

DETERMINATION OF ORGANIC PRIORITY POLLUTANTS AND EMERGING COMPOUNDS IN WASTEWATER BY MICRO SOLID PHASE EXTRACTION COUPLED TO GCMS

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References:

1. Prieto A, Schrader S, Moeder M. (2010); *J Chrom A*, 1217: 6002–6011

A new fully automated procedure for the simultaneous determination of 41 multi-class priority and emerging organic pollutants in water samples is presented combining micro solid phase extraction (MEPS) with large volume injection–GC-MS.

In compliance with national and international directives, regular environmental monitoring is demanded which requires appropriate analytical methods for fast and sensitive detection of relevant compounds such as the priority pollutants polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) or endocrine disrupting compounds.

Miniaturization, particularly of included sample preparation, is a key feature in the development of automated analytical protocols and in this context, MEPS™ is emerging as a novel and promising tool. The list of target compounds included PAHs, PCBs, phthalate esters (PEs), nonylphenols (NPs), bisphenol A (BPA) and selected steroid hormones.

The developed methods were applied to the determination of the target analytes in snow and wastewater samples.



MEPS™ Procedure

Microextraction was performed using MEPS™ (SGE Europe). A 100 μL or 250 μL gas-tight syringe is equipped with a small container incorporated into the needle (Fig 1). The MEPS syringe was used in connection with a large volume injector type CIS 4 (Gerstel) and samples were fully automatically processed by a Multi Purpose Sampler MPS 2 (Gerstel) and controlled by Gerstel Maestro software.

Standard SPE was performed with a Visiprep SPE manifold (Supelco) using 200 mg of C18 sorbent (polar plus® C-18 bonded phase, J.T. Baker, USA) in 2 mL cartridges.

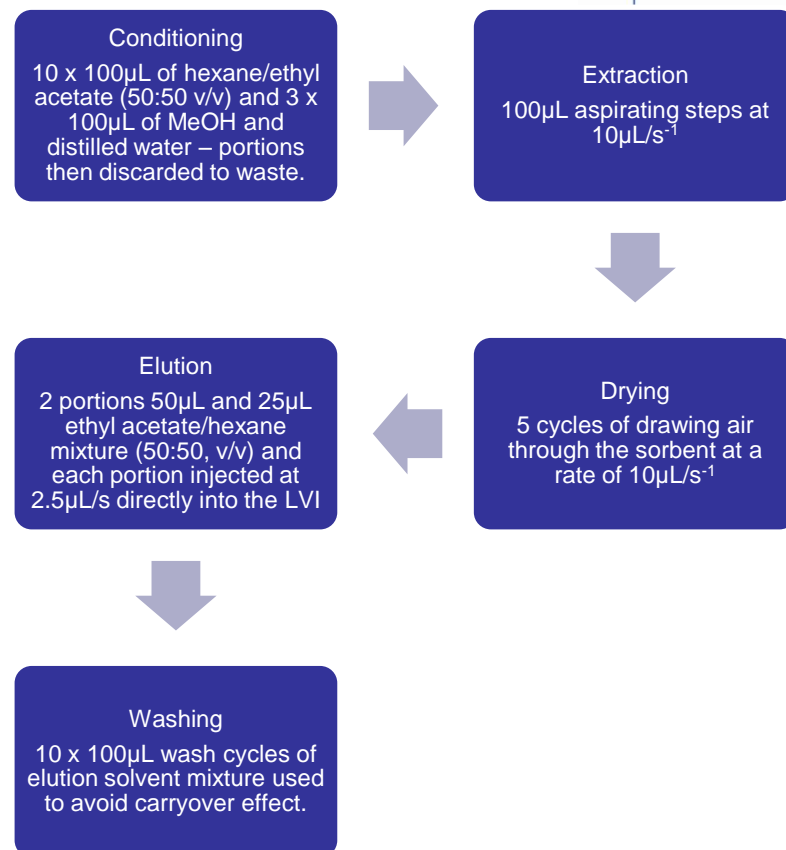
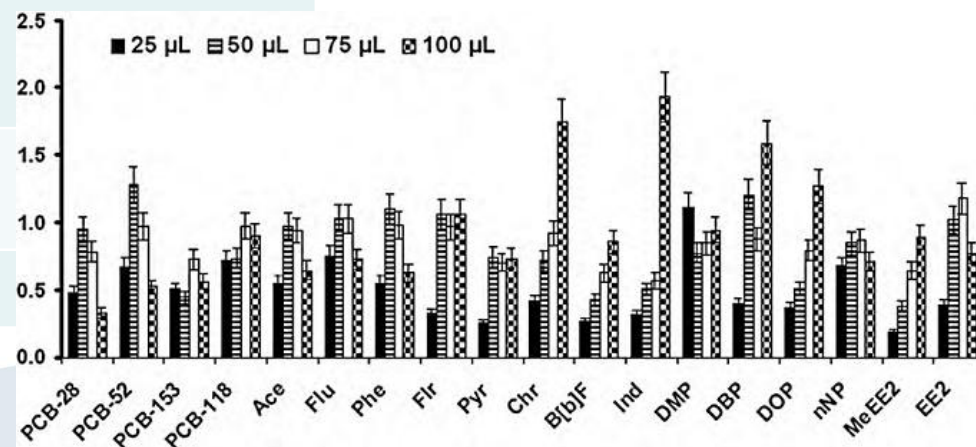


Figure 1. The MEPS™ syringe and SPE cartridge or BIN “Barrel Inset and Needle” filled with 2 mg of sorbent commonly used for SPE.

