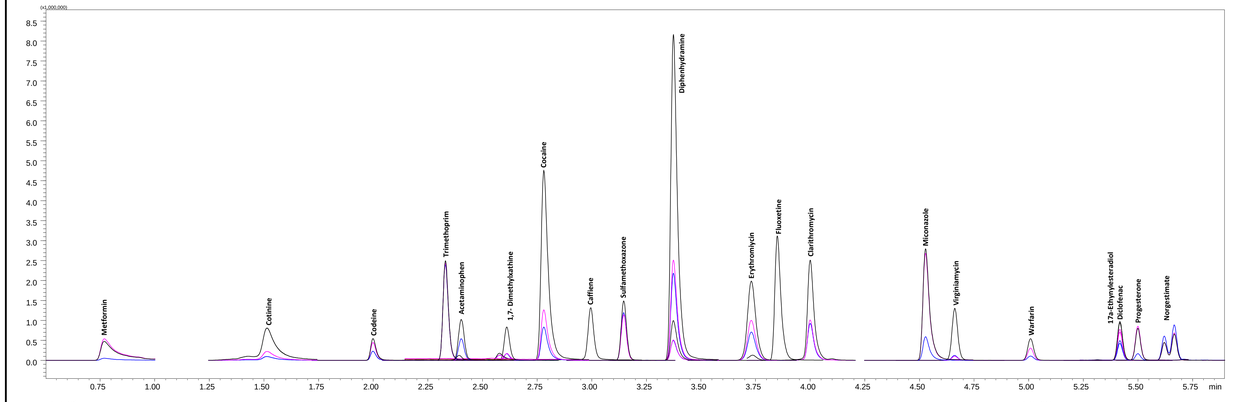
Methods

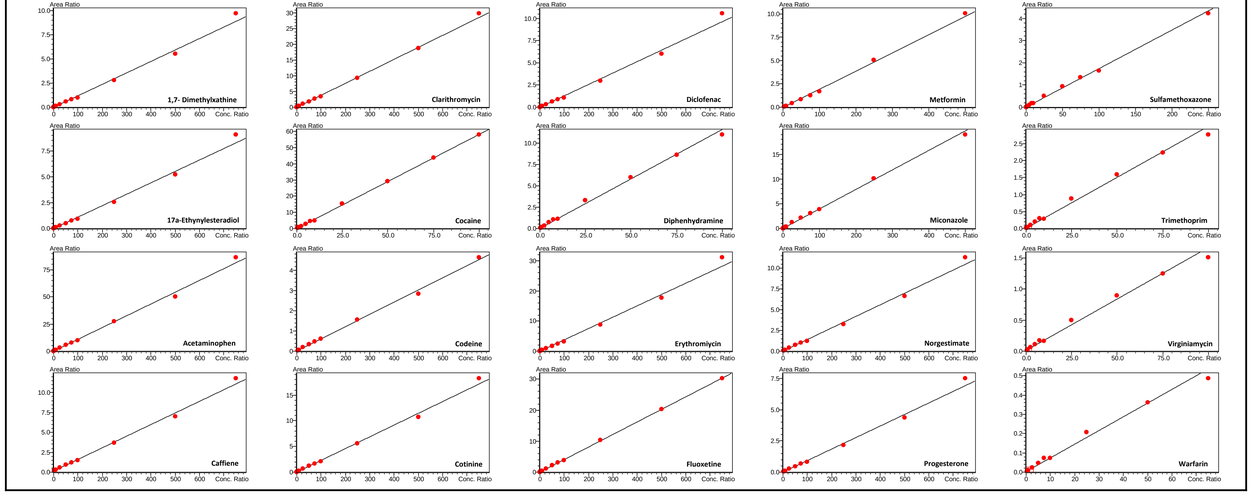
Twenty compounds and two internal standard were analyzed from various drug classes including broad-spectrum antibiotics, antifungals, stimulants, opiates, alkaloids, antihistamines, biguanides, and progestins. Heated Electrospray Ionization (hESI) was used in positive and negative mode to ionize all of the compounds. Each analyte was optimized and separated using a binary gradient with reversed phase chromatography on a Shim-Pack XR-ODS column, in a single 6.5 minute method.

