AUTOMATED ONLINE SPE/TANDEM MS ANALYSIS OF TRACE ORGANIC CONTAMINANTS IN DRINKING WATER

Agilent Ultivo Triple Quadrupole LC/MS System

Figure 1A. Agilent Ultivo Triple Quadrupole LC/MS.

Figure 1B. Agilent 1290 Infinity FlexCube.

Introduction

A variety of organic molecules originating from pesticides, pharmaceuticals, personal care products, and industrial chemicals used in daily life can be introduced into the environment through domestic and industrial wastewater sources. These molecules are a subclass of compounds collectively known as Trace Organic Contaminants (TOrCs), commonly found in a variety of potable and non-potable water resources. Although not acutely dangerous as highly dilute individual entities, the effects of long-term synergistic exposure due to mixtures of these compounds are still to be determined[1]. While characterization for long-term and chronic toxicity are yet to be established, it is important to monitor their presence in current water resources[2].

Using the online SPE capabilities of the Agilent 1290 Infinity Flexible Cube with the analytical power of the Agilent Ultivo Triple Quadupole LC/MS, we have demonstrated a rapid and sensitive method for automated analysis of trace organic contaminants in drinking water without tedious offline enrichment.

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Methodology

The Agilent 1290 Infinity Flexible Cube Online SPE dual cartridge configuration (Figure 2) allows injection volumes of up to 900 µL for sample enrichment with minimal user intervention, improving accuracy and reproducibility. The dual cartridge setup allows for enhanced sample throughput by equilibrating one cartridge as the other is cartridge is being eluted.

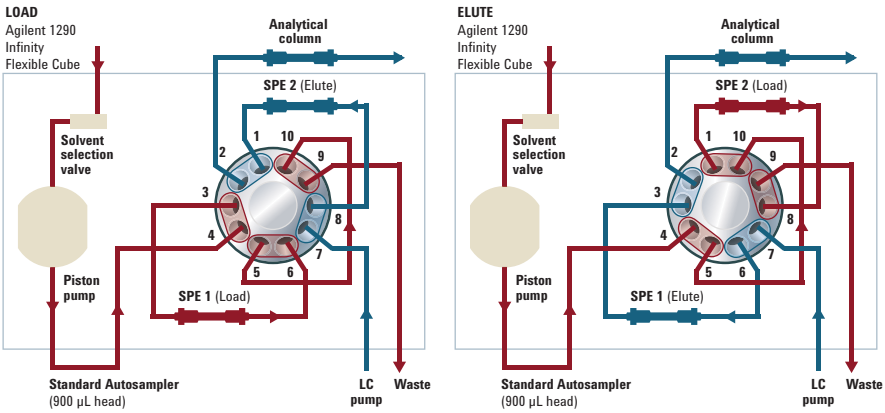
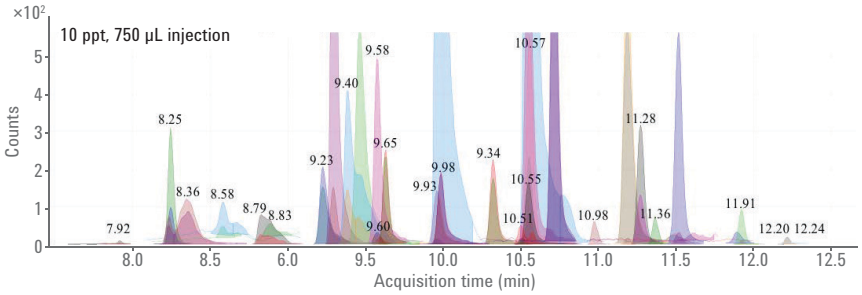


Figure 2. Valve diagram for dual cartridge Online SPE.

In this experiment, a selection of 31 representative TOrCs (listed in Figure 3) were analyzed in spiked water samples from 0.5–200 ng/L (ppt) in concentration. Sample volumes of 750 µL were introduced onto the SPE cartridge for enrichment, then eluted at the 4-minute mark, triggering the start of the HPLC linear gradient. Detection of analytes was carried out on the Ultivo Triple Quadrupole LC/MS using dynamic MRM for maximized sensitivity.



