On-line SPE coupled to UHPLC MS/MS for analysis of multiple TOrCs in water using simultaneous positive and negative electrospray ionization

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Introduction

The presence of pharmaceuticals, personal care products, pesticides, hormones, and other organic contaminants collectively termed as trace organic contaminants (TOrCs) in water has been reported at concentrations varying from a few ng/L to several µg/L in wastewaters. Public concern has risen since the effects of these compounds on humans are largely unknown while adverse effects to aquatic wildlife have been reported. The increasing push for water reuse has made it paramount that not only the analysis be sensitive and robust but also exigent. The growing number of samples along with continuous monitoring associated with water reuse schemes requires rapid and fully automated analytical techniques for the simultaneous analysis of these compounds from vastly varying sub-groups that comprises the TOrCs.

In this study, a single fully automated analytical method for the extraction and analysis of 26 TOrCs using on-line SPE coupled to a tandem mass spectrometer is shown. The method analyzes compounds in both positive and negative electrospray ionization mode simultaneously so each sample is injected only once and allows for significant time and solvent savings. The runtime including extraction and analysis of sample is less than 20 minutes.

The method reporting limits (MRL) for the target analytes varied from 0.1 – 15 ng/L. Further, the method uses only 1.5 mL of sample as compared to the conventional offline SPE method for analysis of water that requires 1000 ml to achieve similar MRLs. Method validation studies were performed with a compound spike in deionized, ground and surface water with recoveries of 70-130% for all compounds. The results of a wastewater effluent were compared to the conventional off-line SPE method and were found to provide similar results when the analysis was corrected for surrogate recovery. However, the online SPE method had significantly less ion suppression than the conventional SPE method.

