



Comparison of Modern LC-MS/MS Techniques for Analysis of TOrCs in Water

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NEMC 2014





Introduction

Pharmaceuticals lurking in U.S. drinking water

AP probe found traces of meds in water supplies of 41 million Americans

Painkillers found in drinking water of 15 Ontario cities, study reports

By The Canadian Press
HAMILTON

A new study reports finding traces of painkillers and other drugs in drinking water from 15 southern Ontario cities.

The places are not identified but all are said to be within easy reach of Environment Canada's National Water Research Institute in Burlington.

Most compounds were reduced to

trace or non-detectable levels after passing through water treatment plants, but the researchers say the fact any chemicals were found is a sign of potential exposure to many more.

The study, by University of Waterloo researcher Mark Servos, appears in the current issue of the Water Quality Research Journal of Canada.

Compounds detected include painkillers such as ibuprofen, chole-

sterol-lowering drugs and the common household antibacterial agent triclosan.

This study follows recent U.S. findings of a vast array of pharmaceuticals in the drinking water of at least 41 million Americans.

A spokesperson for the Ontario Environment Ministry says results of a study it conducted on water from 17 municipal plants are under review and will be released "sometime this year."

Study: India's Water Contains Highest Levels of Pharmaceuticals in World

Published January 26, 2009 / Associated Press

£30bn bill to purify water system after toxic impact of contraceptive pill

Drug firms oppose an EU call for controls on potent chemicals that have been blamed for the gender mutation of freshwater fish

theguardian

The Washington Post

Six years later, gender-bending fish in our water supply remain a mystery

271M Lbs Of Pharmaceuticals In Our Water

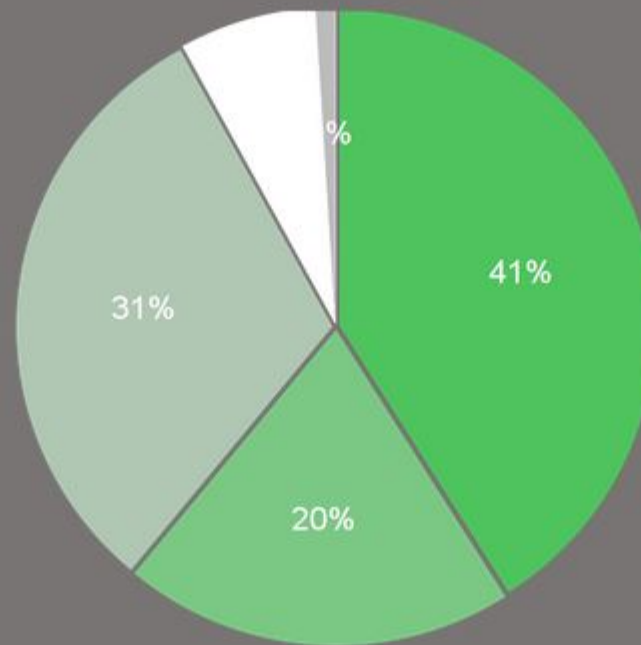


Current Trends

Science Advisory Board

C Preferred Focus of Future Development of Linked Separation/Analysis Technologies

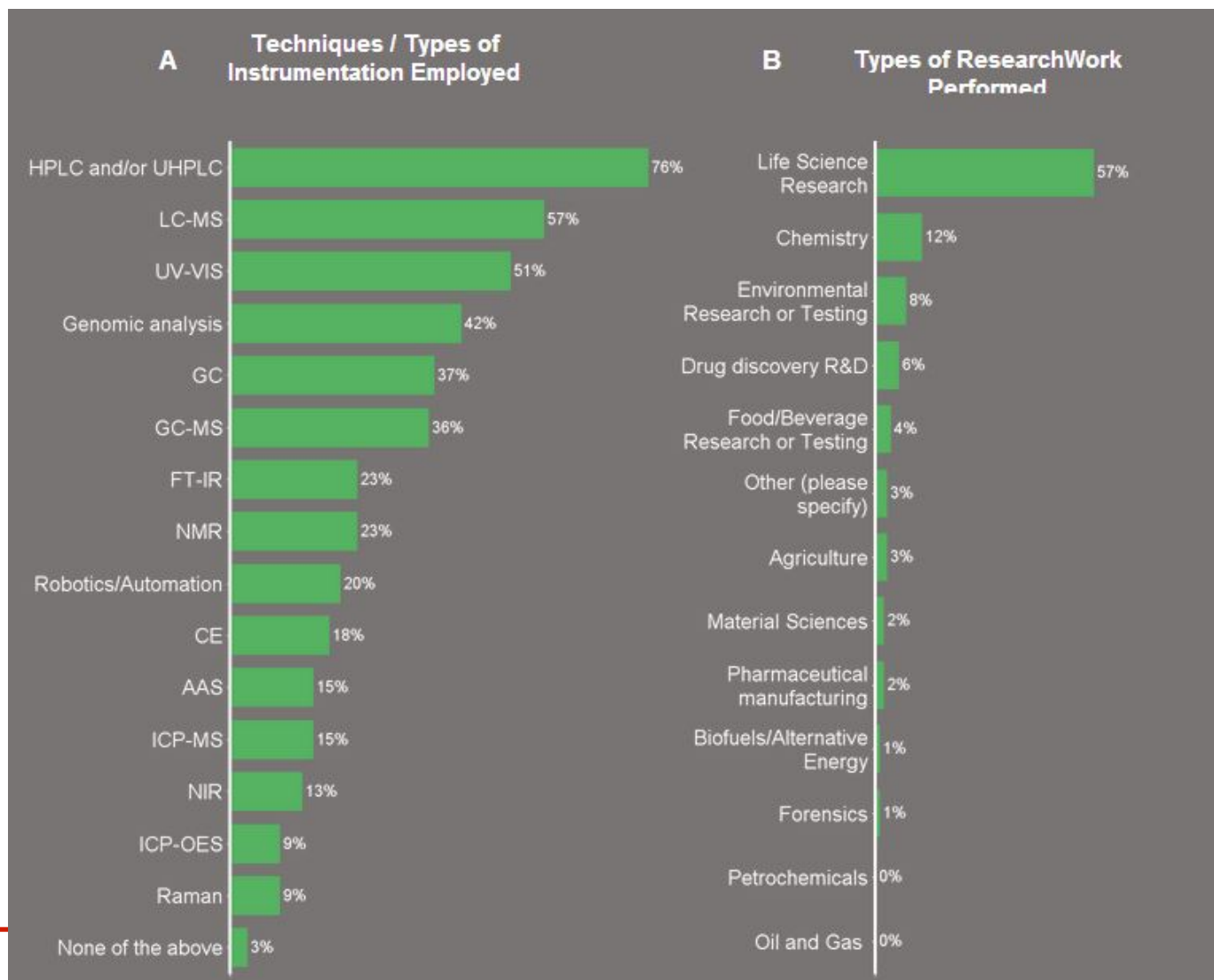
- Enhanced detection technologies
- Increased sample throughput
- Separation technologies
- Validation of technologies for regulatory or other needs
- Other



Respondents
1492



Current Trends





Automation

①

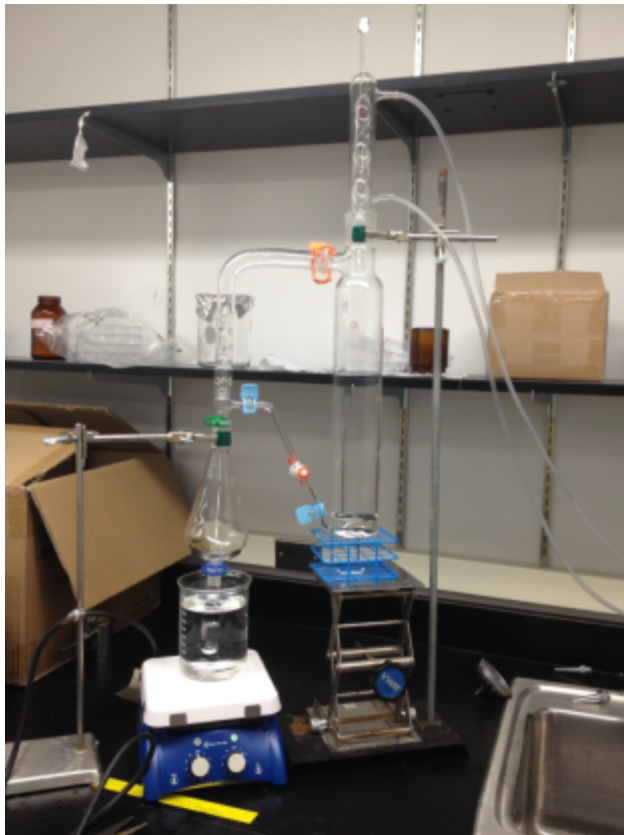
Nothing can stop automation





Traditional Extraction Techniques

Analysis of TOrCs in Water



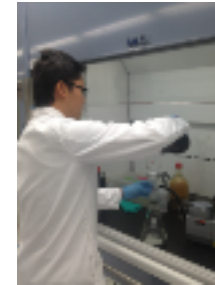
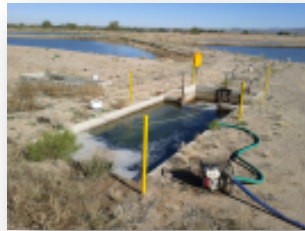
Liquid-Liquid Extraction



