Combination of online SPE and direct injection to widen the coverage of HRMS screening of drinking water

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Introduction

Water safety and quality are fundamental to human development and well-being. Safe and readily available water is important for public health, whether it is used for drinking, domestic use, food production or recreational purposes. Over the past 20 years the routine analytical challenges have significantly evolved and today routine labs have to cope with more than 1000 compounds, which puts a significant burden on how they run their lab infrastructure. Targeted acquisition methods are increasingly complemented by untargeted acquisition methods due to increasing screening requirements as well as to increasing interest in the occurrence of contaminants of emerging concern to support next generation time series analysis.

The sensitive analysis of polar and semi-polar compounds in one analytical run is challenging. Online SPE reduces time and labor and enhances the sensitivity, but is facing one challenge: the affinity of polar compounds to a non-polar stationary phase is weak and they will break through the sorbent bed even with water as the loading solvent. With direct injection, polar compounds can be accounted for, but those compounds which would be amenable to SPE, show low sensitivity and exhibit low response, thus their LOD/LOQ will be higher.

The aim of this work was to take profit of the sensitivity enhancements of online SPE in combination with direct injection to retain polar compounds and to develop a multi-residue high resolution mass spectrometry (HRMS) based screening method for the determination of pesticides of a wide polarity range with a single analytical run.

Experimental

Hardware

The configuration of the LC system used was based on the Agilent InfinityLab Online SPE system.

- Agilent 1260 Infinity II Multisampler (G7167A) with 900 µL loop and metering device, standard wash
- Agilent 1260 Infinity II Quaternary Pump VL (G7111A)
- Agilent 1290 Infinity Thermostatted Column Compartment (G1316C)
- Agilent 1290 Infinity Binary Pump (G4220A)
- Agilent 1290 Infinity Flexible Cube (G4227A) with two valve drives:
  - Agilent 2-position/-port duo valve head (5067-4244) with two additional 100 µL loops and SPE cartridges
  - Agilent 2-position/10-port valve (5067-4240)
- Agilent 1290 Infinity Valve Drive (G1170A) with Online SPE High Volume Injection Kit (G4745A) with 2-position/6-port valve and a 5 mL loop
- Agilent 6550 LC/Q-TOF system (G6550BA)

Samples and methods

Bottled water (France), tap water (Germany), and surface water (Germany) were used.

QTOF Instrument parameters

Gas Temp:	200°C
Gas Flow:	16 L/min
Nebulizer:	30 psi
Sheath Gas Temp:	350°C
Sheath Gas Flow:	12 L/min
Capillary Voltage:	4000 V
Nozzle Voltage:	500 V
Fragmentor Voltage:	380 V

Positive ionization mode

Acquisition mode:	All Ions
Collisions Energy:	0, 20, 40 V
Mass Range:	30-1050 m/z
Acquisition Rate:	4 spectra/sec
Funnel Voltages:	150/60 V

Software

- Agilent MassHunter Acquisition B.08.00
- Agilent MassHunter Qualitative Analysis 10.0
- Agilent MassHunter Quantitative Analysis 10.0

Experimental

Online SPE Chromatographic Method

Column	Raptor ARC-18 2.7 µm, 100 x 3 mm
SPE cartridge	PLRP-S Cartridges, 4.6 × 12.5 mm, 15 to 20 µm (5982-1270)
Solvents	A: H2O + 5 mM NH_4HCO_2 B: MeOH:ACN (50:50) + 5 mM NH_4HCO_2
Gradient	0 – 19 min: 0 % B 19 – 19.50 min: 60 % B 19.50 – 26.20 min: 75 % B 26.20 – 26.4 min: 100 % B 26.40 – 31 min: 100 % B
Flow rate	350 µL/min
Col. Temp.	25 °C
Injection	Injection volume: 2 x 900 µL on SPE cartridge and 100 µL in extended loop, Needle wash: 3 s H2O:MeOH (10:90)

Enrichment:
0 – 18 min: 2 mL/min H2O + 10mM NH_4HCO_2
18 – 19 min: 2 mL/min H2O + 10 mM NH_4HCO_2 (switch SPE)
19 – 22 min: 2 mL/min H2O + 10 mM NH_4HCO_2/ACN (1:1)
22 – 25 min: 2 mL/min ACN
25 – 26 min: 2 mL/min H2O + 10 mM NH_4HCO_2