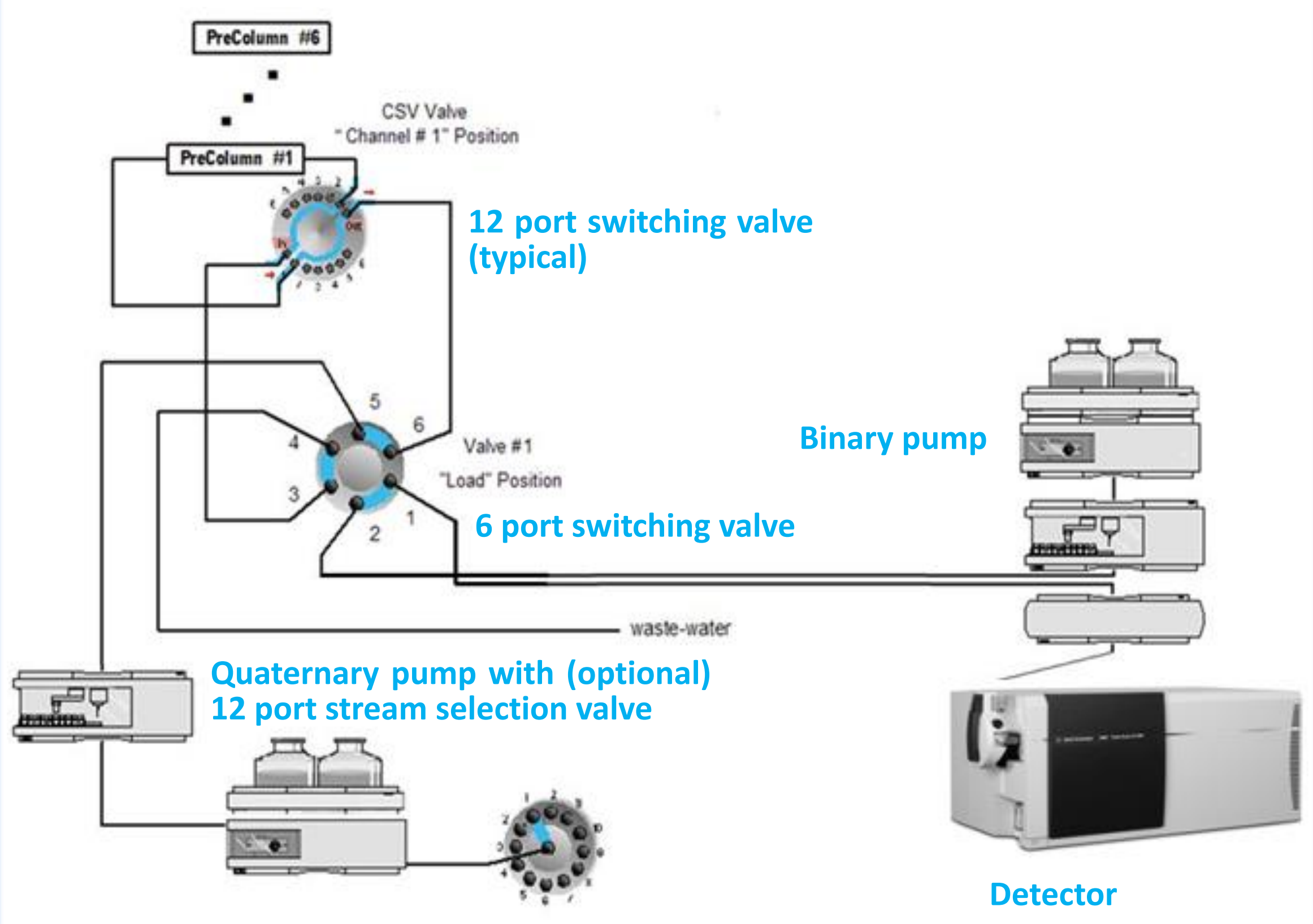
Target Analytes

Compound	Use	MRL (ng/L)	Compound	Use	MRL (ng/L)
Atenolol	β-blocker	5	Meprobamate	Anti-anxiety	0.5
Atrazine	Herbicide	1	Naproxen	Pain-reliever	10
Benzophenone	UV-inhibitor	5	PFOA	Fluoro-surfactant	10
Benzotriazole	Corrosion-inhibitor	10	PFOS	Fluoro-surfactant	10
Bisphenol A	Plasticizer	20	Primidone	Anti-convulsant	15
Caffeine	Stimulant	0.5	Simazine	Herbicide	2.5
Carbamazepine	Anti-convulsant	2.5	Sulfamethoxazole	Antibiotic	2.5
DEET	Insect-repellant	0.1	TCEP	Flame-retardant	1
Diltiazem	Anti-angina	2.5	TCPP	Flame-retardant	0.5
Diphenhydramine	Anti-histamine	1	Testosterone	Hormone	2.5
Fluoxetine	Anti-depressant	10	Triclocarban	Anti-microbial	1
Gemfibrozil	Anti-cholesterol	2.5	Triclosan	Anti-microbial	5
Ibuprofen	Analgesic	10	Trimethoprim	Antibiotic	2.5

Instrumentation

SETUP

The system consists of a quaternary pump with a Trace Enrichment Cartridge (TEC), followed by a binary pump to allow for gradient separations. Switching valves allow for automation.

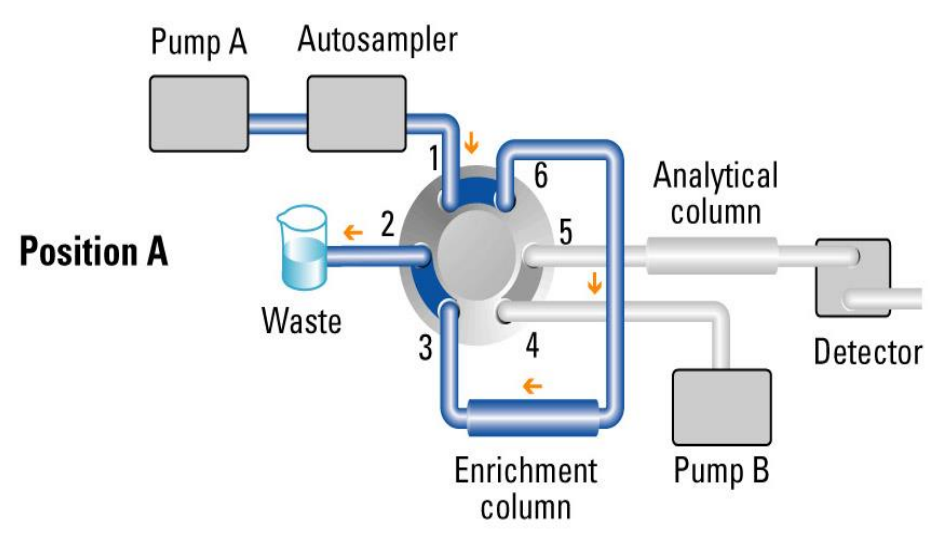


Instrument Configuration and Conditions

SPE system:
- Quaternary pump
- G1329A autosampler with 900 µl head
- 6 port 2 position valve
- 12 port 6 position valve (multiple TEC's)
- 12 port stream selection valve (optional)

RRLC system:
- Binary pump SL
- Well plate sampler SL
- Column department SL

Loading Position:



