Pharmaceuticals and Personal Care Products (PPCPs) in Surface Water

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Novel Aspects

A rapid 8 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 livestock health. The increasing number of individuals who are using these products has been an environmental issue of concern. PPCPs are introduced into the environment via sewage plants and natural disposal e.g. animal excrement and landfill waste. These compounds can then contaminate rivers, aquifers, and soils. This work demonstrates a method for evaluating PPCPs at parts per trillion levels in surface water using liquid chromatography tandem mass spectrometry (LCMS).

Methods

Twenty compounds were analyzed from various drug classes including broad-spectrum antibiotics, antifungals, stimulants, opiates, antihistamines, and progestins. Electrospray Ionization (ESI) was used in positive mode and negative mode simultaneously. Each analyte was optimized and separated using a binary gradient with reversed phase chromatography on a Restek Force Biphenyl column. Surface water samples were collected from various locations across the country and stored following SOP #EH-01 surface water collection using the direct method.

Chromatography Parameters

Column: Restek Biphenyl
100 x 2.1 mm 1.8 um

Column Temp: 55 °C

Injection Volume: 1 µl

Flow Rate: 0.5 mL/min

Mobile Phase A: 5 mM Ammonium Formate
+ 0.1% Formic Acid in H_2O

Mobile Phase B: 0.1% Formic Acid in MeOH

LCMS-8050 Parameters

Nebulizing Gas:	2 L/min
Interface Temp:	300 °C
DL Temp:	250 °C
Heat Block Temp:	400 °C
Drying Gas Flow:	10 L/min
Heating Gas Flow:	10 L/min

Calibration Data

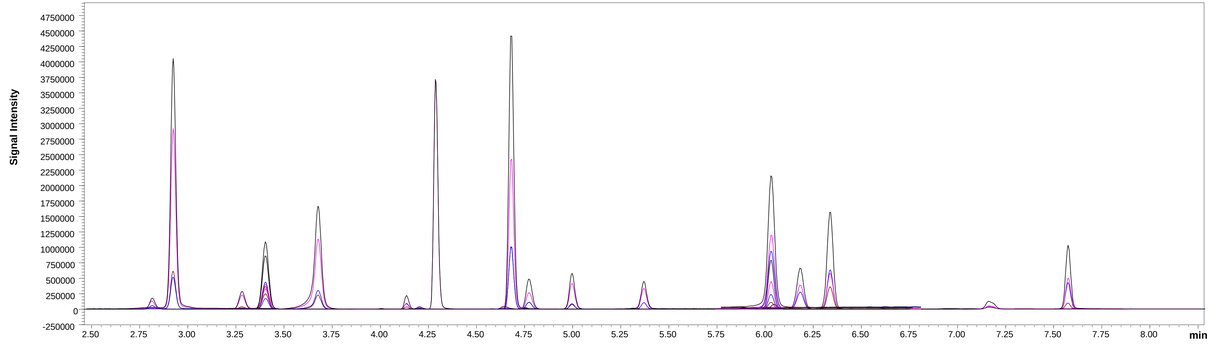
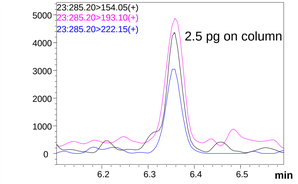


Figure 1: TIC for all compounds

Compound	LOD (ng/mL)	LOD %RSD	LOQ (ng/mL)	LOQ %RSD	ULOQ (ng/mL)	R^2
Atorvastatin	0.25	6.7	0.25	6.7	250	0.997
Diclofenac	0.5	10.7	0.5	10.7	500	0.995
Erythromycin	2.5	0.6	2.5	0.6	50	0.998
Primidone	0.5	8.3	2.5	0.6	500	0.998
Progesterone	0.25	1.6	0.25	1.6	500	0.992
Alprazolam	0.25	0.4	0.25	0.4	500	0.992
Amphetamine	0.25	5.1	2.5	1.1	500	0.991
Buprenorphine	2.5	8.6	5	10.4	500	0.991
Clonazepam	0.5	22.5	2.5	13.7	500	0.998
Diazepam	0.25	14.8	0.25	14.8	500	0.998
Hydrocodone	0.25	0.1	0.5	15.4	500	0.994
Oxycodone	0.25	7.8	0.25	7.8	250	0.996
Cotinine	0.25	6.2	0.25	6.2	500	0.997
1-7 Dimethylxanthine	0.25	12.4	0.5	0.7	500	0.997
Codeine	0.25	14.2	0.25	14.2	500	0.995
Tetracycline	0.25	11.0	2.5	0.6	500	0.992
Virginiamycin	0.25	3.0	0.25	3.0	500	0.991
Minocycline	0.25	0.9	0.25	0.9	500	0.996
Norgestimate	0.25	10.3	2.5	4.8	500	0.999
Diphenhydramine	0.25	11.1	0.25	11.1	50	0.999



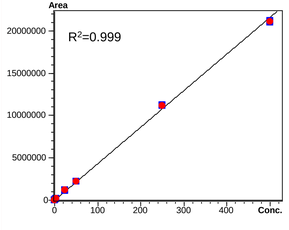
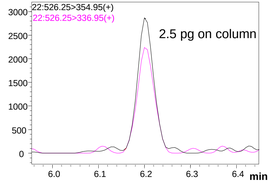


Figure 2: Diazepam LOQ Chromatogram and Calibration Curve



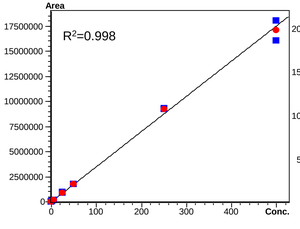
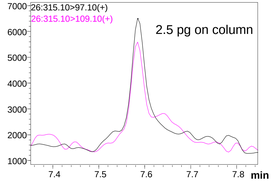


Figure 3: Virginiamycin LOQ Chromatogram and Calibration Curve



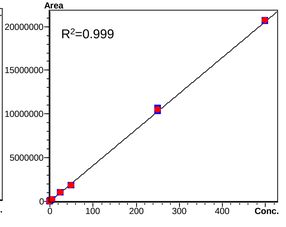


Figure 4: Progesterone LOQ Chromatogram and Calibration Curve

Discussion

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 20% at the LOQ and all of the limits of quantitation were at or below 5 ng/mL. Linearity is demonstrated with all compounds within the reported ranges with a r^2 value of 0.99 or better with $1/C^2$ weighting.

Water samples taken from Maryland and Texas did not show any compounds within the quantifiable range. Water sample taken from Arizona contains amphetamine at 0.343 ng/mL. This is shown in Figure 5 below (Black). The LOQ (Black) chromatogram is also shown for comparison.

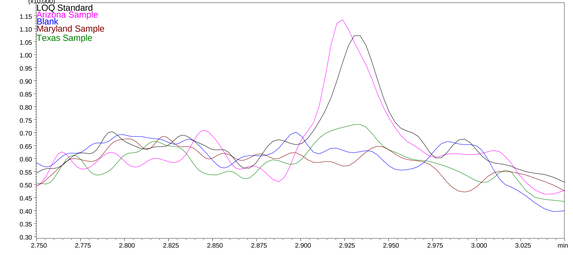


Figure 5: Amphetamine chromatograms from samples taken from various locations. The chromatogram in black represents the sample Arizona. The chromatogram in pink shows the LOQ for amphetamine as comparison.

Conclusion

A robust and rapid 8 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 0.25 ng/mL and 5 ng/mL Amphetamine was the only compound detected in samples taken from the western part of the US. Samples from the Midwest and the eastern part of the US did not test positive for the reported compounds.