Solid Phase Extraction



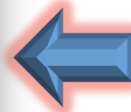
Analysis of TOrCs by C-SPE



Surrogate
addition



Extraction
(SPE) by
Autotrace



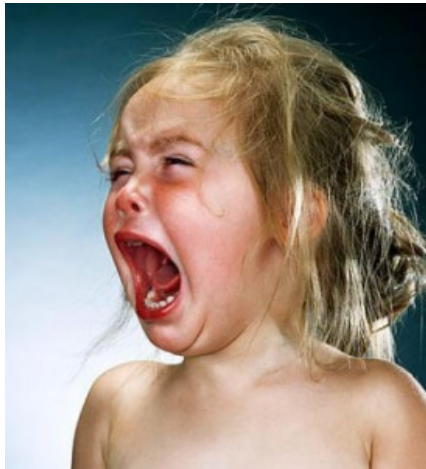
Evaporation



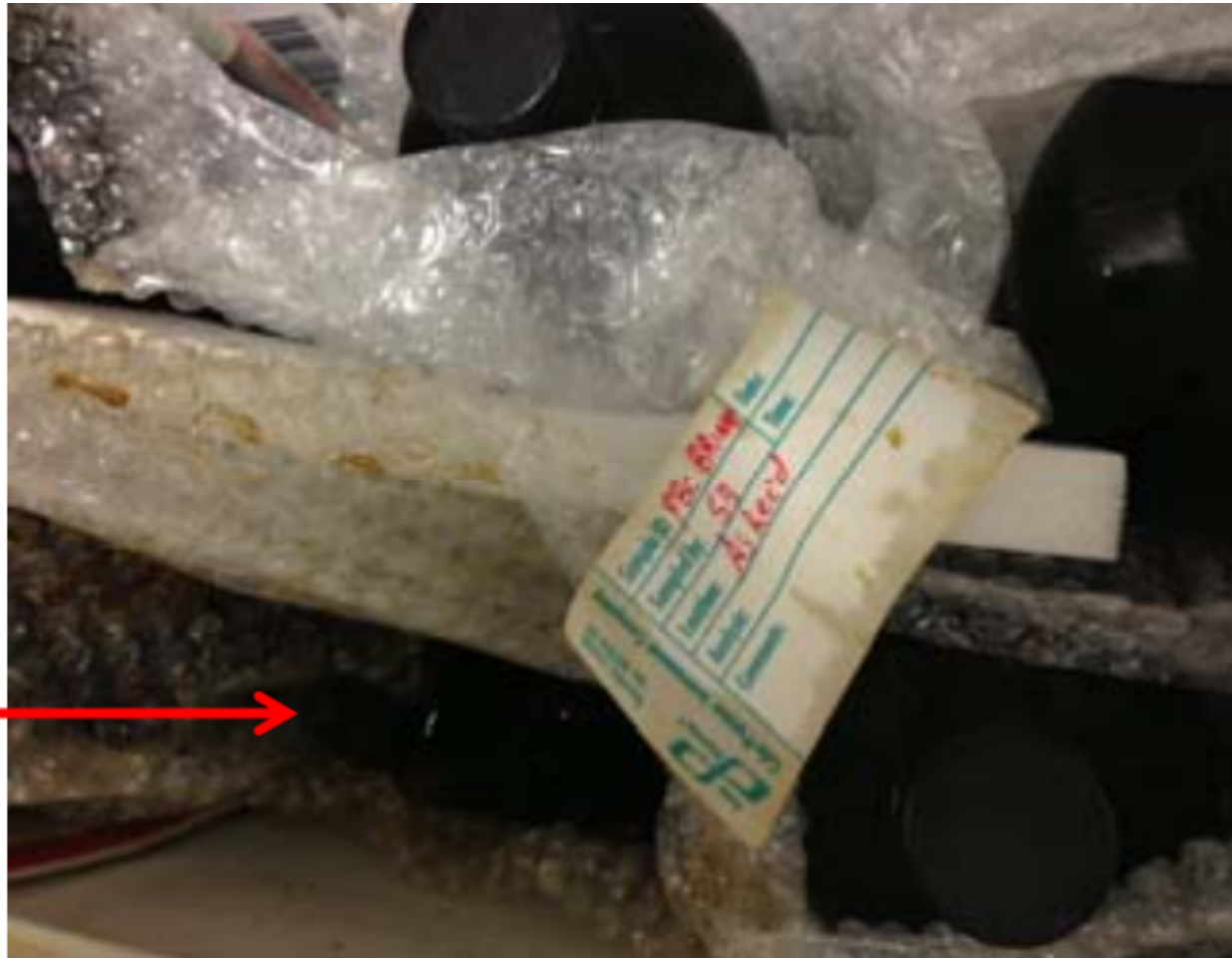
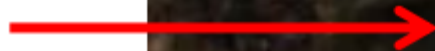
Analysis



Sample Transport



Broken
Sample



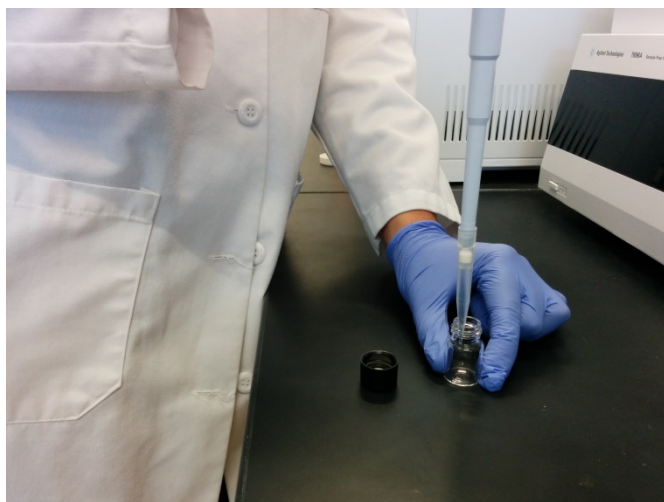


Sample Volume





Analysis of TOrCs by OSPE



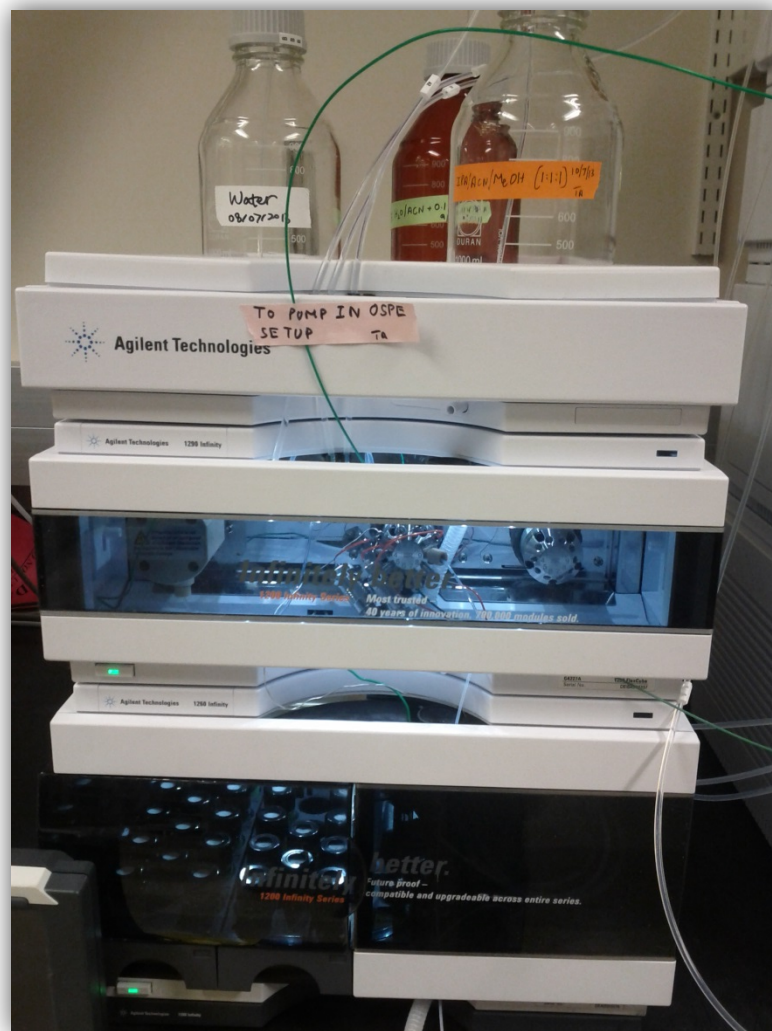
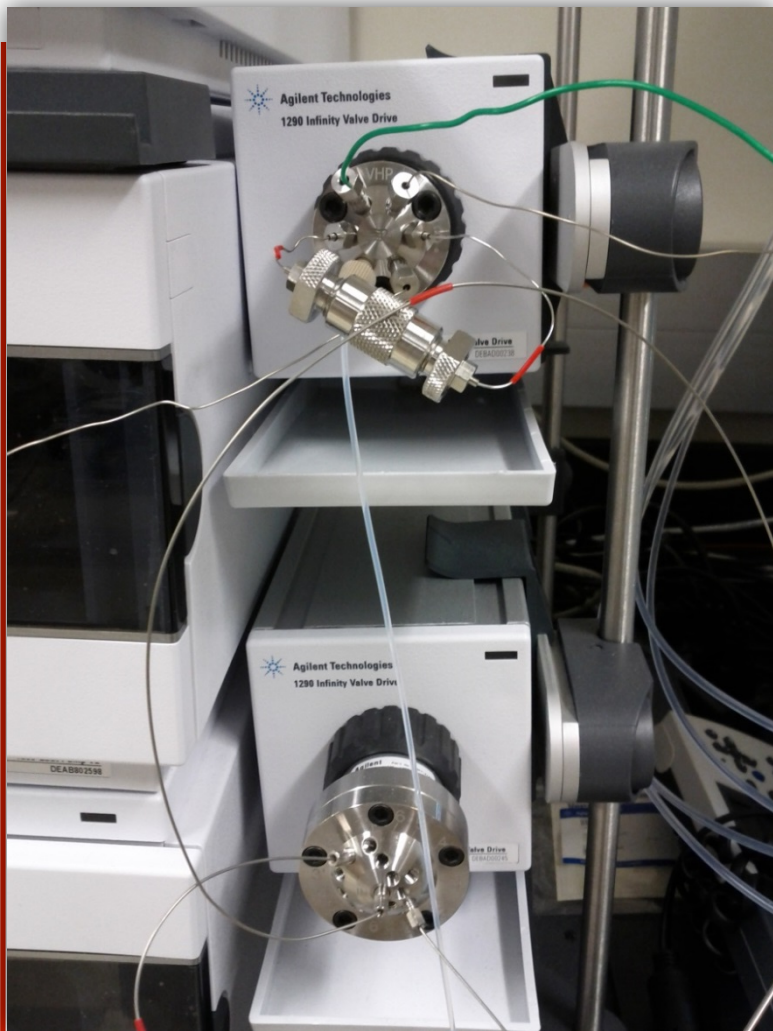
Surrogate Addition into 5 mL of sample



