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Rapid Trace Analysis of Synthetic Pyrethroids in Stormwater Using On-line Pre-concentration followed by Liquid Chromatography-Tandem Mass Spectrometry

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Introduction

Background

Synthetic pyrethroids (SPs) are a class of pesticides for which there is an emerging concern, particularly in urban areas where they are used predominantly for structural pest control in homes and businesses. The toxicity to *Hyalella Azteca* for SPs range from 1-40ng/L (see refs. 1-6). For this reason, some SPs are written into Basin Plans, MS4 permits, and NPDES permits. However, there is no standard reference method encompassing the 8 most used SPs, although some have adapted EPA 625/8270. This involves using a large volume of sample, typically 1 liter, and a laborious extraction where low level analyte loss can occur.

Objectives

- Develop an analytical method for SPs using liquid chromatography tandem mass spectrometry (LC/MS/MS)
- Perform sample preparation on the instrument (online pre-concentration) and analysis in 20 minutes or less.
- Be able to achieve a reporting limit of 1.0ng/L for all SPs
- Validate the method (demonstration of capability, MDL study, synthetic matrix spike study)

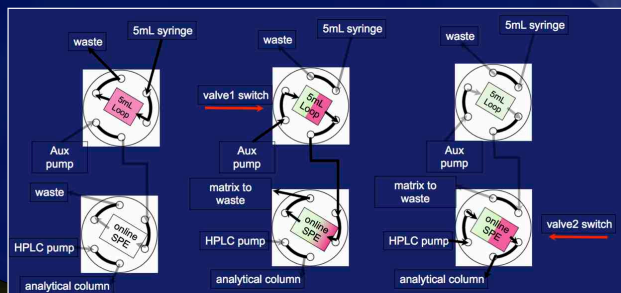


Approach

Online pre-concentration (SPE - solid phase extraction)

Online preparation is a 3-step process; load, transfer, elute.

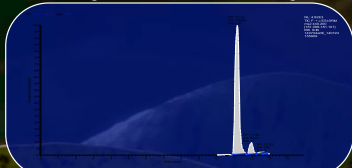
1. An auto-sampler equipped with a 5mL syringe loads a stainless steel loop (top valve) with unpreserved water sample.
2. Switching of the top valve allows an aux pump to back-flush the loop transferring the sample to the online SPE.
3. Switching of the bottom valve allows a second LC pump to back-flush the online SPE column.



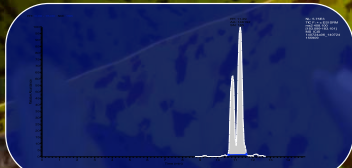
Equipment

- CTC Autosampler equipped with two injection valves
- Thermo Accela 600 (SPE) and Accela 1250 (LC) quaternary pumps
- Thermo Triple-Stage Quadrupole (TSQ) Quantum Ultra with HESI-II probe in SRM Mode

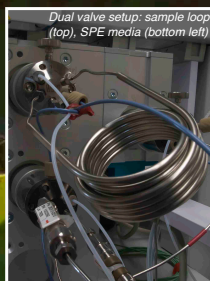
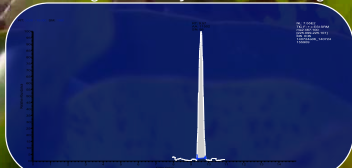
Chromatogram of Bifenthrin at 1.0ng/L



Chromatogram of Permethrin at 1.0ng/L



Chromatogram of λ-Cyhalothrin at 1.0ng/L



Results

Figure 1 - Recoveries of SPs in Reagent Water at 10ng/L

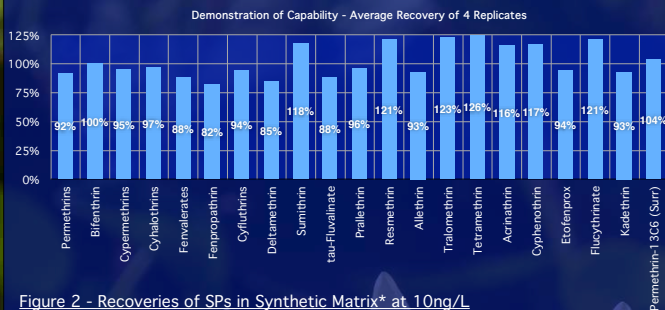


Figure 2 - Recoveries of SPs in Synthetic Matrix* at 10ng/L

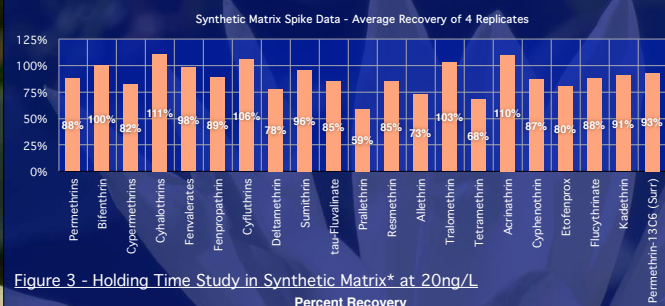
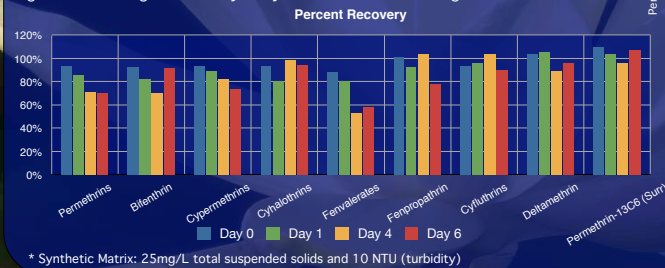


Figure 3 - Holding Time Study in Synthetic Matrix* at 20ng/L



* Synthetic Matrix: 25mg/L total suspended solids and 10 NTU (turbidity)

Discussion

Triple-stage quadrupoles have become more common in environmental laboratories for the analysis of emerging contaminants, pharmaceuticals, personal care products, and for EPA drinking water methods (UCMR3-uncontrolled contaminant monitoring rule ver. 3). Analysis of SPs by Online-SPE LC/MS/MS offers some significant advantages over continuous liquid-liquid extraction (LLE) and gas-chromatography mass spectrometry (GC-MS).

By sampling two 40mL VOA vials, a sample can be analyzed along with a matrix spike/duplicate while having extra sample for redundancy (in case of breakage). This means reduced shipping costs compared to shipping 3 liters of sample. For sites where limited volume is available, a lower required sample volume means that minimum reporting limits for a project can still be met. The performance of this method indicates that, not only can analytes be recovered in lab reagent water, analytes can be recovered with adequate accuracy and precision in sample matrices containing moderate total suspended solids and turbidity including storm water.

Secondary benefits of this method include lower labor costs to the laboratory and faster turn-around time of results. Also, because technical mixtures of synthetic pyrethroids contain multiple stereoisomers which are not equally toxic, the method is adaptable to chiral separation by simply changing the analytical column. Chiral analyses on a GC are generally extremely lengthy with analysis times close to an hour per sample. Also, the lab reduces solvent usage which are used in significant volume during LLE lowering environmental waste output.

One deficiency noted is the holding time study that was performed. Ideally, this study should be redone with analysis performed daily for 7 days on a simulated matrix.

References

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6. EPA Aquatic Life Benchmark List http://www.epa.gov/oppfed1/ecorisk_ders/aquatic_life_benchmark.htm

Questions regarding this article can be submitted to dschiessel@babcocklabs.com