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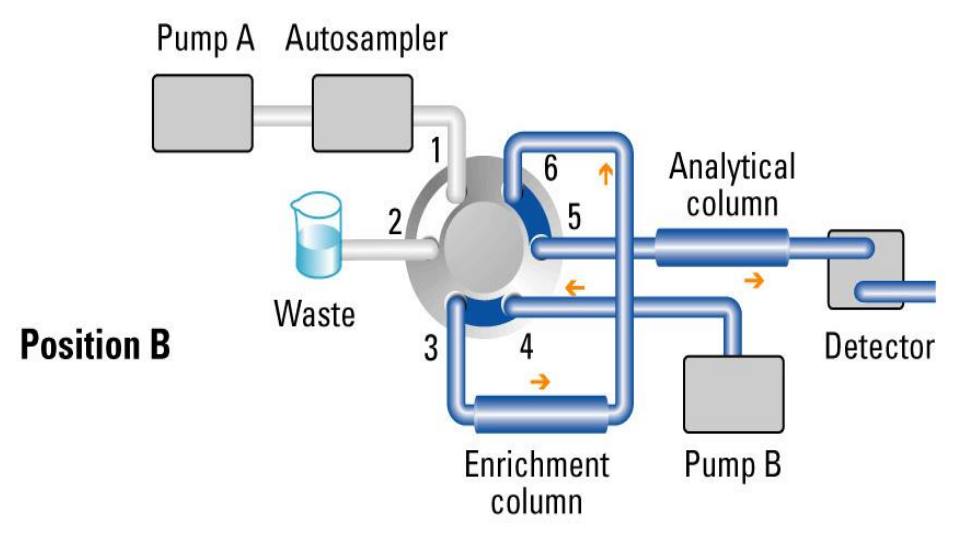
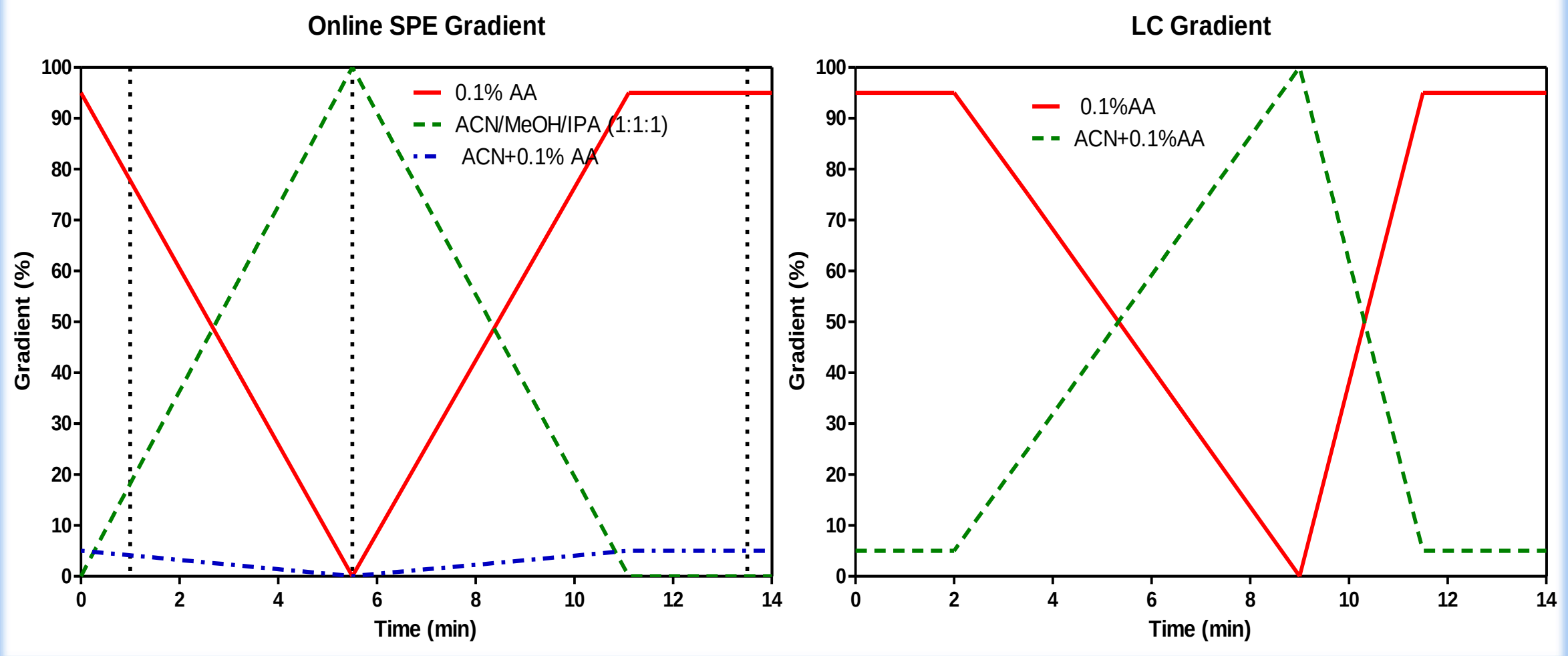


Parameter	Online SPE conditions	LC conditions
TEC/Analytical column	PLRP-S 10 x 2 mm, 15-25 µm	Agilent Poroshell EC120 C18 2.1 mm x 50 mm, 2.7 µm
Temperature	Ambient	30 C
Flow rate	0.7 mL/min	0.35 mL/min
Runtime: 14 min + 1.5 min Post-time		

Gradient:



Results & Discussion

A fully automated online SPE method using the Agilent 6460 LC MS/MS coupled to a 1200 series LC pump has been developed for 26 TOrCs in water with detection limits of 0.1 – 20 pg/mL using a sample volume of only 1500 µL.