Analysis (1700 μ L injection volume)



Instrument Setup





Instrument Setup

Agilent Flexcube connected to 6460 MS/MS

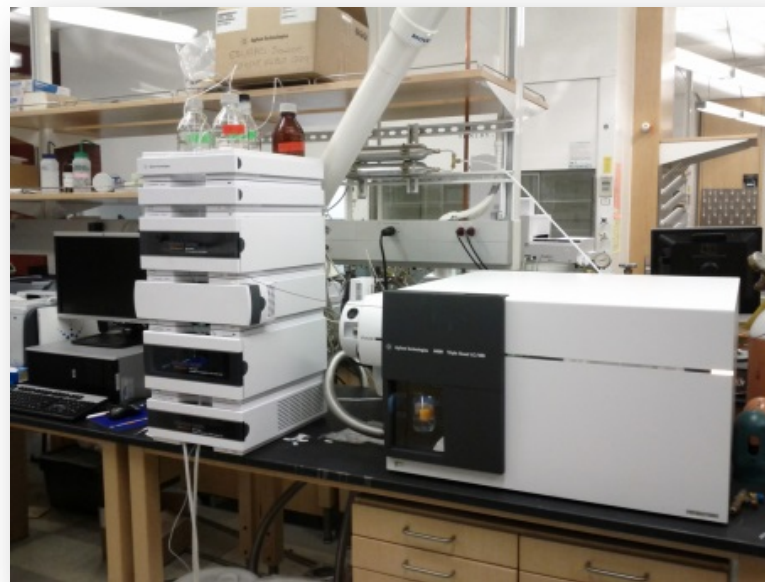




Large Volume Direct Injection



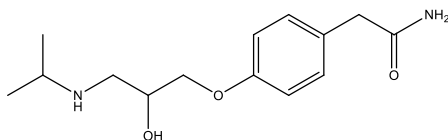
Surrogate Addition into 1 mL of sample



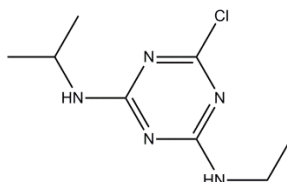
Analysis (100 μ L injection volume)



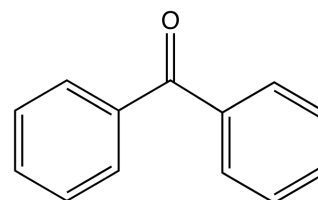
Trace Organic Chemicals



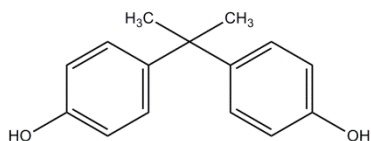
Atenolol (β -blocker)



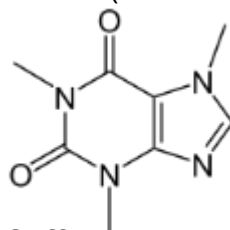
Atrazine (Herbicide)



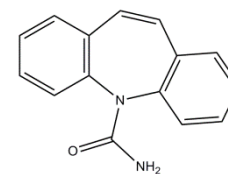
Benzophenone (UV-blocker)



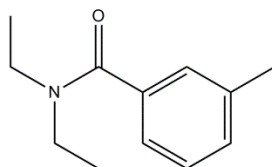
Bisphenol A (plasticizer)



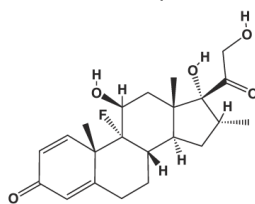
Caffeine (stimulant)



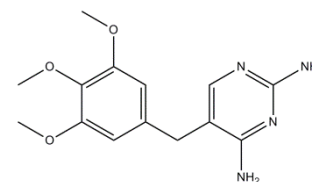
Carbamazepine (Anti-seizure)



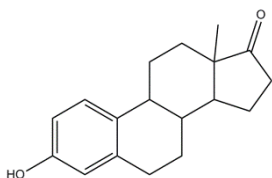
DEET (Insect-repellant)



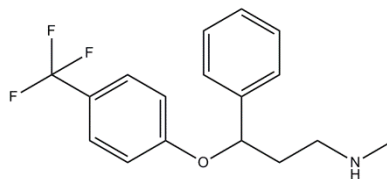
Dexamethasone (glucocorticoid)



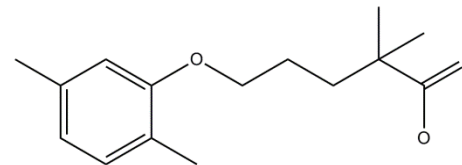
Trimethoprim (Antibiotic)



Estrone (Hormone)



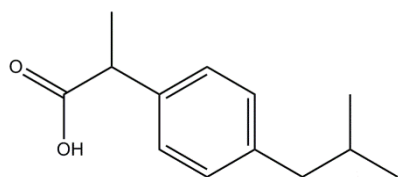
Fluoxetine (Anti-depressant)



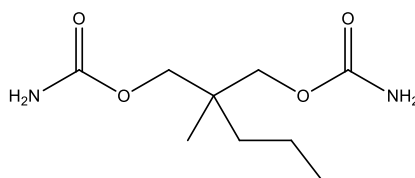
Gemfibrozil (Anti-cholesterol)



Trace Organic Chemicals



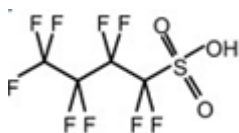
Ibuprofen (Analgesic)



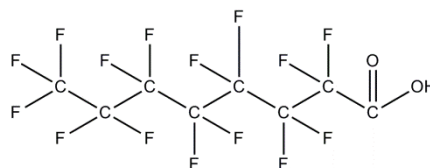
Meprobamate (Anti-anxiety)



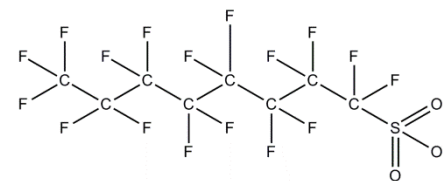
Naproxen (Pain-reliever)



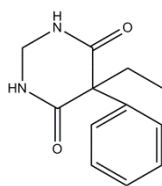
PFBS (Fluoro-surfactant)



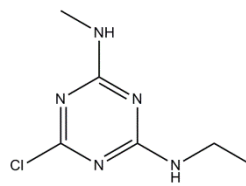
PFOA (Fluoro-surfactant)



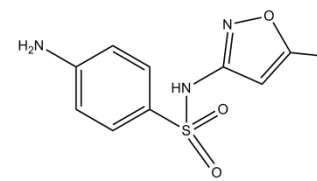
PFOS (Fluoro-surfactant)



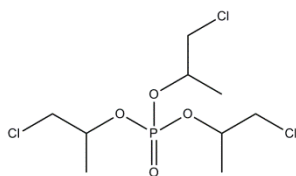
Primidone (Anticonvulsant)



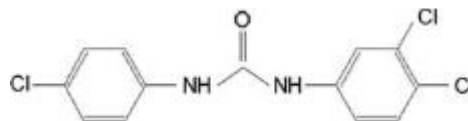
Simazine (Herbicide)



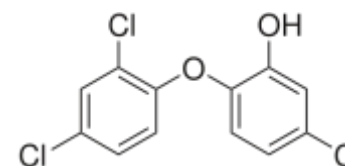
Sulfamethoxazole (Antibiotic)



