TECHNICAL ARTICLE

Evaluation of a New Technique in Semi-Automated, Miniaturized Solid Phase Extraction

INTRODUCTION

Solid phase extraction (SPE) is a very popular method of sample preparation. Conventional SPE is performed by passing a liquid sample across a sorbent bed to retain analytes of interest. Once bound to the adsorbent material, the sample can be further concentrated or washed to eliminate interferences. Conventional SPE has several advantages over liquid-liquid extractions, namely time and solvent savings, SPE methods can still be tedious and time consuming when performed manually. Sample prep as a whole remains a limiting factor in sample throughput in today's laboratory.

Micro Extraction by Packed Sorbent (MEPS™) is a new development in the field of SPE. The MEPS technology consists of a modified removable needle syringe and a needle assembly that contains the SPE sorbent material. MEPS performs the same function as SPE, namely the purification or speciation of samples, and works on smaller samples volumes than conventional SPE. Subsequently, MEPS reduces the volume of solvents needed, from milliliters to microliters, and is much faster - literally minutes per sample preparation.

Since the MEPS technology is syringe based, it is compatible with many common liquid handling systems, thus the extraction procedure can be fully or semi-automated which creating a seamless technique that reduces sample processing time and minimizes operator intervention.

In this study, we demonstrate an existing conventional SPE method converted to a MEPS procedure and semi-automated using a hand held, electronically controlled dispensing device (eVol®).

BACKGROUND

Sample Preparation

Sample Preparation has three objectives:

- Transition analytes of interest into solution.
- Removal of interferences found in the sample matrix.
- Focus analytes to a concentration that the analytical instrument can detect.

MEPS is the miniaturization of packed bed solid phase extractions. The sorbent has been integrated into a modified removable syringe needle. Having a syringe format leads to ready integration into automated sampling systems with extracted volumes compatible with online use in both GC and LC (see Figure 1).

Figure 1. MEPS™ Syringe.

Figure 2 demonstrates how MEPS and conventional SPE function in the same manner, using the same phases. Current SPE methods simply require scaling down of the volumes of sample, wash, and solvent to endable use with MEPS.

Coupling the miniaturized SPE with a hand-held, programmable analytical syringe can offer the user the advantage of programmability and controlled flow rates through the digital drive complimenting the flow rate dependent SPE technique.

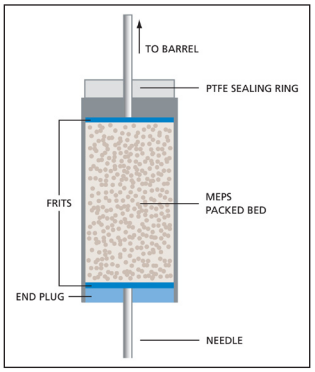


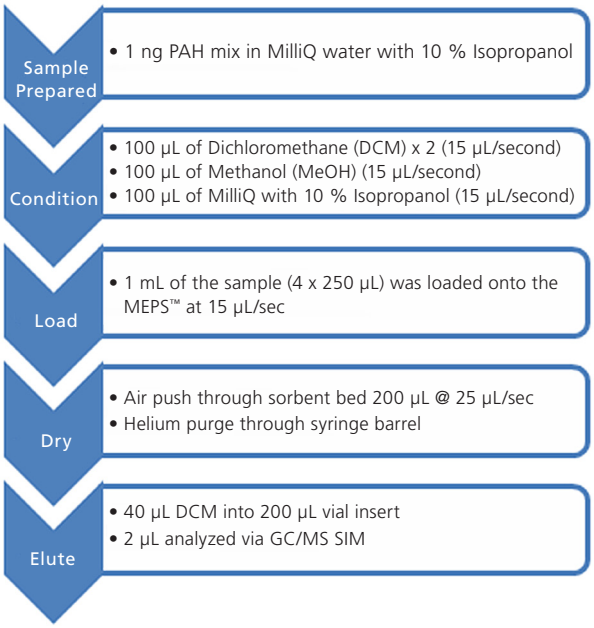
Figure 2. Schematic of the MEPS™ stationary phase within the syringe needle - SGE's patented 'Barrel Insert and Needle' (BIN) configuration.