Compound	RT (min)	Compound	RT (min)	Compound	RT (min)
Atenolol	7.92	Clofibric acid	9.60	Propylparaben	10.57
Caffeine	8.25	Hydrocortisone	9.97	Testosterone	10.72
Trimethoprim	8.36	Carbamazepine	9.98	Diclofenac	10.98
Benzotriazole	8.58	Fluoxetine	9.98	TCPP	11.19
Hydrochlorothiazide	8.82	Simazine	10.01	Norgestrel	11.28
Primidone	8.84	TCEP	10.34	Ibuprofen	11.36
Propranolol	9.23	BPA	10.51	Gemfibrozil	11.91
Meprobamate	9.30	Benzophenone	10.52	Triclocarban	12.20
Sulfamethoxazole	9.40	Naproxen	10.53	Triclosan	12.24
Diphenhydramine	9.51	DEET	10.55		
Diltiazem	9.60	Atrazine	10.57		

Figure 3. Signal response after sample enrichment of a 10 ppt spiked water sample with 750 µL injection.

Online SPE, HPLC, and MS parameters

Table 1 lists Online SPE, HPLC, and MS instrument parameters.

Table 1. Instrument conditions.

Online SPE conditions		
SPE Cartridge	Agilent ZORBAX Extend C18, 4.6 × 12.5 mm, 5 µm	
Agilent 1290 Infinity Flexible Cube solvents	A (Load): H_2O with 0.1 % v/v formic acid B (Elute): 1:1 ACN/IPA	
Sample volume	750 µL	
SPE Elution gradient	0 minutes: Load - Pump for 240 seconds H_2O with FA at 1.5 mL/min 4 minutes: Valve Switch (Elute) - Pump for 360 seconds 1:1 ACN/IPA at 1.0 mL/min 8 minutes: Equilibrate - Pump for 240 seconds of H_2O with FA at 1.5 mL/min	
HPLC Conditions		
Column	Agilent ZORBAX RRHD Eclipse Plus C18, 3.0 × 50 mm, 1.8 µm	
Mobile phase	A) H_2O with 0.2 mM NH_4F B) ACN with 0.2 mM NH_4F	
Flow rate	0.350 mL/min	
HPLC Elution gradient	Time (min) 0 4 11 12.5	Mobile phase 5 %B 5 %B 100 %B 5 %B
Run time	4 minutes (sample enrichment) + 8.5 minutes (HPLC gradient) + 2.5 minutes (post run) = 16 minutes total	
MS Conditions		
Gas settings		
Drying gas	11 L/min at 250 °C	
Sheath gas	12 L/min at 375 °C	
Nebulizer	45 psi	
Source voltage		
Capillary voltage	4,000 V(+), 3,500 V(–)	
Nozzle voltage	500 V(+), 500 V(–)	

Quantitative linearity over 0.5–200 ng/L concentration range

Figure 4 illustrates highly linear calibration curves (R^2 >0.99) for a quantitation range of 0.5, 1, 2, 5, 10, 20, 50, 100, and 200 ng/L after Online SPE sample enrichment.