TCPP (Flame-retardant)



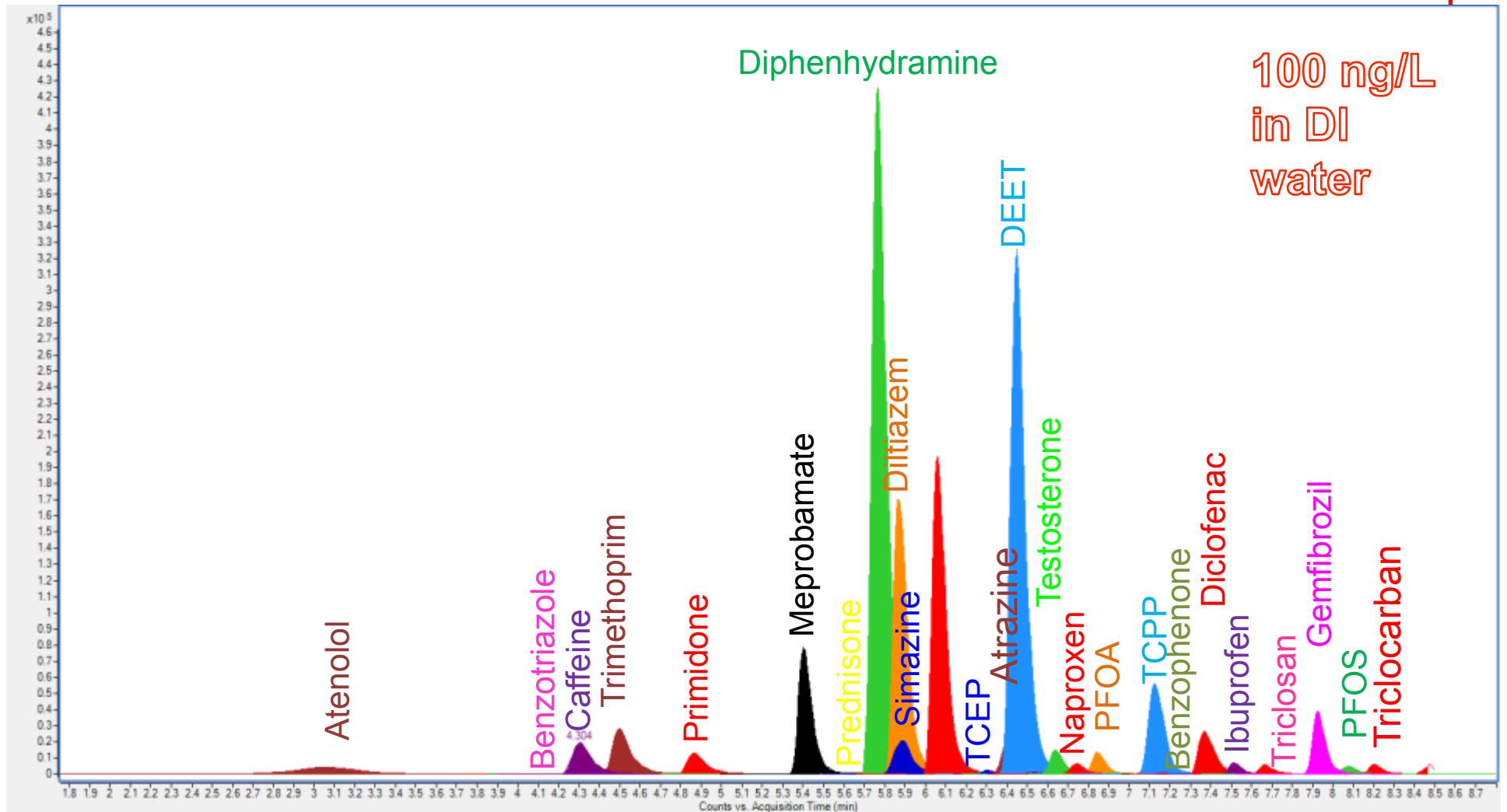
Triclocarban (Anti-microbial)



Triclosan (Anti-microbial)

