MULTI-RESIDUE METHOD FOR PESTICIDES, PHARMACEUTICALS AND PERSONAL CARE PRODUCTS (PPCPs) IN WATER BY DIRECT INJECTION USING UHPLC-MS/MS

Waters Corporation, Wilmslow, UK

INTRODUCTION

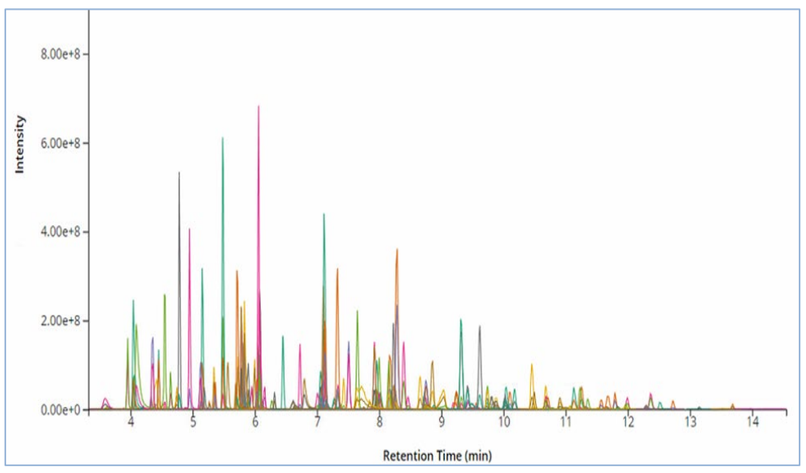
- In recent years, there has been increasing concern about the presence of pesticides, pharmaceutical and personal care products (PPCPs) in water bodies throughout the world. The effect of these emerging contaminants on human health and their potential impact on the environment is not yet fully understood. As concerns continue to grow, many government agencies around the world are funding studies to assess if PPCPs can cause harmful ecological effects.
- Many publications have shown that PPCPs are present at parts-per-trillion (PPT) levels in rivers and streams highlighting the need for methods that are able to detect compounds at these trace levels. In addition to the low-level detection of these compounds, a major analytical challenge for analysis lies in the wide chemical diversity of compound classes and structures, examples of which are shown in *Figure 1*. Furthermore, the complexity of the water samples requiring analysis can be very diverse.
- The recast Drinking Water Directive entered into force in January 2021 and is the EU's main law on drinking water. It commits EU member states to achieve a common goal of 'good chemical and good ecological status' for all ground and surface waters. It concerns the access to, and the quality of water intended for human consumption in order to protect human health and ensures an integrated approach to water management, respecting the integrity of entire ecosystems, and by regulating individual pollutants and setting corresponding regulatory standards.
- Another layer committing to water quality is a watch list mechanism which was established to improve the information around identifying and monitoring emerging substances of concern. Member states must monitor the listed substances at least once a year for up to four years. The watch list was established in 2015, and updated most recently in 2022, and on these lists are increasing amounts of pharmaceuticals as well as personal care products.

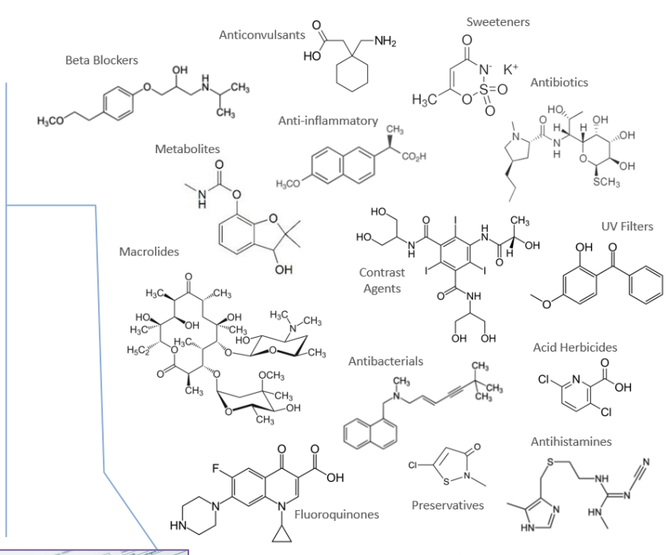
METHOD

Sample preparation, extraction and analysis:

Water was collected from sources of known soft and hard water areas and from surface water locations in the UK. Mineral water was purchased from a UK retail outlet and stored in its original container. All samples were stored at refrigerated conditions. Prior to analysis acetic acid to the equivalent of 0.01% was added to the samples.