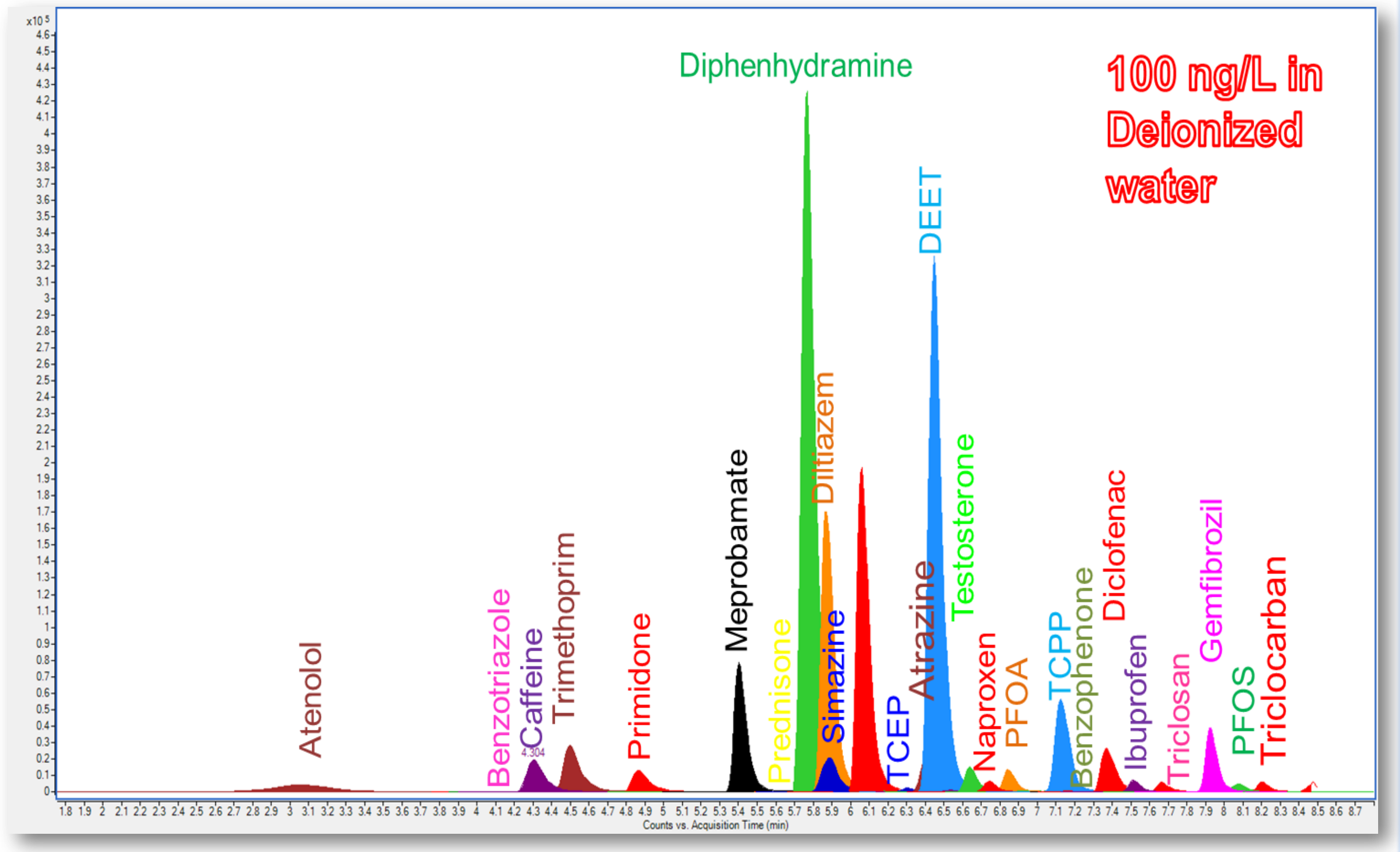
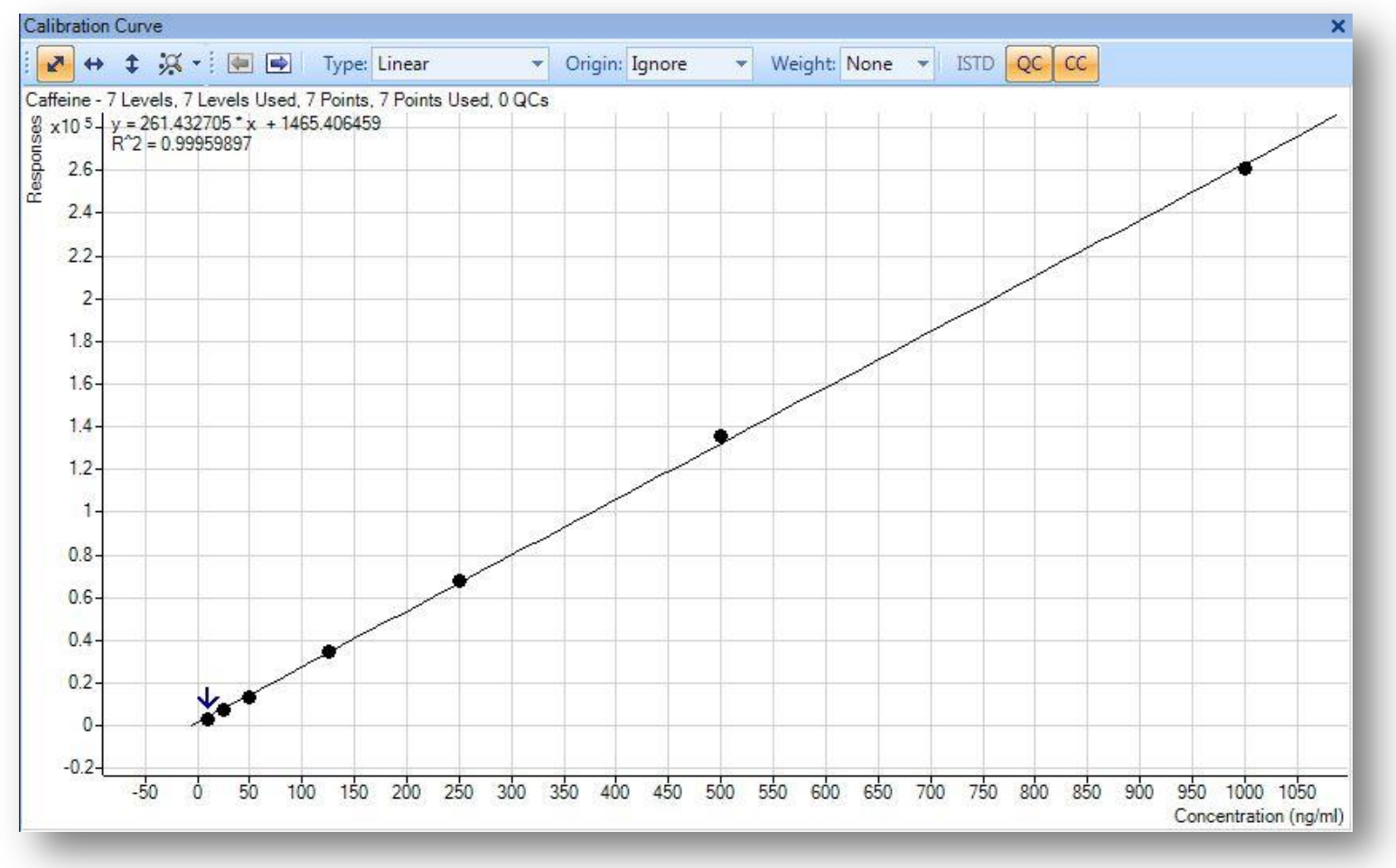