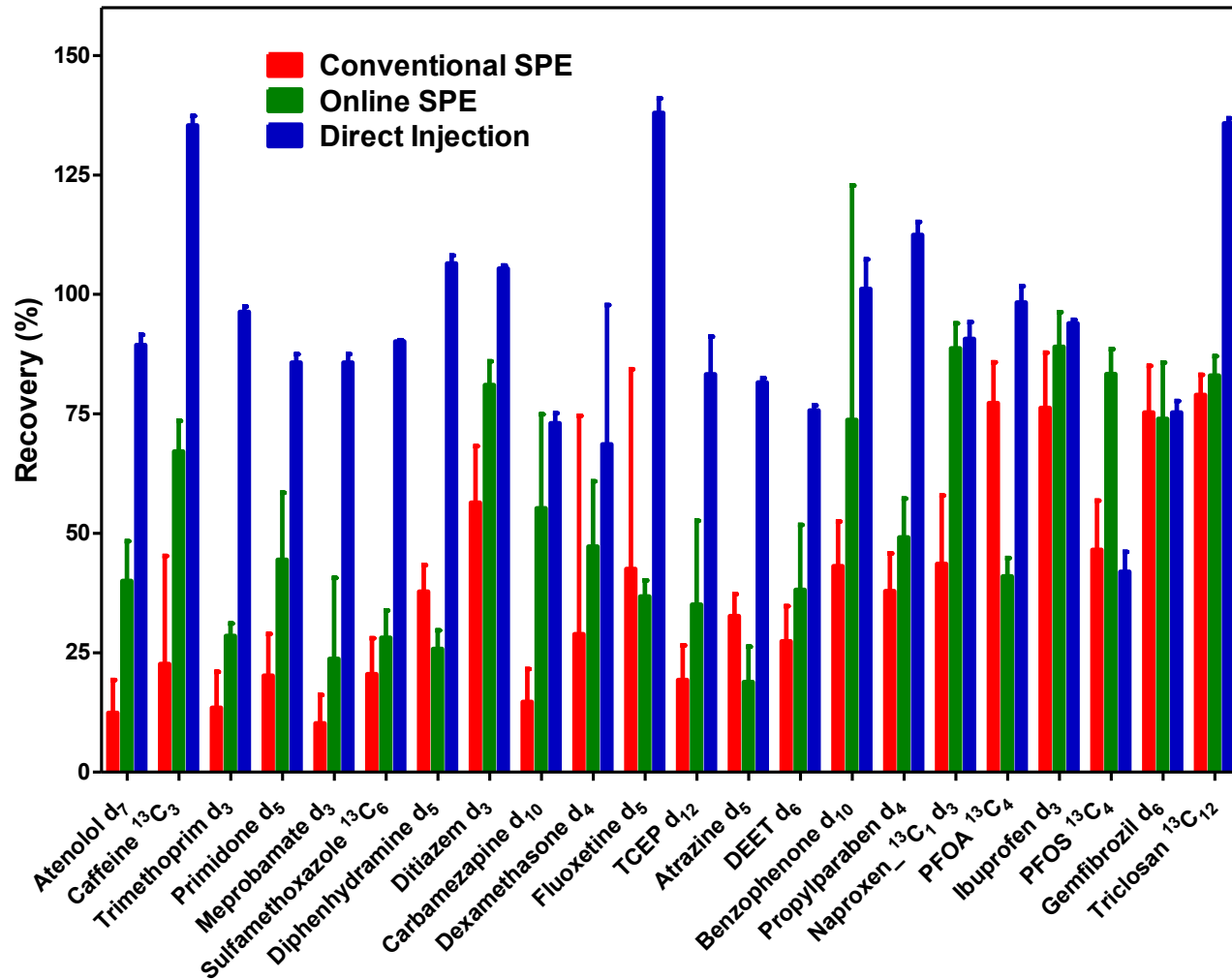


Analytical Method





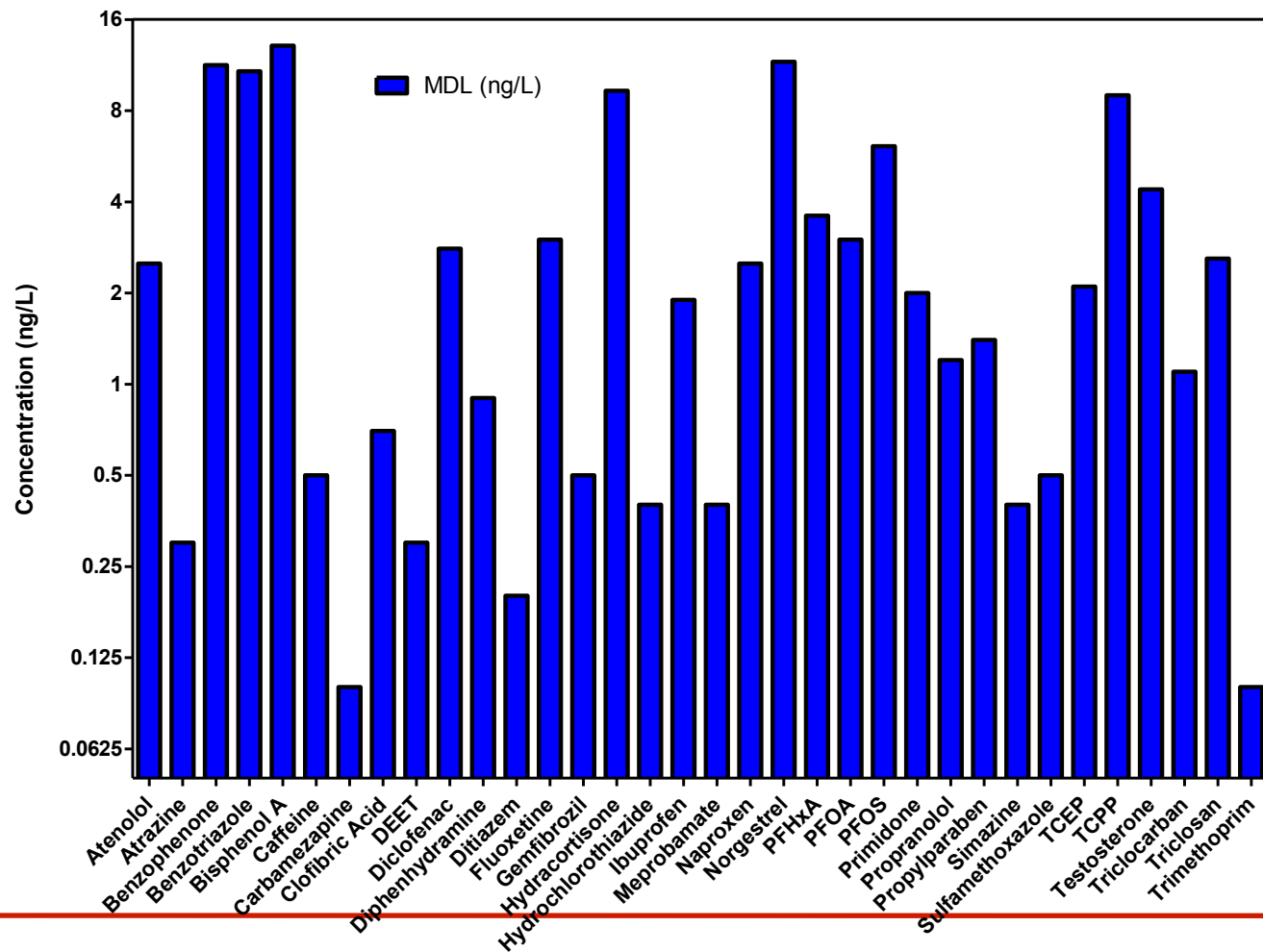
True Recoveries in WW





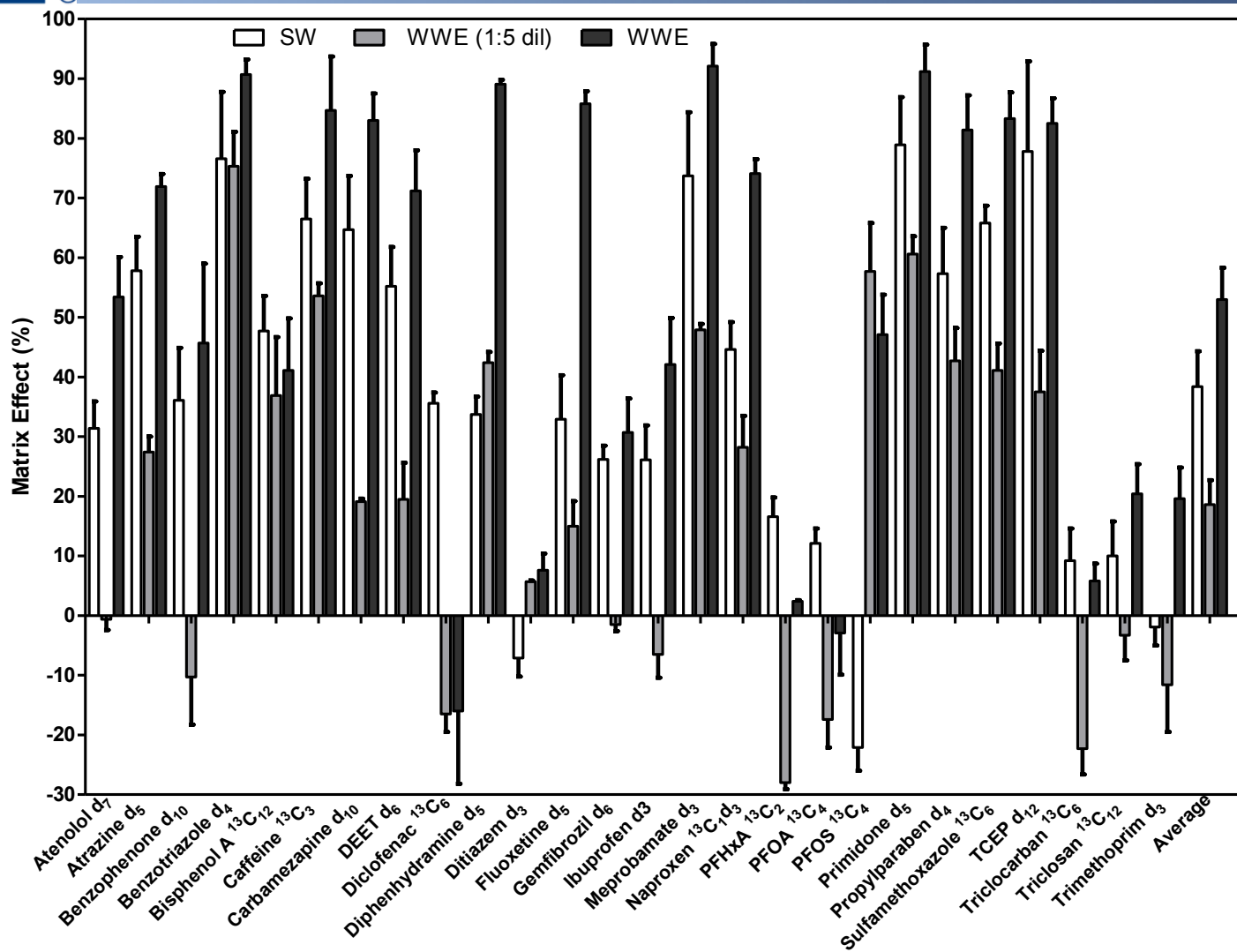
Method Detection Limit

8 replicates using Glaser et al. method



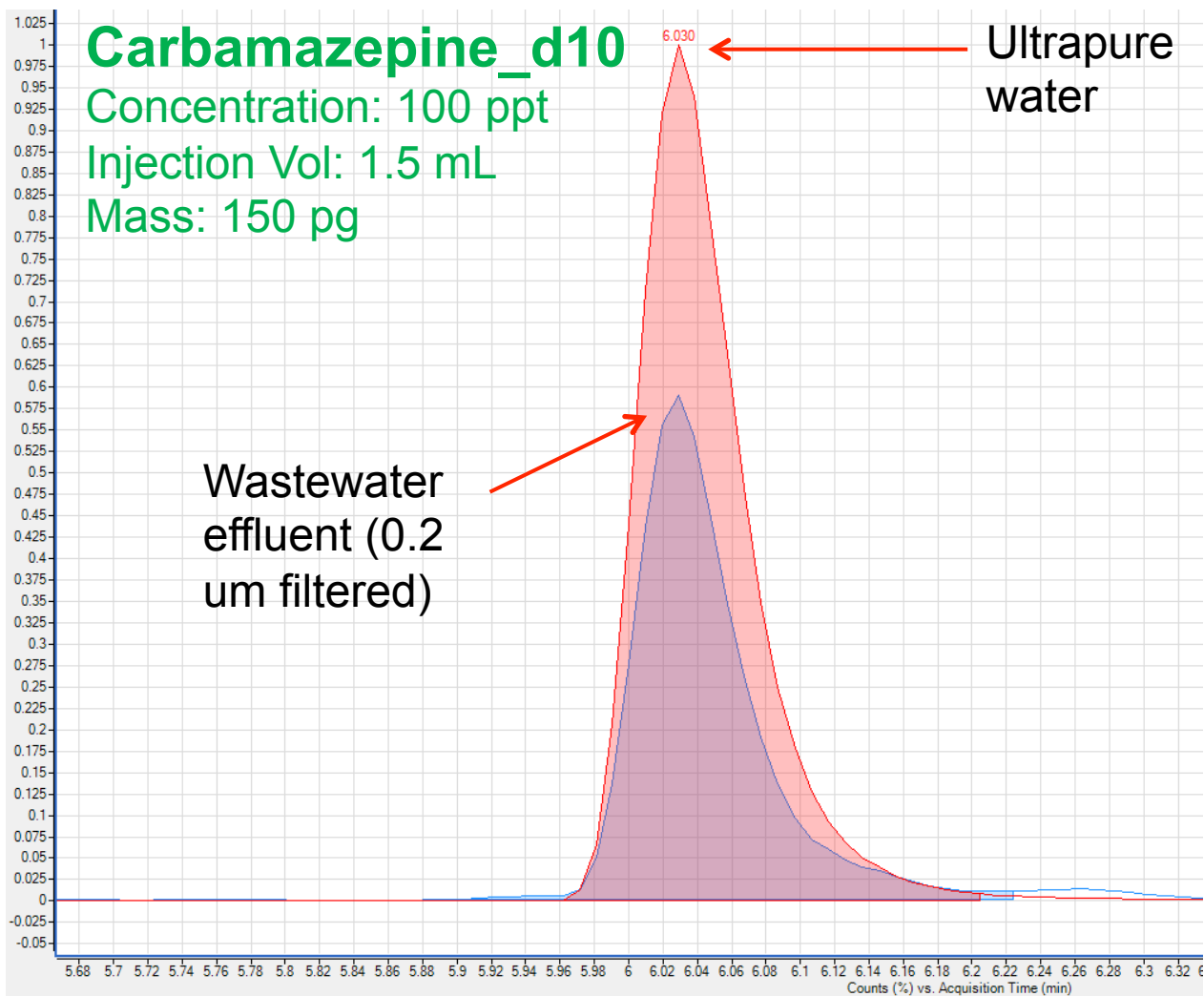


Matrix Effects



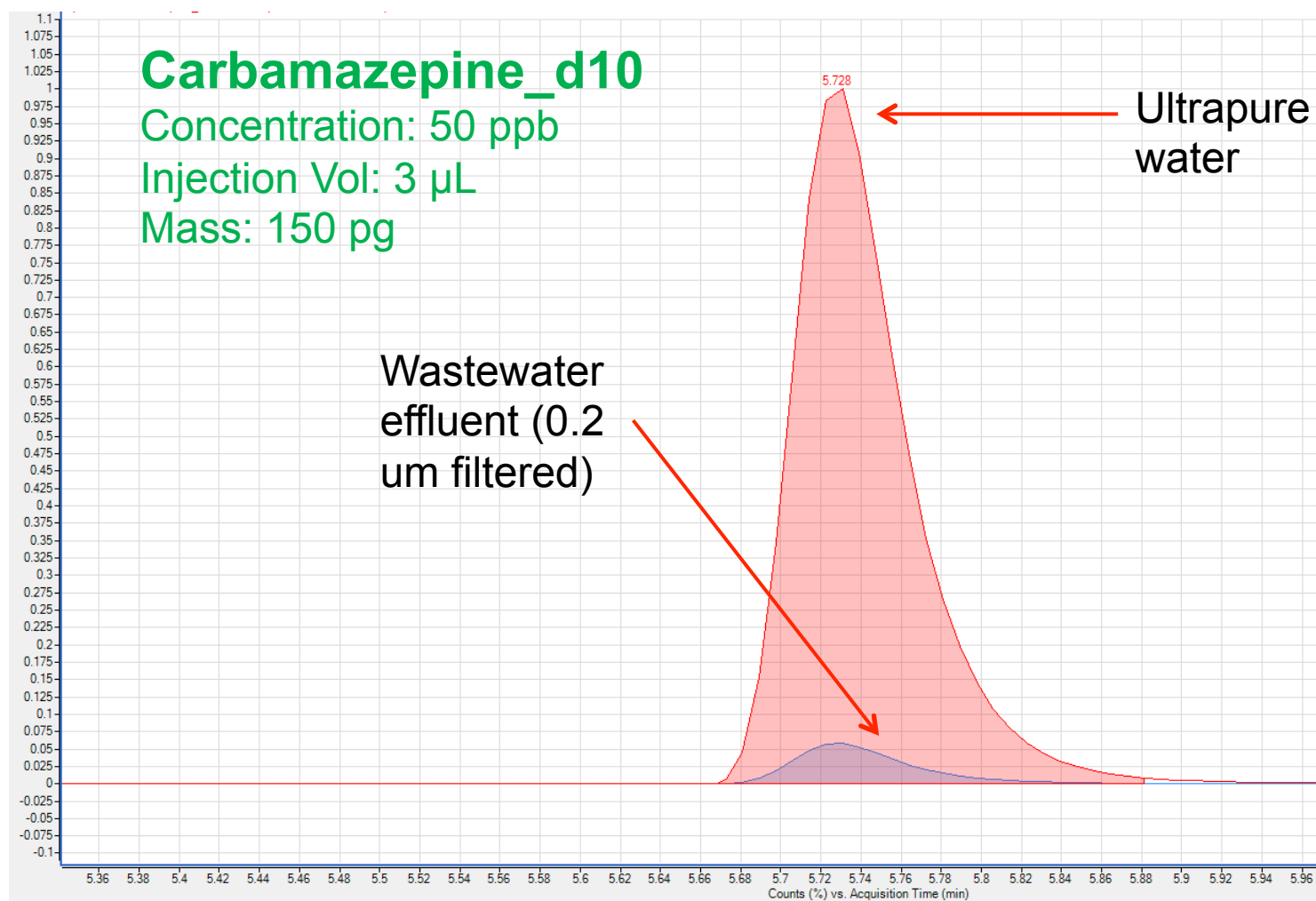


Ion Suppression: Online SPE



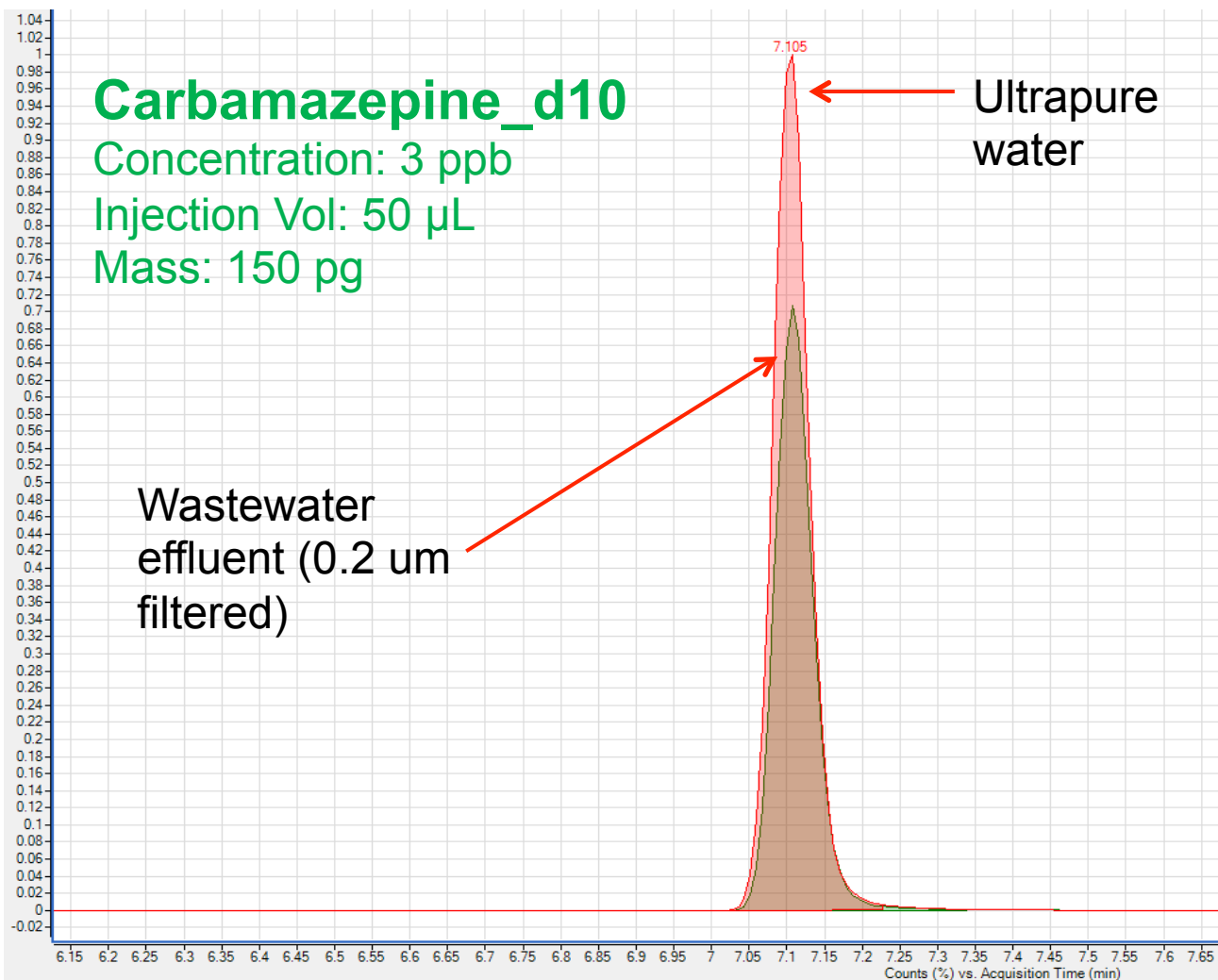


Ion Suppression: Conventional SPE





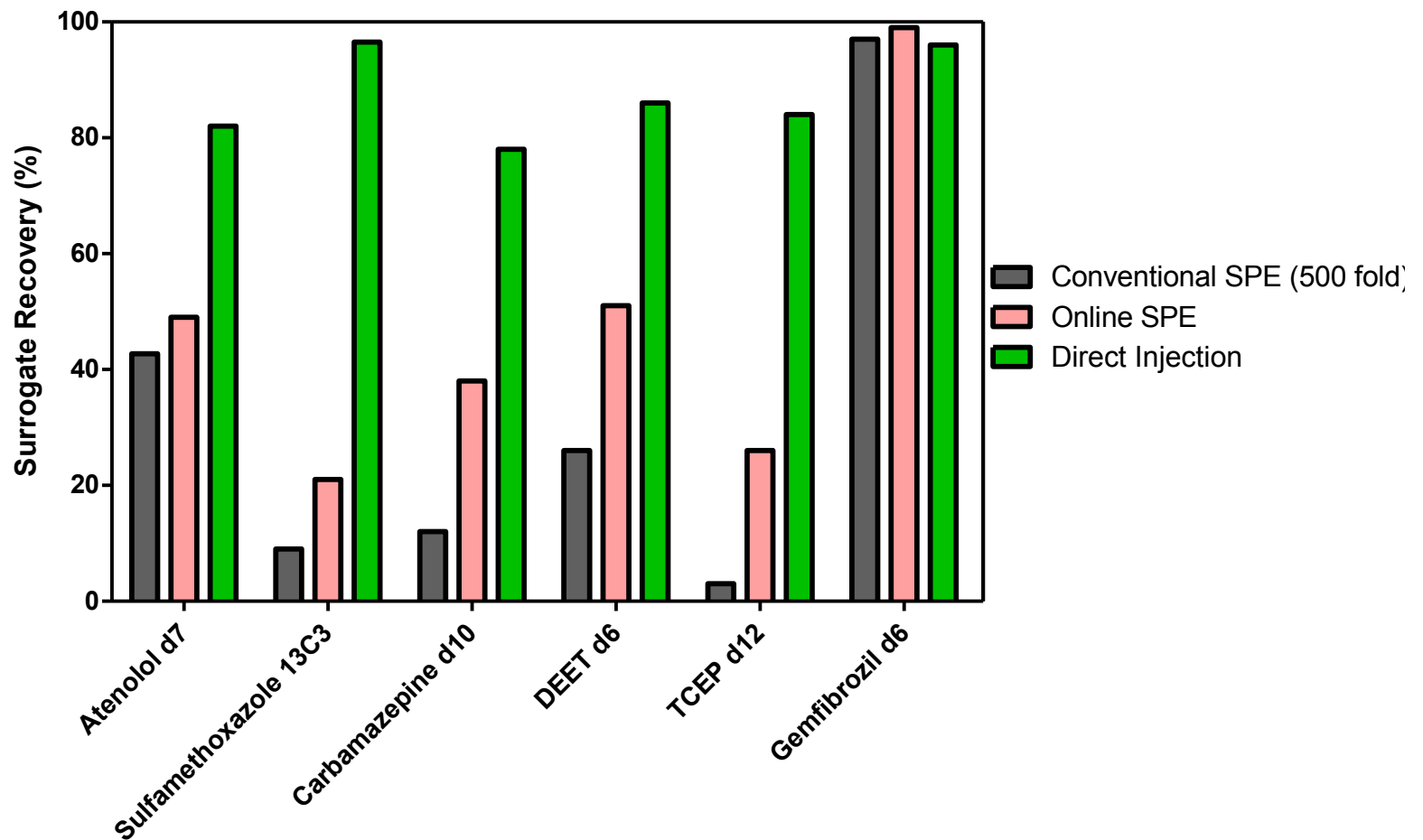
Ion Suppression: Direct Injection