A calibration range of 5 to 1000 ng/L was used for all analytes. Quantification of spiked samples fortified at 10, 20 and 100 ng/L were calculated by matrix matched bracketed calibration prepared in respective matrix extracts.





Instrumental conditions:

UHPLC System:	**ACQUITY™ Premier System**
Column:	ACQUITY Premier HSS T3 Column 1.8 µm, 2.1 x 100 mm (p/n: 186009468)
Mobile Phase A:	0.01% acetic acid in water
Mobile Phase B:	0.01% acetic acid in 50:50 v/v methanol:acetonitrile
Column Temp:	45˚C
Injection Volume:	50 µL

Full MRM parameters will be detailed in an upcoming application note at www.waters.com

MS System:	**Xevo™ TQ Absolute MS**
Ionisation Mode:	ESI+ and ESI-
Acquisition:	MRM
Capillary Voltage:	0.5 kV (pos and neg)
Desolvation Temp:	550˚C
Desolvation Gas Flow:	1000 L/Hr
Source Temp:	140˚C

Figure 1. ACQUITY Premier LC System paired with a Xevo TQ Absolute MS to analyse 200 compounds of varying physiochemical properties within a 19-minute run.

RESULTS AND DISCUSSION

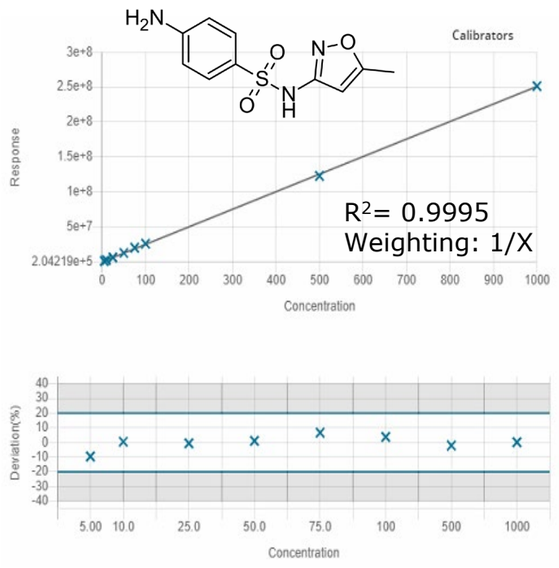
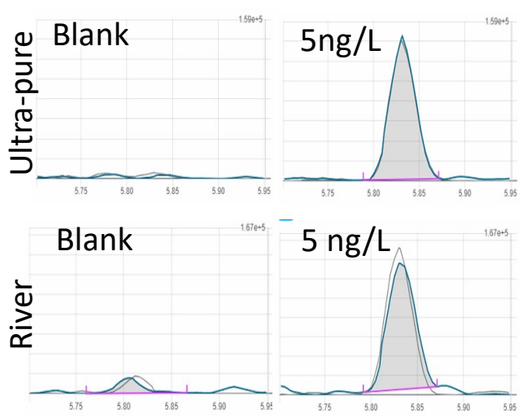


Figure 2. Sulfamethoxazole calibration curve (linear range from 5 - 1000 ng/L) in ultra-pure water, including blank and 5 ng/L chromatograms in ultra-pure and river water samples.



S/N ratio (PtP) >100 at 10 ng/L in ultra-pure, hard tap, mineral and river water matrices

>70% of compounds passed criteria in preliminary studies:

- Deviation of calculated residual concentrations were within 20%.
- Linearity was calculated with at least 6 levels achieving a mixture of linear and quadratic regression using 1/X and 1/X2 weighting with R^2 values ≥0.995 as seen in the example of Sulfamethoxazole in *Figure 2*.
- Overall retention time demonstrated stability over the study regardless of water type as shown in an example of Metconazole in *Figure 3*.
- Compounds, levels and matrices gave an average recovery by compound between 80 and 120%.