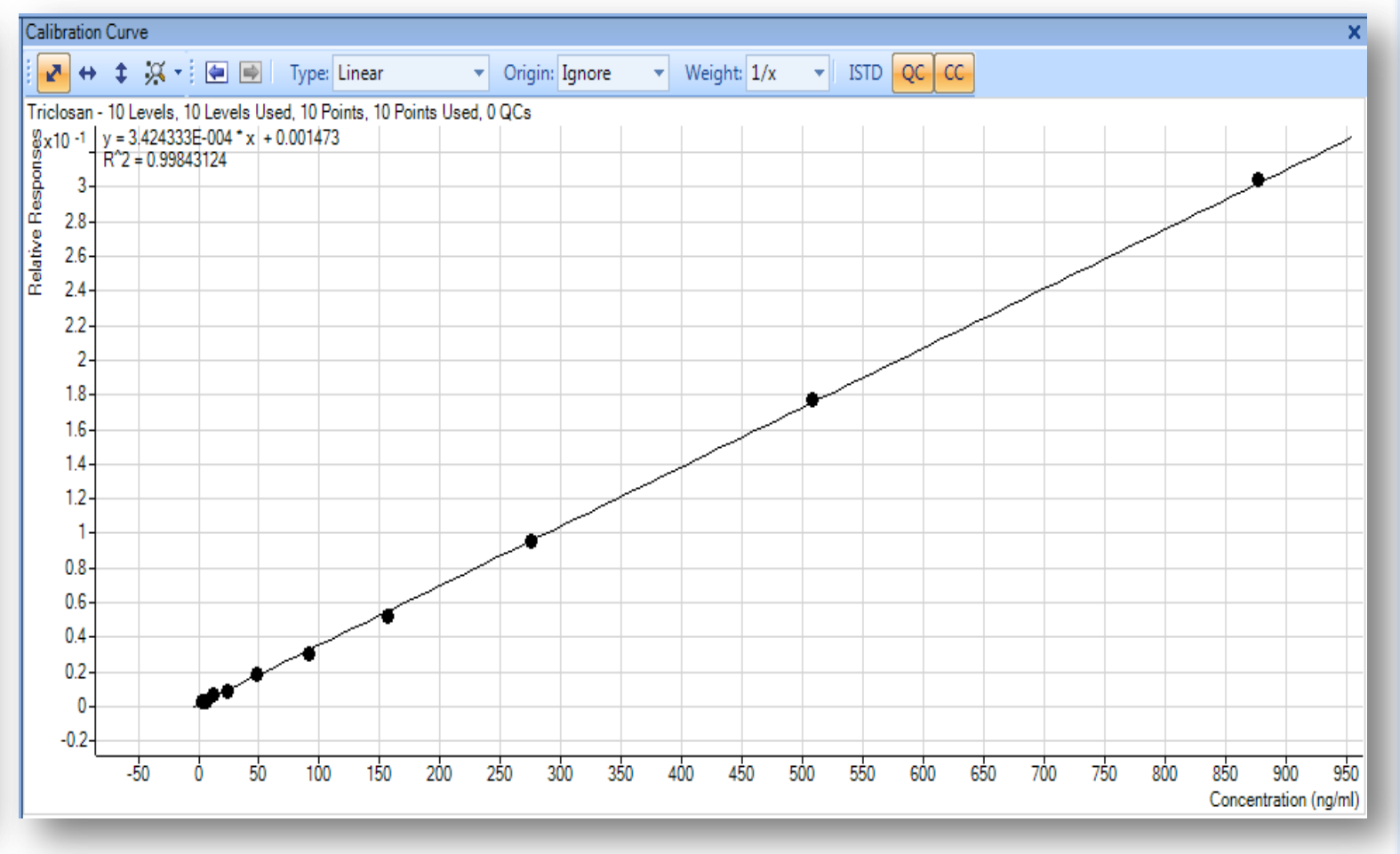