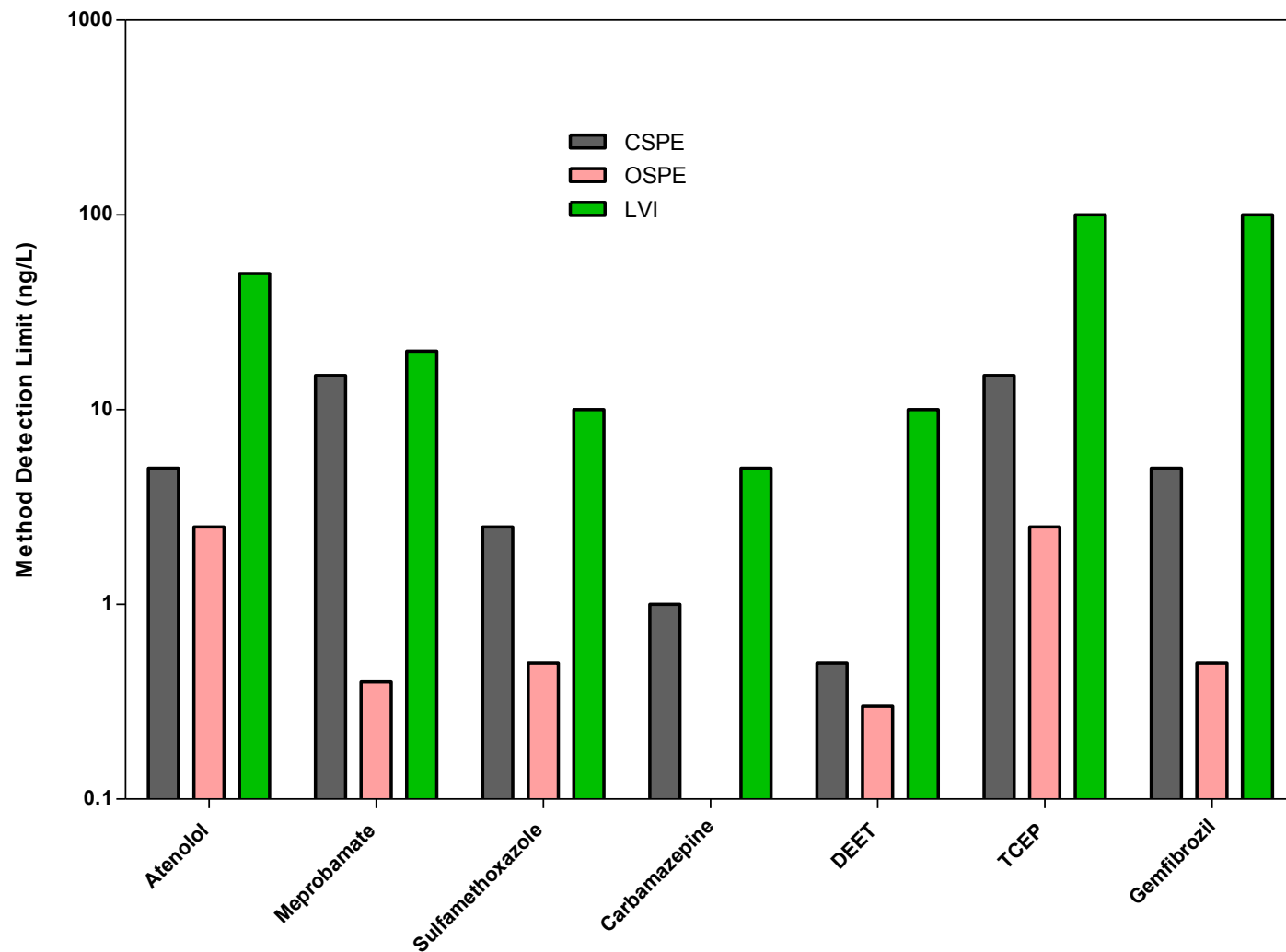
Ion Suppression Effects

Comparison of 3 methods



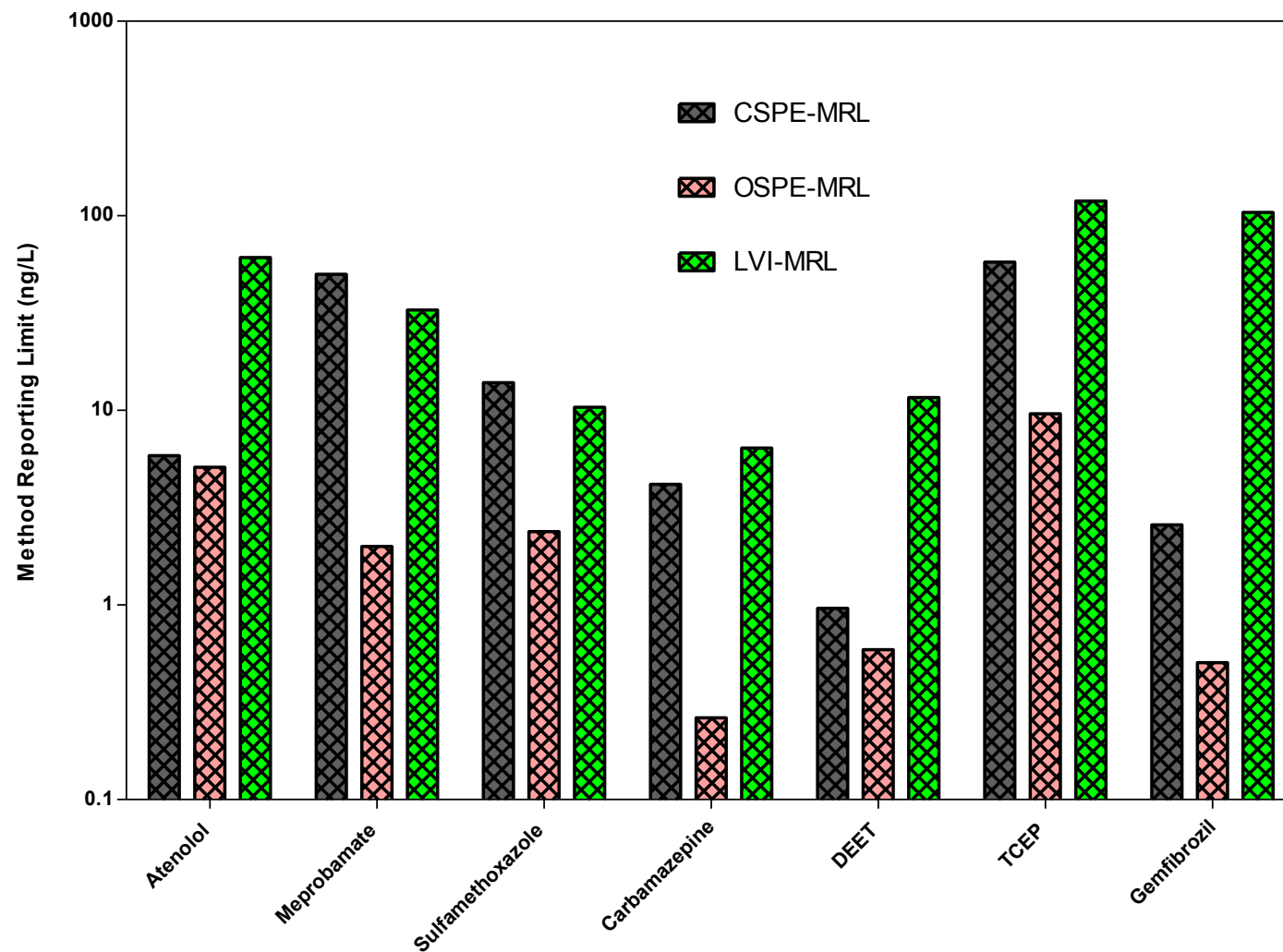


Ion Suppression Effects





Ion Suppression Effects





Analysis of Emerging Contaminants in Water

Conventional SPE Method

Online SPE Method

Direct Injection Method



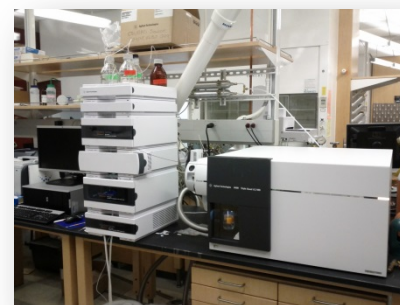
1 L sample



1.5 mL sample



0.1 mL sample



High Sensitivity HPLC Analysis of Contaminants of Emerging Concern (CECs) in Water Using the Agilent 6460 Triple Quadrupole LC/MS System

Application Note