Sample diluent influence on peak shape and sensitivity: for maximum comprehensive performance, a careful balance is required when simultaneously analysing for a variety of compounds with a range of physiochemical properties.

- Highest overall sensitivity was seen when a higher aqueous sample composition was used, and this was essential for compounds such Acephate and Trimethoprim.
- Compounds that are less soluble in water such such as β-Estradiol, Erythromycin and Phenol require an elevated organic content but ratios of 10 % acetonitrile and above in the injected sample were not optimum for the majority, especially when this composition created solubility issues and distortion in chromatography for the earlier eluting compounds.

Desolvation and source temperature investigation: Some compounds were difficult to detect at 10 ng/L. Upon troubleshooting, lower desolvation temperatures were studied and compounds such as MCPB gave a better response at 300°C compared to compounds such as Diazepam which favoured 650°C. Soft transmission was also investigated, and sensitivity improvements were seen in labile compounds such as Dicamba that benefit from a gentler StepWave environment.

There are many benefits to running multi-residue screening methods including streamlined workflows and more efficient asset utilisation. These methods can also be further customised to accommodate challenging compounds with specific preferences to parameters such as sample composition and source temperatures that deviate from that of the majority.

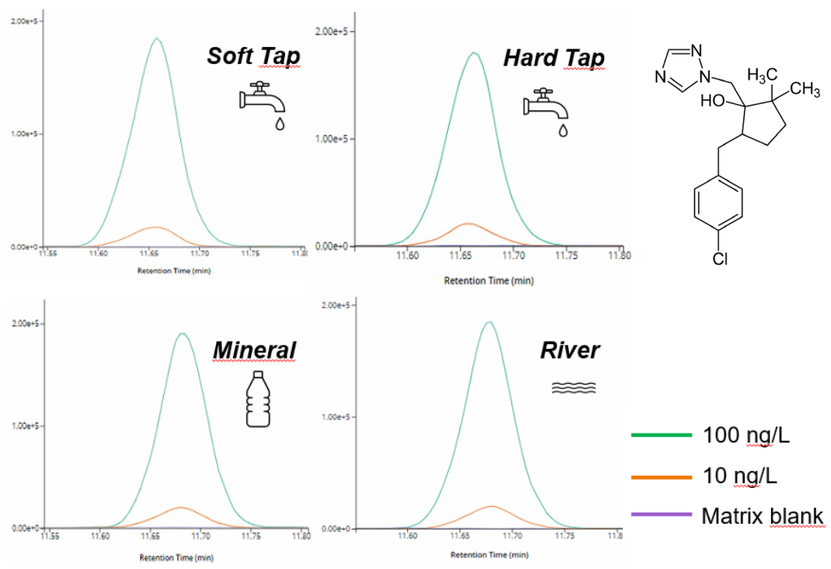


Figure 3. Peak response of Metconazole over a range of matrix types demonstrated at blank, 10 ng/L and 100 ng/L levels. *S/N ratio >100 at 10 ng/L for all matrices.*

CONCLUSIONS

- A sensitive multi-method has been developed to determine residues at concentrations as low as 5 ng/L in drinking and surface water without the need for lengthy clean-up or concentration steps.
- 200 compounds can be quantified at ≥100 ng/L and 181 compounds at ≥10 ng/L, this exceeds the EU Drinking Water Directive requirements, and the proposed levels in the Water Framework watch list and Environmental Quality Standard Directive for many relevant compounds.
- This method offers sufficient chromatographic retention, separation and detection for compounds in matrix-matched calibrants.
- Multi-methods are a useful screening tool and can be customised to accommodate for challenging compounds where optimum conditions may deviate from the overall suite. You can find many out of the box solutions and resources on the Waters website which can be adapted or used as starting points of reference.