METHODOLOGY AND RESULTS

Manual MEPS PAH Method Development on C18

Polycyclic Aromatic Hydrocarbons (PAH) are common environmental contaminants, comprised of fused benzene rings with naphthalene being the smallest of the PAHs with two fused benzene rings. There are several test methods listed by the EPA for the analysis of the 16 priority pollutants - for trace level analysis, GC-MS in SIM mode is the preferred choice for low level water analysis.

Using manual MEPS the operator must perform all the steps with the modified analytical syringe. Typically, inter-operator variations include the flow rate - fundamentally the force used on the plunger.



Method
Shimadzu QP-2010

Injection
Pulsed Splitless (35 psi 1 min)
2 µL injection + 1 µL DCM Flush (w/ 2.5 ng IS)
Injection Port 300 °C

Column and Oven Conditions
P/N 054742
BPX50 – 20 m x 0.18 x 0.18
Helium 1.1 mL/min Constant Flow
60 °C (hold 1 min)
35 °C/min to 230 °C (hold 0)
6 °C/min to 240 °C (hold 0)
50 °C/min to 265 °C (hold 0)
4 °C/min to 320 °C (hold 1)

Mass Spec
Autotune; 219 m/z
Mode – SIM
Interface 300 °C
Ion Source 260 °C

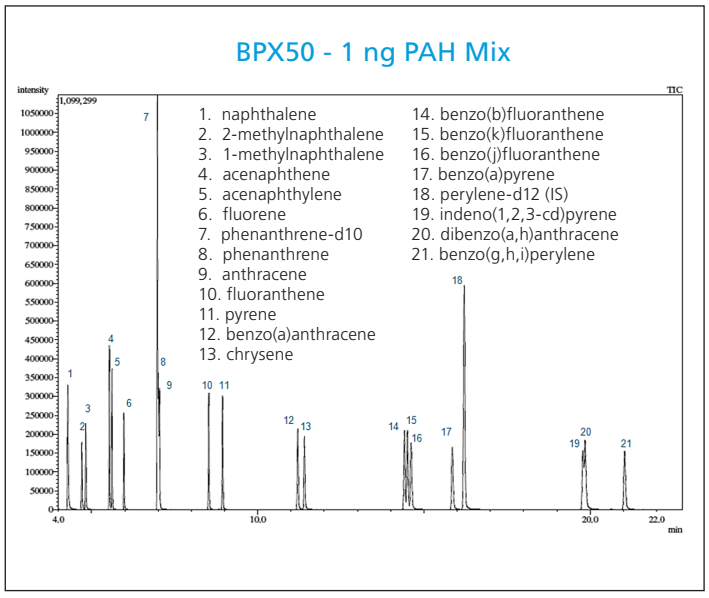


Figure 3. PAH evaluation on BPX50 using GCMS with Manual MEPS™ extraction.

Note: ERA Low-Level PAH Quality Assurance Performance Evaluation Test recovery = 77.8 %.

eVol MEPS Method Development on HDVB

eVol MEPS works via essentially the same process as manual MEPS where the primary difference involves the use of a hand-held automated analytical syringe. This facilitates control over aspiration and dispense volumes, flow rates and method repeatability.

eVol® Custom Method

Sample Prepared
- 1 ng PAH mix in MilliQ with 10 % Isopropanol

Condition

Step	Prompt	DCM	Speed
1	Aspirate	250	1
2	Dispense	250	1
	Prompt	MeOH	Speed
3	Aspirate	250	1
4	Dispense	250	1
	Prompt	H2O	Speed
5	Aspirate	250	1
6	Dispense	250	1

- 250 µL of DCM (16.67 µL/second)
- 250 µL of MeOH (16.67 µL/second)
- 250 µL of MilliQ with 10% Isopropanol (16.67 µL/ second)

Load

Step	Prompt	SAMPLE	Speed
7	Aspirate	500	1
8	Dispense	500	1
9	Aspirate	500	1
10	Dispense	500	1

- 1 mL of the sample (2 x 500 µL) was loaded onto the MEPS™ at 16.67 µL/sec

Dry

Step	Prompt	DRY	Speed
11	Aspirate	500	10
12	Dispense	500	10
13	Aspirate	500	10
14	Dispense	500	10
15	Aspirate	500	10
16	Dispense	500	10
17	Aspirate	500	10
18	Dispense	500	10
19	Aspirate	500	10
20	Dispense	500	10

- Air push through sorbent bed 2500 µL @ 400 µL/sec

Elute

Step	Prompt	ELUTE	Speed
21	Aspirate	100	1
22	Dispense	100	1

- 100 µL DCM into 200 µL vial insert
- 1 µL IS (phenanthrene-d10) added
- 50 µL analyzed via GC-MS SIM

eVol PAH extraction with MEPS

Figure 4, shows the GC-MS analysis of 500 pg PAH extracted by the eVol MEPS program on HDVB.