Figure. TIC of 100 ng/L standards in Deionized water

Calibration curves for all compounds had $R^2>0.99$ with more than 3 orders of linearity



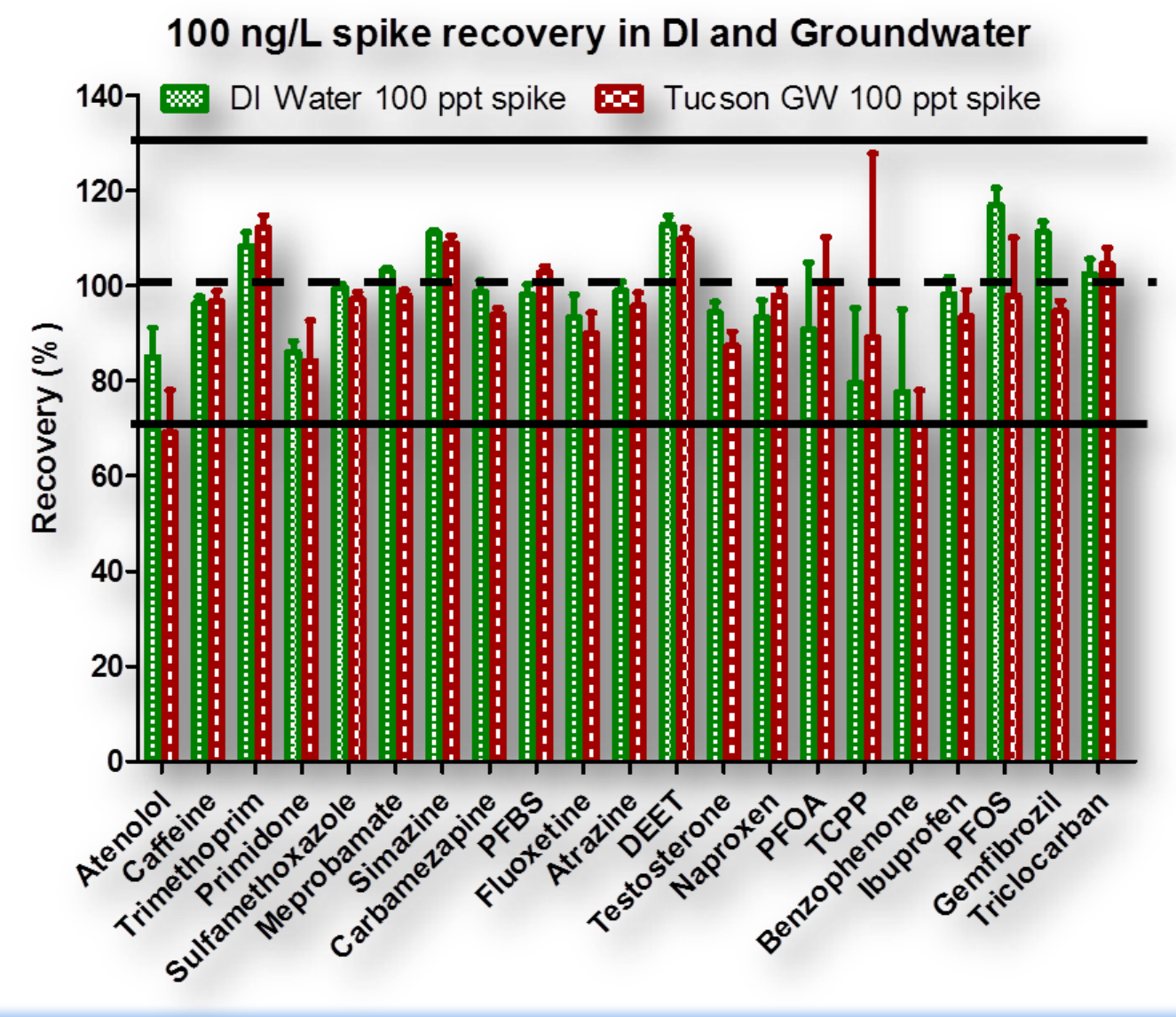
Calibration curve for Caffeine from 5-1000 ng/L

