THE APPLICATION OF MEPS FOR THE ON-SITE PREPARATION OF WATER SAMPLES

Paul Wynne, Roy Hibbert, Peter Dawes
SGE Analytical Science, 7 Argent Place, Ringwood VIC 3134 AUSTRALIA
Toll Free: 1800 800 167 - Tel: +61 (0) 3 9837 4200 - Email: support@sge.com

Introduction and Discussion

MEPS uses a barrel insert and needle (BIN) device to reduce Solid-Phase Extraction (SPE) to a micro-scale suitable for small volume samples and for the on-line adaptation of conventional SPE techniques. Because the SPE cartridge (BIN) is incorporated into the needle assembly of a gas-tight syringe, MEPS is also a simple field-portable SPE device that may be operated manually without need for sampling pumps or, alternatively, may be incorporated into robotic samplers.

To demonstrate the application of MEPS we report the qualitative field use of C18-MEPS for the sampling of water bodies in both industrial and urban environments. Water samples were extracted on-site and then the MEPS syringes were transported back to the laboratory overnight for elution and analysis of the retained components. C18-MEPS was used to extract samples (100-1000 µL) of water from industrial drains and stormwater pipes to recover semi-volatile residues for GCMS analysis (Fig 1-3). The technique was also applied to sampling droplets on surface extracts of paint for non-destructive surface profiling (Fig 2). Analysis of the unknown samples was qualitative but sufficiently sensitive to detect industrial discharge residues associated with grinding coolants, packaging materials and other contaminants. Naturally occurring leachates from vegetation were also detectable. Droplet extraction of a painted surface was performed in reversed-phase mode (water extract on C18 sorbent) and allowed the surface to be profiled for comparative purposes. The same technique could be applied in normal phase (data not shown) using an organic solvent and a silica or C2 sorbent.

MEPS devices are of glass and stainless steel construction allowing them to be fully immersed for sampling at depth or, alternatively, used at needle depth to avoid perturbing the stream from which the sample was drawn. An extension pole allowed MEPS to be used to sample back along pipes or down inspection vents. When sampling from drainage pits and open sumps, there was minimal requirement to remove grates to gain access. An extension pole also allowed sampling from outflows that were offensive and could be readily adapted for safe sampling of toxic materials or where the sample was hot or otherwise dangerous.

Conclusion

MEPS was found to be suitable for the in-field extraction of water samples with the stages of sample loading (field based) and clean-up and elution (laboratory based) separated. Manual operation of the syringe pump allowed sampling without the need for portable power supplies or other sampling paraphernalia. Where testing protocols allow, the field portability of MEPS can eliminate the need to recover and stabilize samples for transport to the laboratory. Specifically, we have made use of the small size, ease of use and mechanical stability of the MEPS syringe to allow us to demonstrate the provision of a sampling service to a remote site without the need for transporting hazardous materials or unstable samples.

MEPS Online Kit.
This solution pack provides all the hardware, software and support needed to add online SPE capability to your CTC platform, using the MEPS SPE system.

HERBICIDE RESIDUE IN ROADSIDE DRAIN

Storm water (1 mL total volume, 10 x 100 µL at 10 µL/sec) on a methanol conditioned C18-BIN MEPS device. The sorbent was dried with air (3 x 100 µL at 100 µL/sec) and returned to the laboratory. Immediately prior to analysis, the MEPS was eluted with methanol (20 µL) and 2 µL of sample analyzed by GCMS. By using only a portion of the MEPS eluate, the amount analyzed was the equivalent of 100 µL of stormwater. The water sample showed the presence of the herbicide simazine as well as hydrocarbons typical of mineral diesel fuel (road surface and air), plastics residues (plastic waste and packaging) and flame retardant used in polystyrene and other applications (packaging and other refuse). Simazine is likely to have been applied to weeds in nearby industrial land or roadside areas. No weed growth was evident within 5 m of the sample collection area nor was the water flow from a weed affected area.

MEPS was found to be suitable for detecting residues from land management and commercial activities in storm water. Enhanced concentration of analyte can be achieved using MEPS in combination with a larger volume syringe and/or more sampling cycles and by analyzing a greater proportion of the MEPS eluate.

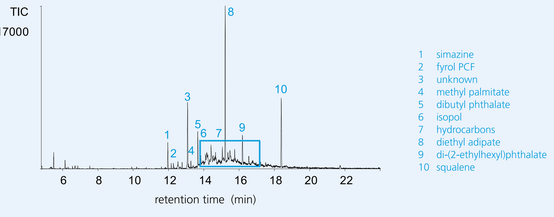

Figure 1: Analysis of road side drain showed the presence of hydrocarbon (enclosed in dotted line), flame retardant and herbicide.