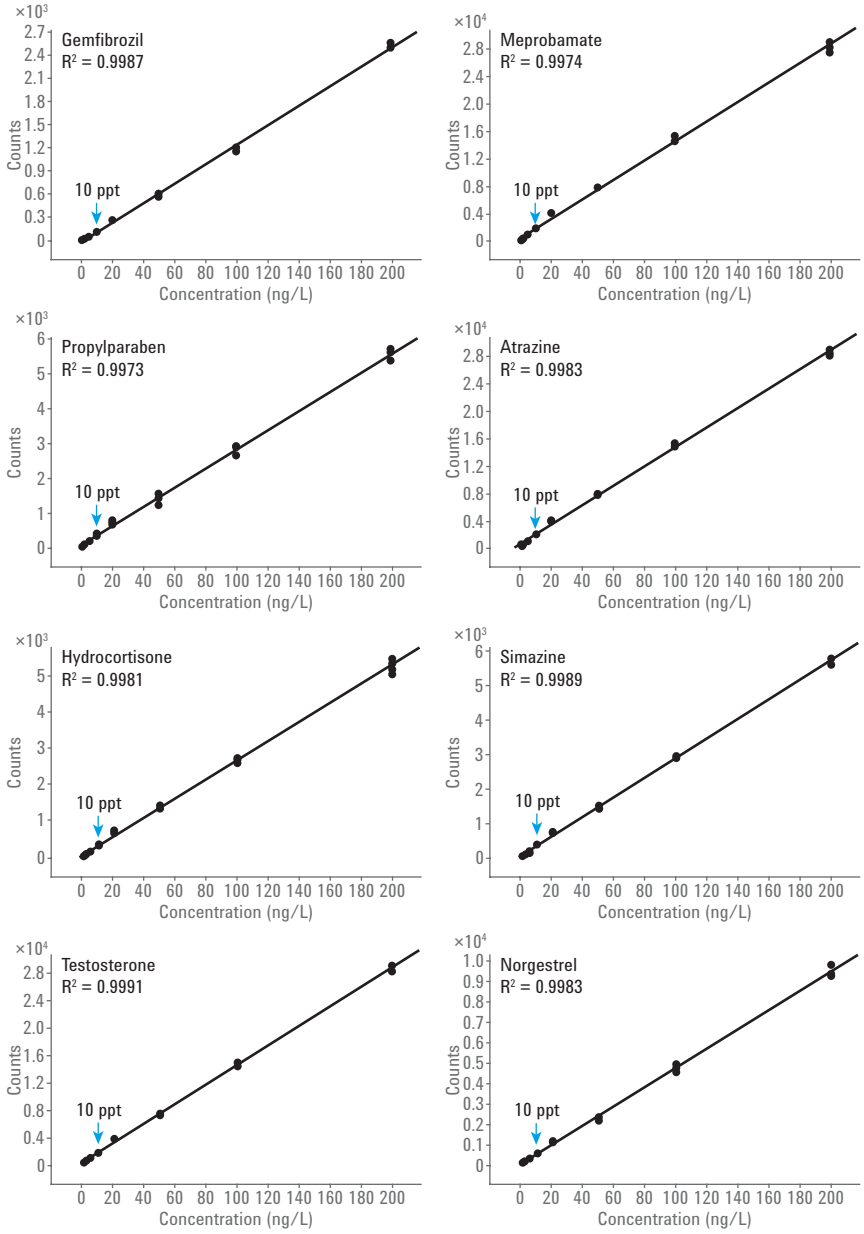


Figure 4. Selected calibration curves demonstrating a high degree of sensitivity and linearity for quantitative analysis.

Chromatographic peak reproducibility over various concentration levels

Chromatographic peak overlays in Figure 5 demonstrate the robust retention time stability and peak shape of the dual cartridge Online SPE setup over a large concentration range (0.5–200 ng/L) for a total of 54 injections.