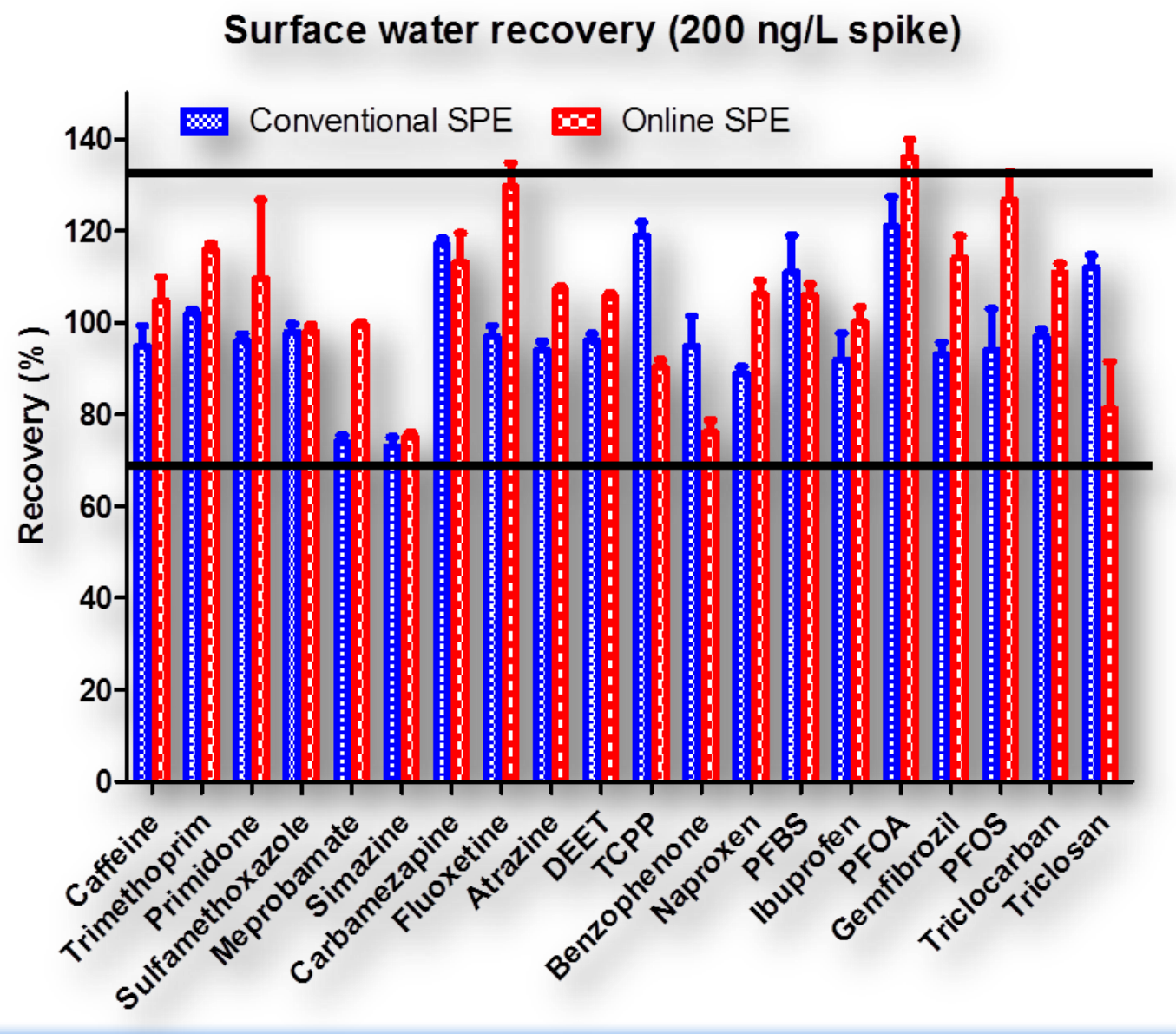


Calibration curve for Sulfamethoxazole from 3-900 ng/L

Method Validation

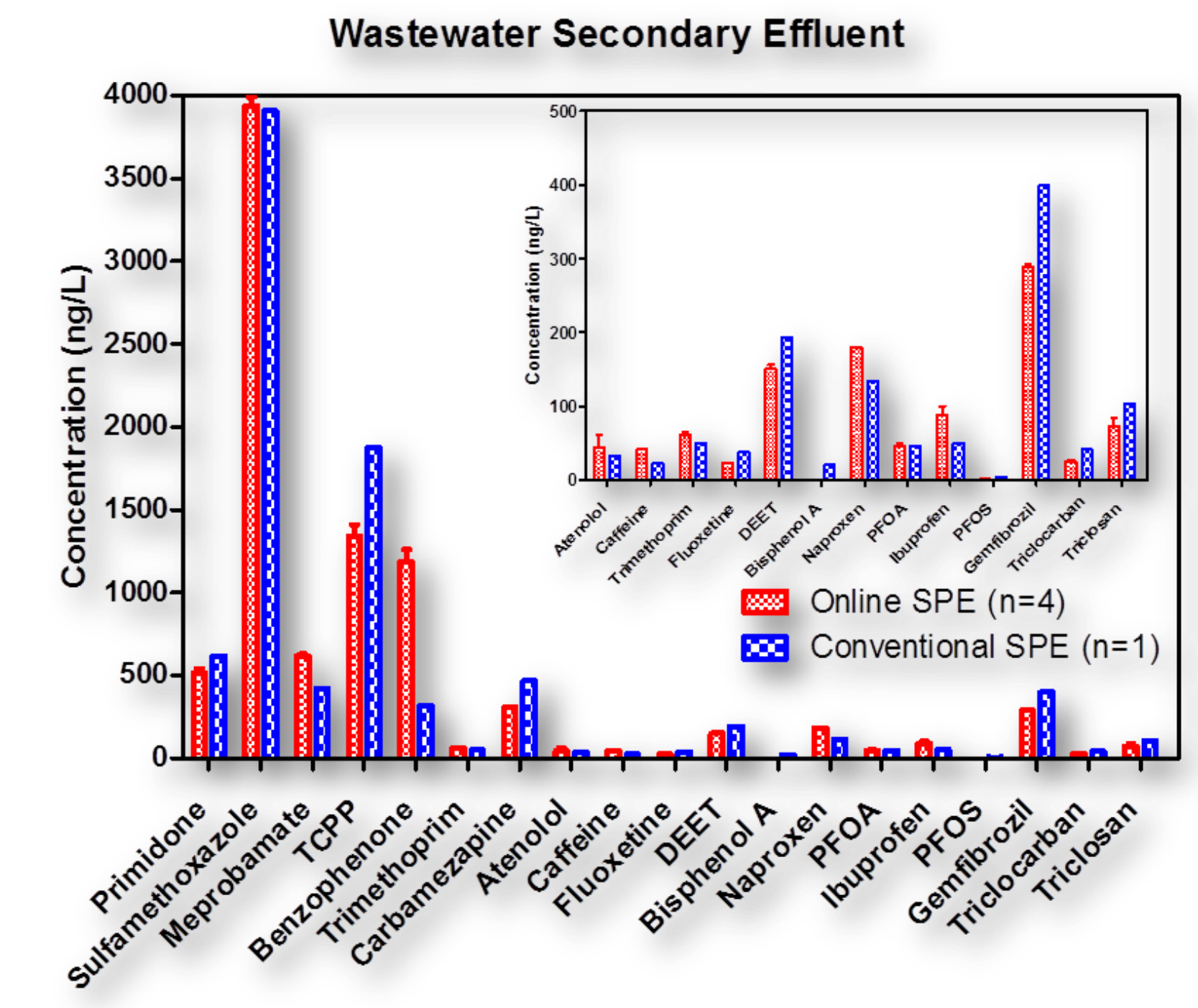
Matrix spike recoveries in different water matrixes provided 70-130% recovery for all compounds and very good comparison between online SPE and conventional offline SPE was found in a surface water.