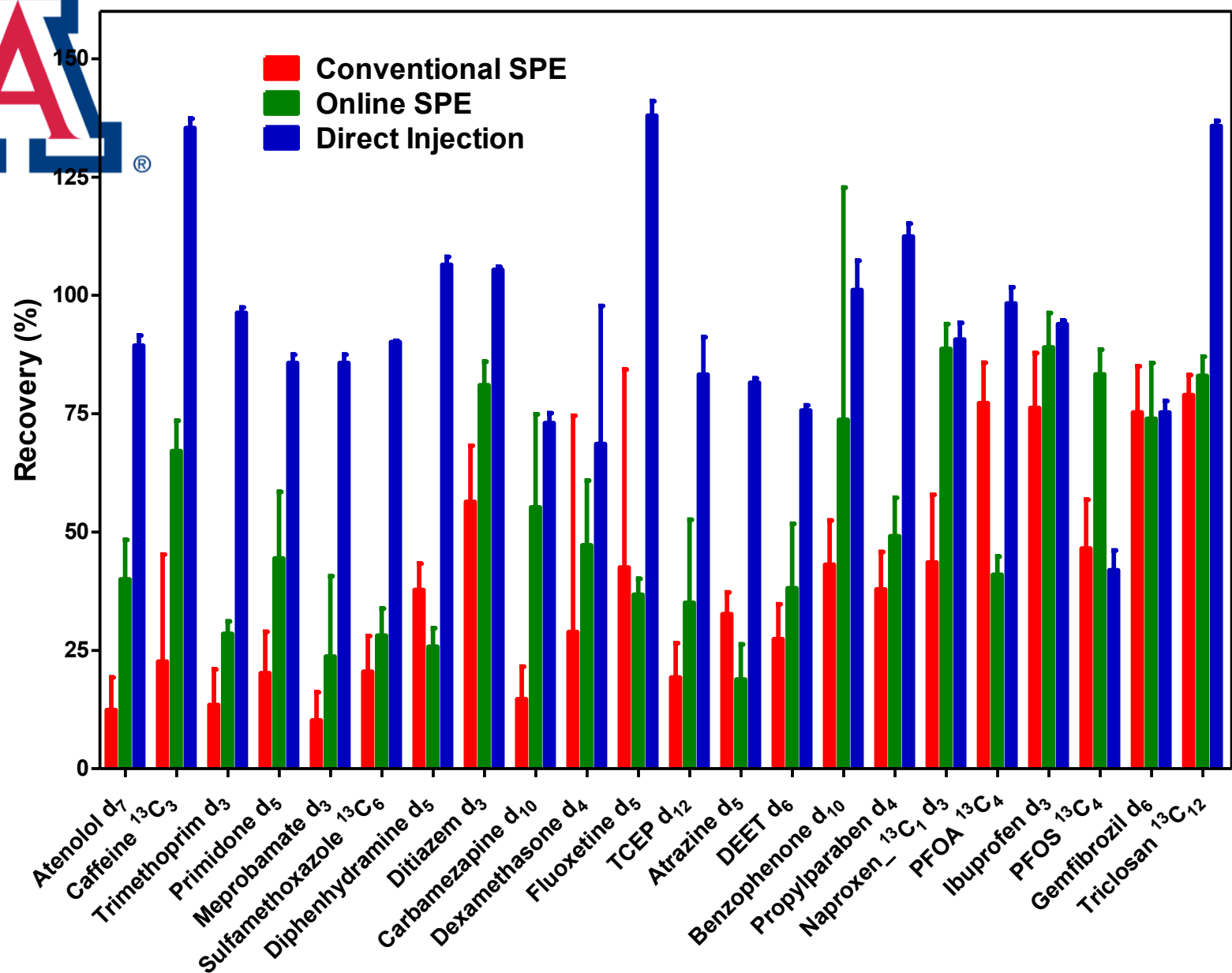
Sensitive LC/MS Quantitation of Trace Organic Contaminants in Water with Online SPE Enrichment

30 min

0.1-20 ng/L

Analysis of Trace Organic Contaminants in Water by Direct Injection Using Agilent 6490 LC/MS/MS with Pos/Neg Switching

15





Conclusions

- ☐ Online SPE allows sensitive analysis of trace organics in water while allowing significant time and labor savings.
- ☐ Method has been proven to be robust in several different water matrixes.
