Poisoned water: An investigation into the Detection of Pesticides with a Novel Approach to SPE

Matthew Diplock[1], Raquel Gonzalez de Vega[1], Andrew Minett[2], Philip Doble[1],
[1] School of Mathematical and Physical Sciences, Faculty of Science, University of Technology Sydney, Ultimo NSW 2007, Australia; [2] Eprep Pty Ltd, Mulgrave VIC 3170, Australia
Email: raquel.gonzalezdevega@uts.edu.au

Introduction

Sample preparation is vital for reliable and accurate analyses. Automation of sample preparation minimises errors and eliminates manual liquid handling tasks. Micro Solid-Phase Extraction (µSPE) is a novel automated technique that uses low bed volumes and small (<3 µm) particle sizes enabling the manipulation of microlitre volumes.

µSPE offers an alternative strategy for quantification of analytes where surrogate or deuterated standards are not available. This workflow involves passing the standards through µSPE prior to construction of the calibration curve and may be applied to detection of the ever-growing list of pollutants in both environmental and food samples.

Figure 1 µSPEed cartridges with one-way check valves and ePrep sample preparation Workstation

Methods

µSPEed Extraction Workflow
Aqueous samples were loaded onto µSPEed cartridges, C18RPS-3µm/120Å (Eprep), washed with ultrapure water and then eluted using 100µl of IPA. Conditioning and equilibration steps carried out at 200 µL/min flow rate, all other steps at 60 µL/min. Operational workflow is described in Figure 2.

Chromatography
Instrument: Thermo Scientific Trace 1300 GC
Column: DB-5MS UI Length: 25 m Diameter: 0.25 mm Film: 0.25 µM
Split flow: 50 mL/min
Splitless time: 1.00 min
Purge flow: 5 mL/min
Temperature profile: 25°C/min rise to 9 min, 9°C/min until 25 min, hold for 5 min

Detection:
Detector: Thermo ISQ QD Single Quadrupole
MS transfer line temperature: 270
Ion source temperature: 280
Scan range: 50 - 500
Injection volume: 1 µL

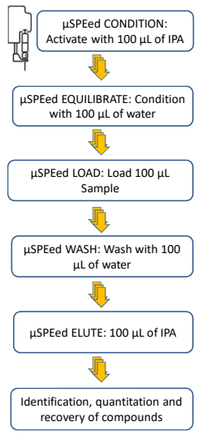

Figure 2 µSPE Workflow

Experimental

1) GC-MS chromatographic separation: Figure 3 shows a typical GC-MS chromatogram for a standard mix containing 20 target compounds at 50 ppb. Each Pesticide compound was identified from 3 major ions and compared to library reference spectra.

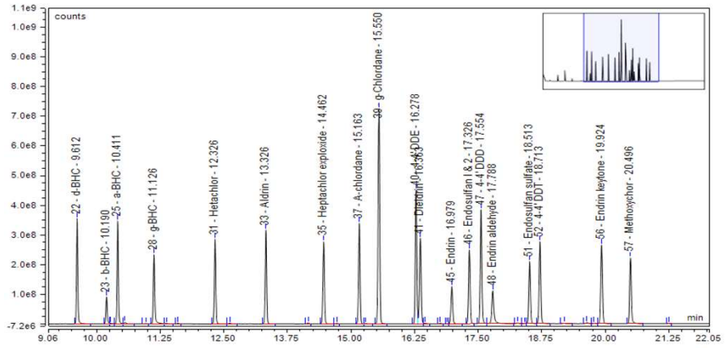

Figure 3 Identification of standard pesticides from a 50 ppb standard by GC-MS

2) µSPEed process validation: Method recovery was investigated by determining a spiked standard in an ultrapure water sample (50 ppb for each pesticide); the recovery range was from 86 to 103% (Table 1) demonstrating that this SPE method provides good selectivity and suitability for the analysis of pesticides in water samples.

Compound	Linearity	%Recovery	%RSD
d-BHC	0.948	88	7.6
b-BHC	0.93	98	6.9
a-BHC	0.943	96	7.9
g-BHC	0.937	99	6.3
Hetachlor	0.94	100	6.2
Aldrin	0.945	96	3.8
Heptachlor exploxide	0.946	100	5.2
A-chlordane	0.933	98	7.2
g-Chlordane	0.936	96	6.5
4-4' DDE	0.946	94	8.3
Dieldrin	0.95	103	4.3
Endrin	0.928	96	4.7
Endosulfan I & 2	0.932	110	9.4
4-4' DDD	0.941	100	8
Endrin aldehyde	0.901	103	7.6
Endosulfan sulfate	0.907	100	8.8
4-4' DDT	0.948	86	8.5
Endrin keytone	0.929	103	4.4
Methoxychor	0.908	100	11.5

Table 1 Linearity and average recoveries of the 20 pesticides after µSPE extraction by GC-MS

3) Application of the developed method to a sedimentary river water sample: Sedimentary river water sample (Figure 4a) was used unfiltered and untreated when passed through µSPEed C18 Cartridges for pesticide trapping. Figure 4b shows sedimentary deposit left in the µSPEed cartridge following load and elution of pesticides; demonstrating that the SPE method can be used without any filtering before trapping and clean up.

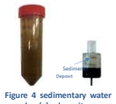

Figure 4 sedimentary water sample (a) deposit on a µPEed cartridge

This method was tested against dirty sedimentary river water samples. These samples had no further clean up procedure other than the SPE method. The resulting chromatogram in Figure 5 shows no interference from humus/sedimentary components on GC/MS analysis of the µSPEed elution of pesticides.

Recoveries of the 20 spiked compounds (Table 2) are lower in sedimentary river water than the ones found in a clean water sample, due to suspected adsorption of the sedimentary components.

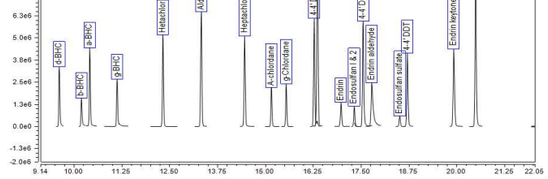

Figure 5 GC-MS Chromatogram of a Spiked sedimentary river water sample

Compound	% Recovery
d-BHC	72
b-BHC	71
a-BHC	97
g-BHC	72
Hetachlor	69
Aldrin	75
Heptachlor epoxide	68
A-chlordane	71
g-Chlordane	66
4-4' DDE	72
Dieldrin	70
Endrin	74
Endosulfan I & 2	73
4-4' DDD	69
Endrin aldehyde	77
Endosulfan sulfate	75
4-4' DDT	76
Endrin keytone	77
Methoxychor	74

Table 2 Average recoveries from spiked sedimentary river water samples after µSPE extraction

Conclusions

µSPEed cartridges have the ability to reduce the amount of sample required, concentrating a 100 mL sample into just 50 µL while eliminating the need for large and complex elution steps with incredibly small effective elution volumes. The high efficiency of the µSPEed cartridges combined with the small particle size (3 µm) of the sorbent bed allows almost a complete elimination of any other sample preparation techniques like filtering or centrifuging, with the entire sample simply being loaded onto the cartridge.

This work demonstrates a simple way to use this method, combined with an accurate and fast automated system and highly efficient µSPE extraction methods to quickly, accurately and rapidly analyse pesticide samples even in the most difficult of water matrixes.