Instrument	GC-MSD instrument (Agilent 6890)		
Injector	PTV injector (CIS 4, Gerstel)		
Detector	Agilent 5973 Mass Selective Detector		
Inlet details	Deactivated baffled liner - Split, 2.5 μ L/s, 50 °C, 87.6 kPa. Solvent vent at 0.7 min for 70 mL/min. Splitless for 1.5 min 720 °C/min to 300 °C and held to 300 °C for 5 min		
Solvent	Ethyl acetate/hexane (50:50, v/v)		
Capillary	HP-5MS (30 m x 0.25 mm, 0.25 μ m)		
Oven	50 °C for 2 min with 15 °C/min to 100 °C with 10 °C/min to 290 °C for 15 min.		
Transfer line	300 °C	Ion source	230 °C
Analyser	150 °C		

Figure 2. Comparison of several elution/injection volumes (25–100 μ L) for selected analytes extracted with MEPS™.

75 μ L (1 \times 25 μ L+1 \times 50 μ L) was chosen as the elution volume in order to avoid peak splitting observed for the most volatile compounds when total volumes higher than 75 μ L were injected consecutively (2 \times 50 μ L) into the PTV.



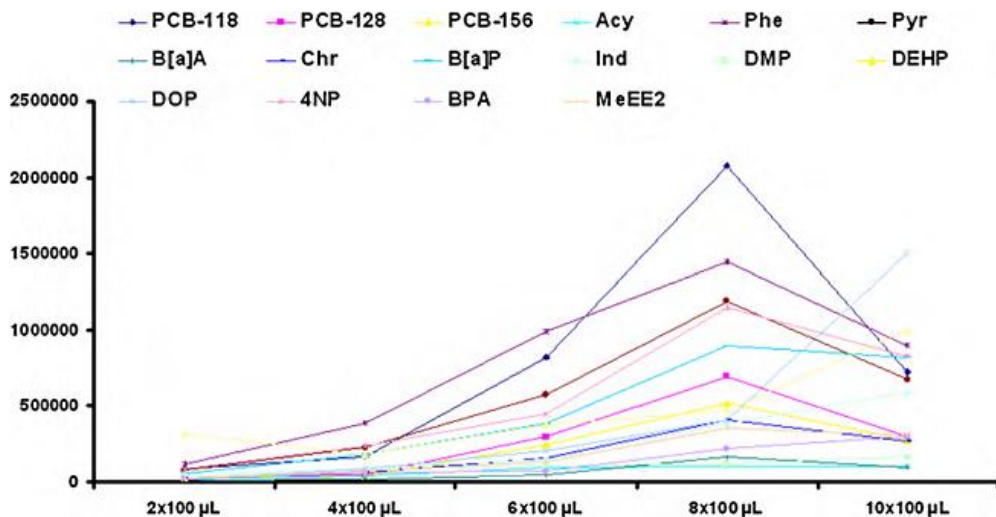


Figure 3. Influence of the number of extraction steps on the responses of selected analytes using MEPS™

The developed MEPS-LVI-GC-MS and SPE-LVI-GC-MS chromatographic procedures exhibited excellent linearity ($R^2 > 0.99$) for the majority of compounds (PAHs, PCBs, phthalate esters and nonylphenols¹). The results demonstrate the high sensitivity of the MEPS™ procedure in comparison to the commonly applied SPE methodology. Furthermore, MEPS™ allows the extraction of only 800 µL of sample volume to detect the target compounds at ng/L concentration level.

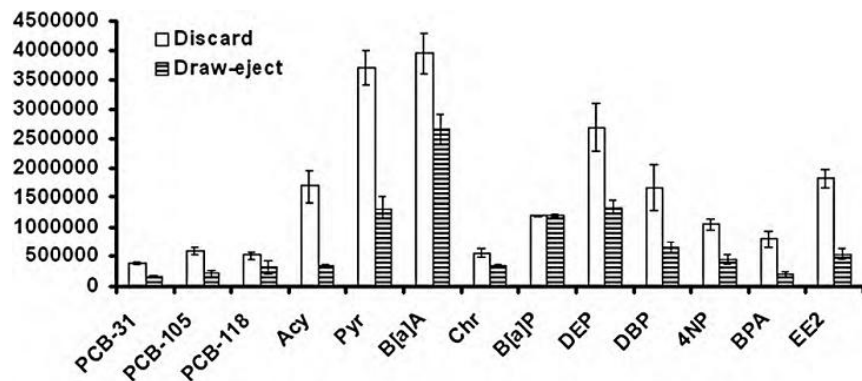


Figure 4. Evaluation of sample loading technique, multiple draw-eject cycle mode vs. extract-discard mode (each sample aliquot pumped only once through the MEPS™-BIN then discarded before the next sample aliquot was pumped). Chromatographic responses of selected compounds.

- Accurate multi-residue determination was achieved for 41 organic pollutants in water at low levels (ng/L) from sample volume of 800 μ L.
- Use of isotopically labelled standards avoided standard addition even for wastewater samples.
- Fully automated multi-residue protocol saves time and solvent compared to standard SPE methodology.
- Unlike conventional SPE cartridges the MEPS™ materials allow multiple use (lifetime depends on sample matrix and analytes).
- LODs for the MEPS™ protocol: 0.2 and 266 ng/L (800 μ L sample) comparable to those obtained by off line SPE (0.2 to 736 ng/L for 100 mL sample volume).
- Recoveries (>75%) and precision of the methods (RSD) was below 21% for all compounds.