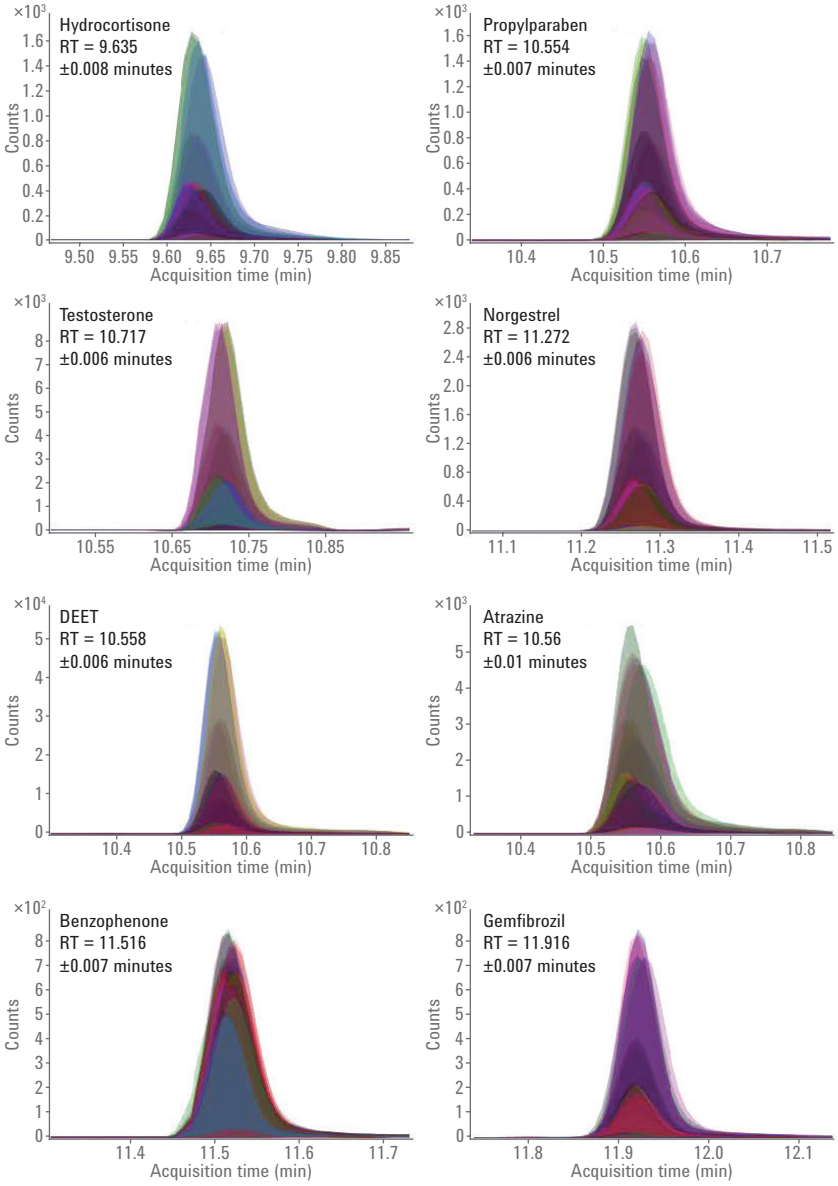


Figure 5. Chromatographic peak overlays and retention times of selected TOrCs.

Limits of detection

Figure 6 illustrates that, of the 31 TOrCs analyzed, 29 compounds have limits of detection that easily fall into the range of 5 ppt or less with only 750 µL of sample.

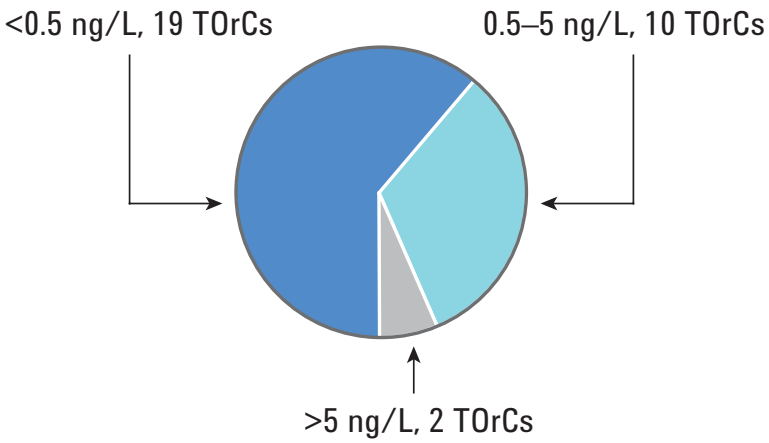


Figure 6. Distribution of the limits of detection of 31 common TOrCs found in water with 750 µL injection.

Conclusions

- The Agilent 1290 Infinity Flexible Cube enables automated Online SPE sample enrichment for trace organic contaminants.
- Enhanced throughput is achieved using a dual-cartridge setup for rapid sample turnaround.
- The Agilent Ultivo Triple Quadrupole LC/MS enables enhanced trace quantitative analysis with a minimized footprint.
- Technical innovations contained in Ultivo provide optimal sensitivity and robustness, without sacrificing the performance of larger instruments.

References

1. C. G. Daughton, T. A. Terhes. Pharmaceuticals and personal care products in the environment: agents of subtle change. *Environ. Health Perspect*. **107**, 907-938 (1999).

2. T. Anumol, S. Snyder. Rapid analysis of trace organic compounds in water by automated online solid-phase extraction coupled to liquid chromatography-tandem mass spectrometry. *Talanta* **132**, 77-86 (2015).

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