Determination of trace (pg/L) levels of Cypermethrin in water using Stir Bar Sorptive Extraction

Kathy Ridgway*, Dan Carrier, Anaïs Maury,
Anatune Ltd, Cambridgeshire, UK.

* Corresponding author email Kathy.ridgway@anatune.co.uk

Introduction

New limits for the levels of permitted pesticides in water present a challenge to the testing laboratories. For Cypermethrin, due to its high aquatic toxicity, a detection limit of 0.01 ng/L is proposed. A method is therefore required that provides a high level of enrichment, in order to avoid the need for large sample volumes using traditional liquid- liquid extraction approaches. The use of a selective GC-MS/MS method further enhances selectivity and hence sensitivity.

A Twister is a glass-encased magnetic stir bar coated with an extraction phase typically polydimethylsiloxane (PDMS), as shown in Figure 1. When the Twister stirs an aqueous sample, analytes are extracted onto the non-polar PDMS phase. Just as in liquid-liquid extractions, analytes partition between the extracted phase, in this case PDMS, and the liquid sample phase (water). The percentage recovery onto the twister bar will depend on the Log K_{ow} for each analyte. Log K_{ow} is the octanol-water partition coefficient. A high Log K_{ow} would suggest the analyte is lipophilic and this would likely be adsorbed onto the twister bar. The Log K_{ow} for Cypermethrin is reported to be 5.3, therefore the theoretical recovery should be >99% for a 50 ml sample (GERSTEL Twister Calc). As a guide, for compounds with a log K_{ow} above 3, recoveries greater than 70% can be achieved.

Cypermethrin Log K_{ow} 5.3

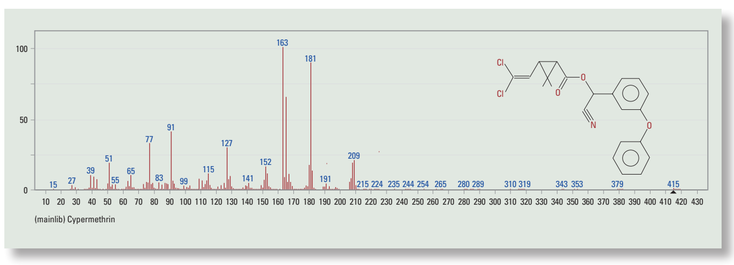

Figure 1 The GERSTEL Twister™ (PDMS)

After the twisters have been stirred for a fixed amount of time, each twister is then dried, and placed into a TDU liner for analysis. The use of Thermal desorption directly into the GC inlet enables complete transfer of extracted analytes.

Figure 2 shows a schematic of how the GC inlet is configured for twister analysis. In order to obtain the selectivity for this work, an Agilent 7000C triple quadrupole mass spectrometer was used, with the GERSTEL MultiPurpose Sampler (MPS 2), as illustrated in Figure 3.

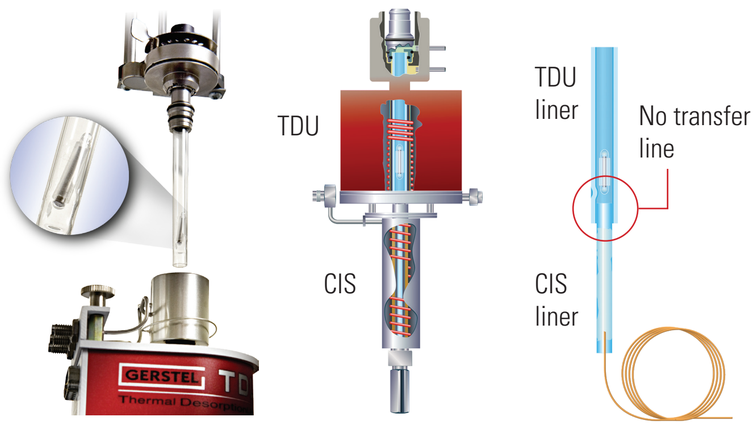

Figure 2 A picture and schematic of GC Inlet for twister analysis

Instrumentation

GERSTEL MultiPurpose Sampler MPS 2 XL
Maestro Version 1.4.25.8/3.5
GERSTEL Thermal Desorption Unit (TDU)
GERSTEL Cooled Injection System (CIS) 4
98 position Twister autosampler tray (VT98t)
Agilent GC 7890B
Agilent 7000C MS/MS

Figure 3 Instrumentation for Twister analysis

Method

Initial experiments were performed using 50 ml aliquots of Bottled spring drinking water, spiking with a technical mix of Cypermethrin isomers at various concentrations.

Extraction was performed for 2 hours using PDMS twisters following addition of salt (sodium chloride) and 5% methanol. Desorption conditions were optimized to ensure complete removal of the cypermethrin from the PDMS Twister and refocussing on the cold CIS inlet. (Figure 4).