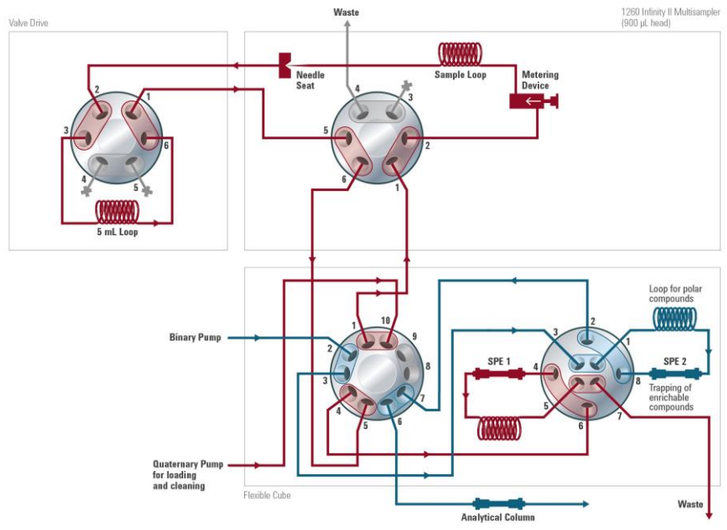

Figure 1: Online SPE setup

Online SPE Method Setup

Run time	0 – 18 minutes	18 – 28 minutes
HPLC Pump	Isocratic hold + post time for analytical column	Gradient run
Online SPE	Injection and loading SPE 1 with 2 x 900 µL plus 100 µL direct injection into loop	Cleaning and conditioning SPE 2

Results and Discussion

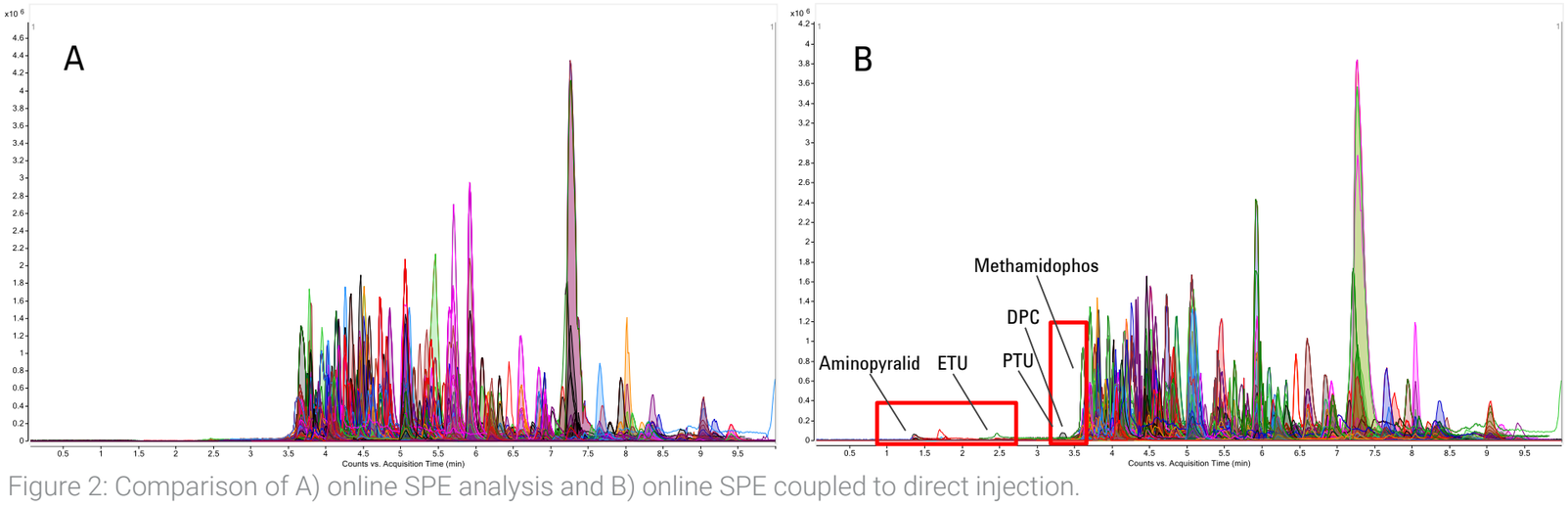

Figure 2: Comparison of A) online SPE analysis and B) online SPE coupled to direct injection.