IN SITU EXTRACTION OF SOLID SURFACES

Sampling of solids for profiling of paint, coatings and environmental residues may be simplified by combining the extraction chemistry with the sampling process. A droplet of water (1 mL) was beaded on the painted surface and allowed to stand for 2 hours. The water droplet (200 µL total volume, 2 x 100 µL at 10 µL/sec) was then extracted using a C18-BIN. The sorbent was dried with air (3 x 100 µL at 100 µL/sec), eluted with dichloromethane (20 µL) and a 2 µL portion was then analyzed by GCMS.

The surface extract showed the presence of a series of phenolic and phenoxypropandiols that are consistent with residual monomers from an epoxy coating. The concentration of benzene sulphonamides, bisphenol A and partially reacted monomers form a profile typical of this particular epoxy location. Tris-(2-butoxyethyl)phosphate is a common flame retardant in floor polishes and polymers and so is also a useful marker. The use of C18-MEPS for in situ sampling of solid surfaces allowed for non-destructive profiling of painted surfaces and other coatings. In this example, water was beaded on the polymer surface and then extracted using a reversed-phase extraction technique. Normal phase methods are also practical using organic solvents and C2- or silica BIN-MEPS devices.

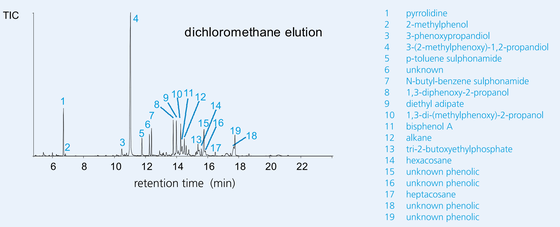

Figure 2: Analysis of water pooled on polymer sealed surface.

AVOIDING CONTACT WITH OFFENSIVE OR UNKNOWN SAMPLES USING MEPS

Water samples were identified as potentially polluting on the basis of their opacity and unusual odor. Extension rods carrying MEPS syringes with C18-BINs that were conditioned with methanol could be used to sample water without perturbing the water flow as only the needle entered the sample path. Water samples (200 µL total volume, 2 x 100 µL at 10 µL/sec) were collected. The needle tips were wiped and the MEPS syringes returned to the laboratory. Before elution, the BIN sorbent was dried with air (3 x 100 µL at 100 µL/sec) and then eluted sequentially with methanol (20 µL) and dichloromethane (20 µL). A 2 µL portion of each sample was then analyzed by GCMS.

The water sample showed the presence of dibutyl glycol and several minor related components, 4-chloro-2-cresol, small chain polyethylene glycols and hydrocarbons. Abrasive mineral particles also collected from the outflow support the suggestion that at least some of the materials were from water soluble or dispersible grinding coolants. C10 to C14 alkanes may have been from coolant or machine oils as the low abundance of other hydrocarbons in the same boiling range ruled out the presence of diesel oil. The components are considered to have low toxicity and so the outflow could be considered acceptable or safe to discharge.

Sequential elution of C18-MEPS with solvents with very different solvating properties was found to be useful in giving some selectivity of sample clean-up and may be useful in multi-eluate approaches to class analysis. Prior elution of the sorbent with hexane or similar hydrocarbon solvents (data not shown) allowed the elution of hydrocarbon materials followed by the elution of more polar components in methanol.

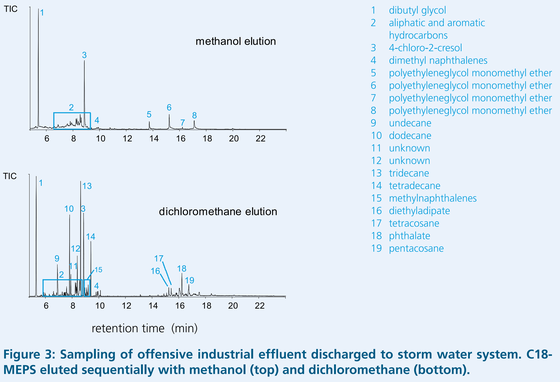

Figure 3: Sampling of offensive industrial effluent discharged to storm water system. C18-MEPS eluted sequentially with methanol (top) and dichloromethane (bottom).

EXPERIMENTAL CONDITIONS

GCMS method for experiments shown in Fig 1-3: Analysis used an Agilent 6890 GC -5973N MSD and a BPX5 column (30 m x 0.25 mm ID with a 0.25 µm film thickness). Injector temperature was 270 °C and injection was splitless. The oven temperature was 40 °C (4 min) then 20 °C/min to 250 °C (10 min). Transfer line was 280 °C, source 230 °C and quadrapole 180 °C. Scan range was 40-500 Da at 2 scan/sec.

SGE Analytical Science
www.sge.com