- ☐ Online SPE is significantly less affected by ion suppression compared with conventional offline extraction techniques.
- ☐ LVI is currently not sensitive enough to attain desired MRLs but offers promise with rapid increase in sensitivity of newer mass spectrometers.
- ☐ Use of online SPE with accurate mass detectors (ToF & Q-ToF) could allow for real-time analysis of trace unknowns in water.

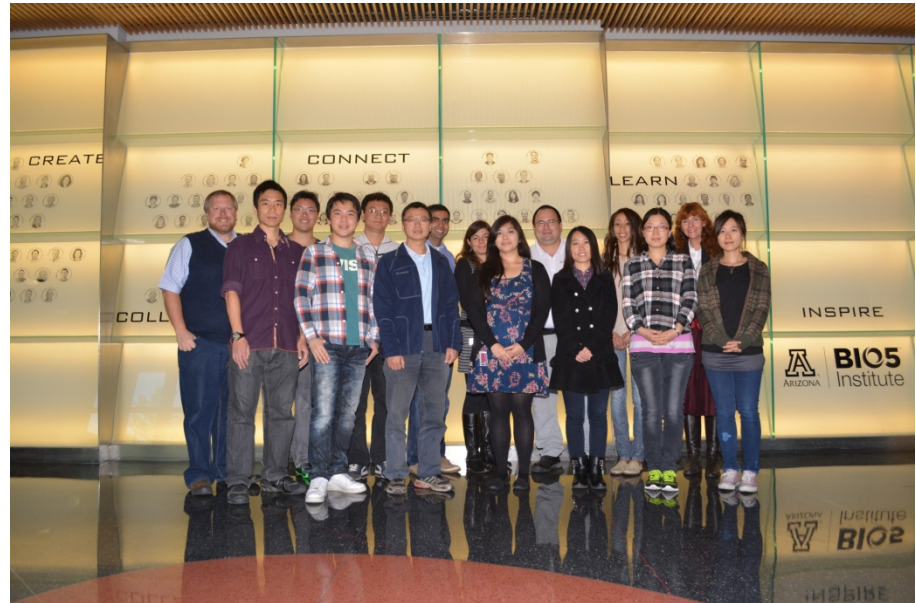


Acknowledgements

Snyder Research Lab

Agilent Technologies

- Joe Weitzel
- Dr. Sheher Mohsin





Questions

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