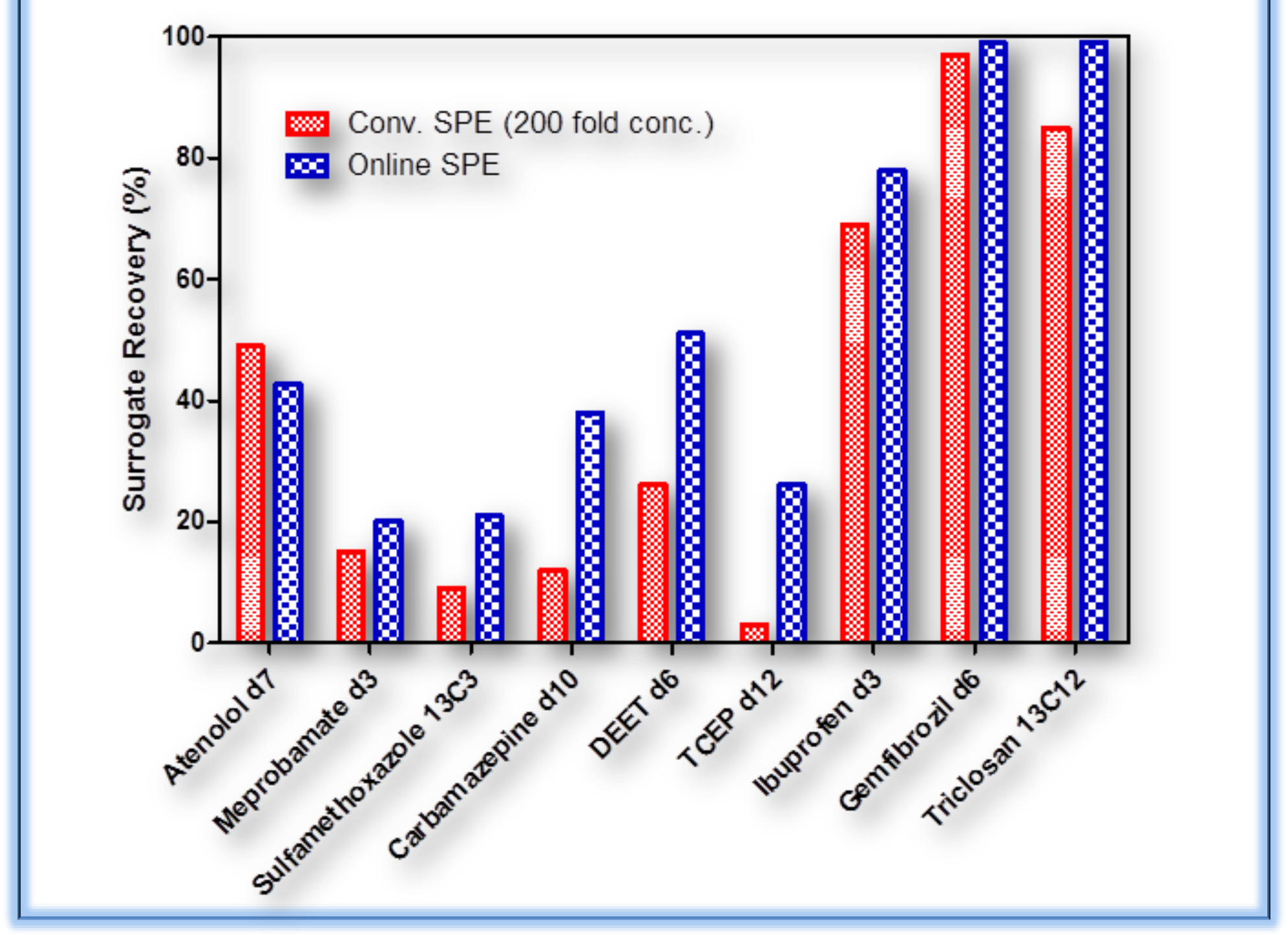
Wastewater Analysis

The method compared well against conventional offline SPE with a 200 fold concentration factor when analyzing wastewater effluent.



ION SUPPRESSION

The online SPE method suffers less ion suppression when compared to the conventional SPE as shown by the recovery of surrogate standards in a secondary treated wastewater effluent



Conclusions

The online SPE using fully automated switching valves, LC dual pump system and a mass spectrometer is capable of sensitive quantification of various trace organic contaminants in water.

The application of this system allows the user significant time, labor and sample savings while not sacrificing sensitivity and robustness.

The method compares favorably to current offline extraction techniques in several different water matrixes.

References

Anumol, T.; Mohsin, S.; Snyder, S., Sensitive LC/MS quantitation of trace organic contaminants in water with online SPE enrichment *Agilent Application Note* **2013**, (5991-1849EN).