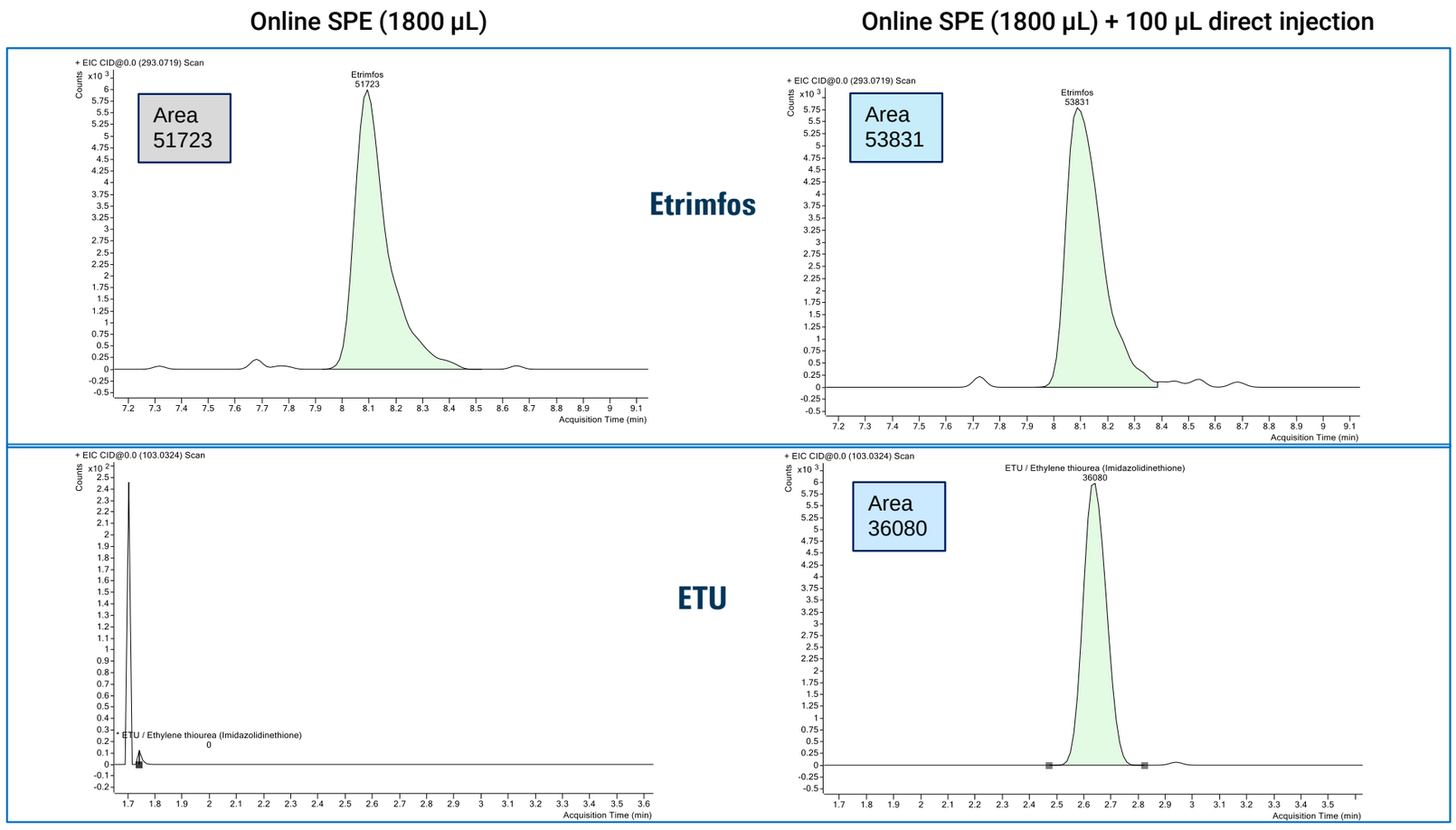

Figure 3: Direct injection coupled to online SPE enables the analysis of polar and semi-polar pesticide simultaneously. Evaluated concentrations were 50 ng/L for ETU (non-SPE amenable) and 2.5 ng/L for etrimfos (SPE amenable).

Conclusions

- Development of a rapid and sensitive multi-residue online SPE LC/MS/MS method for the analysis of relevant pesticides.
- One analytical run to cover polar and semi-polar pesticides by combining direct injection with a high-volume online SPE.
- Combined approach maintains flexibility, reaches high sensitivity and facilities increased throughout.
- Enables the analysis of analytes of different physicochemical properties using an overall run-time of just 31 minutes.