Chromatography Parameters
Column: Shim-Pack XR-ODS
Column Temp: 40 °C
Autosampler Temp: 15 °C
Injection Volume: 1 µl
Flow Rate: 0.6 mL/min

LCMS-8050 Parameters	
Nebulizing Gas:	3 L/min
Interface Temp:	350 °C
DL Temp:	125 °C
Heat Block Temp:	350 °C
Drying Gas Flow:	7 L/min

Results- Calibration and Linearity





Results- Calibration Curve of Neat Samples

			Linearity (n=5)			Precision and Accuracy			
			0.1 ppb – 750 ppb			10 ppb (n=16)		75 ppb (n=16)	
Compound	RT	R^2	Range	LOQ	LOQ %RSD	Conc.	%RSD	Conc.	%RSD
1,7- Dimethylxathine	2.622	0.9941	0.5 - 750	0.5	12.19	8	4.01	52.37	2.05
17a-Ethynylestradiol	5.428	0.9981	0.25 - 750	0.25	13.96	8.4	3.23	72.4	1.8
Acetaminophen	2.41	0.9988	0.5 - 750	0.5	9.05	9.37	6.5	83.29	3.48
Caffeine	3.005	0.9909	2.5 - 750	2.5	3.48	9.09	5.86	65.63	1.49
Clarithromycin	4.014	0.9983	0.1 - 750	0.1	7.92	8.68	1.39	64.27	1.4
Cocaine	2.792	0.9958	0.25 - 100	0.25	8.3	7.59	2.97	74.37	3.2
Codeine	2.008	0.9967	5 - 750	5	2.48	10.11	1.82	74.72	1.21
Cotinine	1.525	0.9937	0.75 - 750	0.75	10.8	9.31	14.03	54.6	12.96
Diclofenac	5.428	0.9924	0.5 - 750	0.5	4.64	8.12	3.09	58.73	1.89
Diphenhydramine	3.384	0.9952	0.25 - 100	0.25	7.18	11.39	1.32	68.02	0.85
Erythromycin	3.742	0.9929	0.25 - 750	0.25	8.18	8.26	2.21	71.77	1.02
Fluoxetine	3.86	0.9988	0.25 - 750	0.25	5.67	9.28	1.58	71.09	0.97
Metformin	0.774	0.9925	2.5 - 500	2.5	5.98	8.03	3.14	58.87	1.21
Miconazole	4.539	0.9985	0.25 - 500	0.25	14.75	9.06	3.59	69.73	1.45
Norgestimate	5.649	0.9912	2.5 - 750	2.5	13.17	8.25	3.2	57.75	2.11
Progesterone	5.483	0.9917	2.5 - 750	2.5	9.1	8.34	3.28	80.15	1.28
Sulfamethoxazone	3.156	0.9969	0.25 - 250	0.25	9.15	9.81	2.56	71.26	1.19
Trimethoprim	2.337	0.9932	0.1 - 100	0.1	7.93	10.76	2.86	76.76	1.16
Virginiamycin	4.671	0.9816	0.75 - 100	0.75	4.83	11.78	1.91	84.17	2.74
Warfarin	5.018	0.9918	0.5 - 100	0.5	7.87	10.27	2.37	80.5	2.05

The calibration curve was made up in mobile phase starting conditions and spiked using a stock solution of the analytes.

All of the analytes had a %RSD of less than 15% at the LOQ and all of the limits of quantitation were below 5 ppb. All of the compounds were weighted 1/C and had a linear line of fit. The linear range was adjusted for each compound due to some source saturation.

A Precision and Accuracy (P&A) study was conducted to gauge the expected performance of the method. Sixteen replicate injections of 10 ppb and 75 ppb were analyzed. The table above lists the detailed results of the P&A study, reporting the average concentration for each compound (n = 16) and the %RSD for all compounds.

Conclusion

A robust and rapid 6.5 minute method for evaluating pharmaceuticals and personal care products was developed using ultra-fast liquid chromatography mass spectrometry. Most analytes had an lower limit of quantitation at a level between 0.1 ppb and 5 ppb.
Miconazole was the only drug detected in the river water samples. The samples may have been too diluted from the excessive amount of rain in the area before sampling occurred.
The method can be used to further test other river water samples when there is a more stable water table to test from.