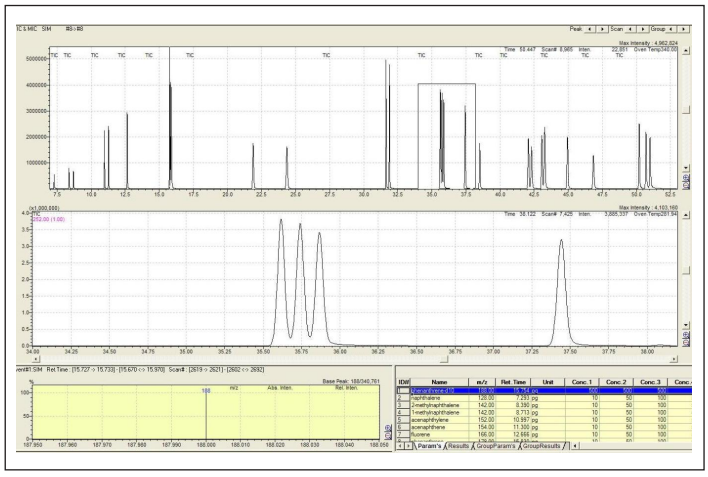


Figure 4. GC-MS with SIM on eVol® extraction with MEPS™.

Method

Shimadzu QP-2010 with AOC-20i

Injection

PTV – LVI Injection
50 µL injection (w/ 0.5 ng IS)
40 °C (hold 0.5 min)
400 °C.min to 300 °C (hold 45 min)

Column and Oven Conditions

P/N 054742
BPX50 – 20 m x 0.18 x 0.18
Helium 1.4 mL/min Constant Flow
40 °C (hold 3 min)
35 °C/min to 120 °C (hold 0.5 min)
8 °C/min to 200 °C (hold 10 min)
11 °C/min to 270 °C (hold 0)
2 °C/min to 300 °C (hold 1 min)
40 °C/min to 340 °C (hold 7 min)

Mass Spec

Autotune; SEI Source
Mode – SIM
Interface 300 °C
Ion Source 260 °C

Table 1, demonstrates the extraction using HDVB with Quality Assurance Performance Evaluation Testing. The average recovery = 73.2 %.

HDVB EXT	Certified	Conc (ng)	% Rec	
acenaphthene	7.71	5.54	71.8%	PASS
acenaphthylene	6.26	5.00	79.8%	PASS
anthracene	1.39	1.16	83.7%	PASS
benzo(a)anthracene	0.787	0.59	74.8%	PASS
benzo(b)fluoranthene	0.824	0.49	59.2%	PASS
benzo(k)fluoranthene	1.62	0.98	60.6%	PASS
benzo(g,h,i)perylene	0.322	0.16	48.7%	PASS
benzo(a)pyrene	0.83	0.43	52.2%	PASS
chrysene	0.685	0.47	68.3%	PASS
dibenz(a,h)anthracene	0.965	0.48	49.7%	PASS
fluoranthene	1.37	1.21	88.3%	PASS
fluorene	5.26	4.57	86.9%	PASS
indeno(1,2,3-cd)pyrene	1.37	0.86	63.1%	PASS
naphthalene	8.26	4.49	54.4%	PASS
phenanthrene	1.82	1.61	88.7%	PASS
pyrene	1.95	1.66	85.0%	PASS

Table 1: eVol® MEPS™ extraction recovery results from ERA test standard.

CONCLUSION

- MEPS enables a convenient format for miniaturization of SPE, with a significant reduction in sample preparation time, sample usage and waste generation.
- Manual MEPS is convenient but the repeatability is operator dependent.
- Semi-automated eVol MEPS, being programmable, is easy and offers high repeatability.
- Fully automated MEPS can be used with CTC-PAL and Shimadzu AOC-20i.

Using eVol MEPS extraction and injection of the sample can be combined in one process with direct injection into the GC via PTV or LVI as well as HPLC.
Importantly, sample preparation time is significantly reduced - eVol extraction ~6 min.

For more information contact our technical customer support team at **techsupport@sge.com**

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