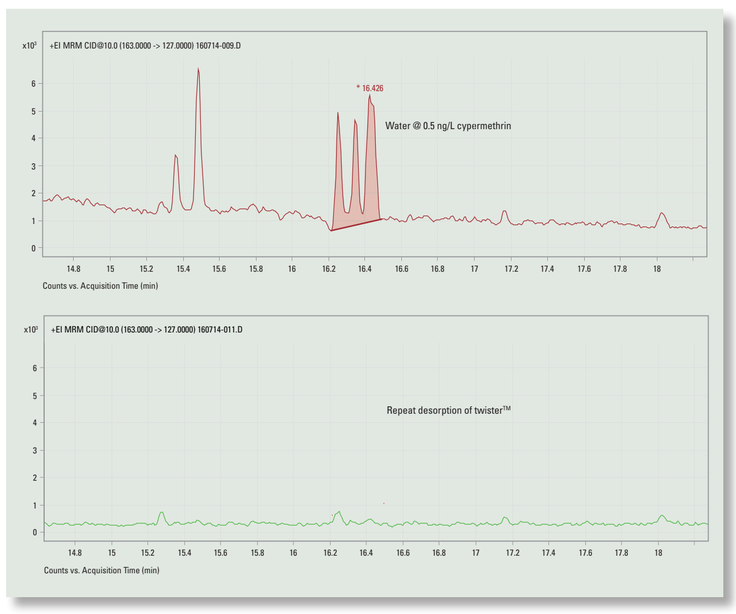

Figure 4 Optimised desorption conditions showing complete transfer.

GC/MS conditions

Column: 30 m x 0.25 mm id, 0.25 µm film thickness DB-5MS (Agilent)

Thermal gradient from 60°C to 310 °C (1 ml/min flow rate)

MRM transitions optimized for Cypermethrin 163>127, 163>91, 164.9>91

TDU temperature program initial 50°C ramped to 280°C with splitless desorption

CIS 4: Temperature Program -100°C to 280°C

Results

Good precision and linearity was achieved over the concentration range tested: 0.1 ng/L to 0.5 ng/L. Figure 5 shows a calibration plot for Cypermethrin using PDMS twisters (correlation coefficient $R^2 = 0.993$).

Six replicate twister extractions of water spiked at 0.1ng/L gave an RSD of 9%, based on total Cypermethrin peak area response ,without the use of an internal standard (Table 1). Overlaid chromatograms following extraction of 50ml sample for 2 hours are illustrated in Figure 6.

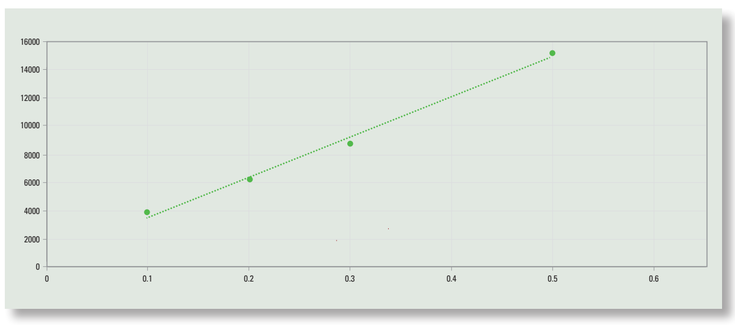

Figure 5 Calibration plot for Cypermethrin.

Replicates (50ml)	Total peak area
0.1 ng/L A	4417
0.1 ng/L B	4781
0.1 ng/L C	5696
0.1 ng/L D	5276
0.1 ng/L E	4986
0.1 ng/L F	4762
Mean	**4986**
SD	**448**
RSD (%)	**9.0%**

Table 1 Repeatability

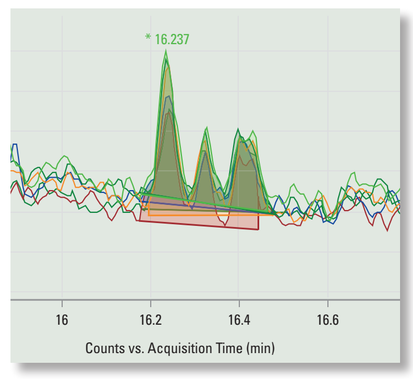

Figure 6 MRM Chromatograms of the 6 replicates at 0.1 ng/L

Method optimisation and further work

Initial results indicate that detection at the proposed levels should be possible using stir bar sorptive extraction with selective detection. In subsequent experiments, by taking a larger sample volume (250ml), we were able to detect Cypermethrin at 0.05 ng/L (Figure 7) .

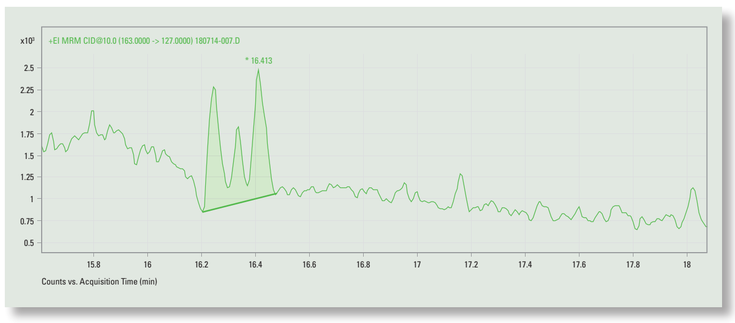

Figure 7 MRM chromatogram following 2 hour twister extraction

Further optimisation experiments are proposed, such as increasing extraction time, and adjusting the concentration of salt and methanol. The use of a labelled internal standard will also be evaluated and linearity extended.

Some extraction of real water samples has been performed, but the method needs further evaluation for a full range of 'dirty' water matrices to demonstrate full fitness for purpose. Considerations for real samples should include evaluation of the effect of pH and consideration of extraction of the complete sample – including sediment.

Conclusion

Good precision and linearity can be achieved with enrichment using twister and selective detection using GC-MS/MS acquisition MRM methods. The technique is simple and avoids the use of traditional liquid-liquid extractions

This initial work has demonstrated the potential of this technique to achieve detection at the proposed limits.

Acknowledgements:

GERSTEL GmbH & Co.KG, for providing images