

SOLUTIONS BY



# DETERMINATION OF PAH In Particulate Matter PM<sub>10</sub> with SPE/EVAporation

## Determination of PAH

### In particulate matter $PM_{10}$ with SPE/EVApuration

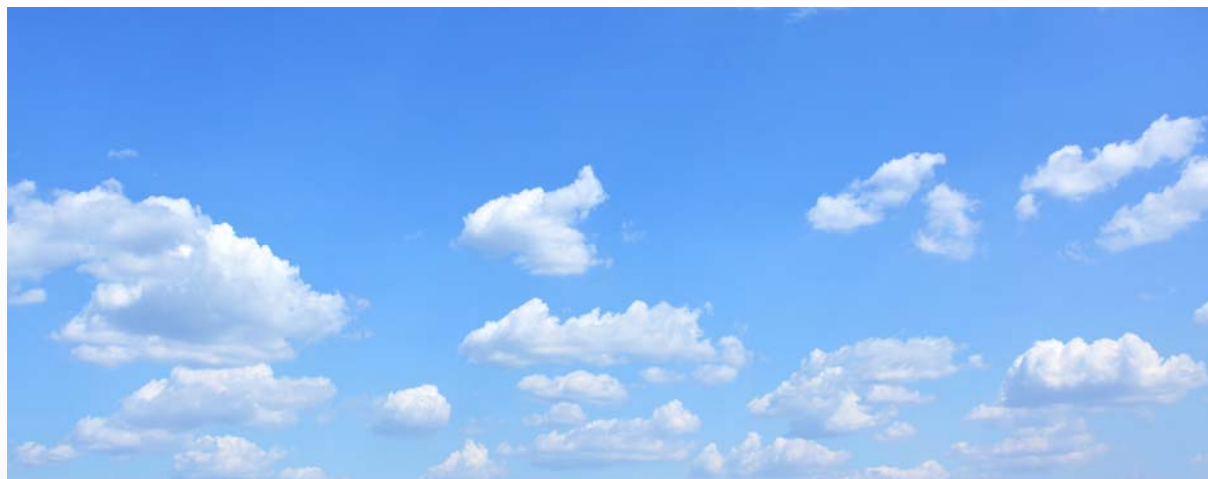
#### Introduction

Outdoor air may contain a number of substances which are hazardous to man's health, either in gaseous form or bound to particles. In order to analyse the outdoor air for PAH, particulate matter  $PM_{10}$ , meaning small particles with a diameter of  $10\ \mu\text{m}$ , are analysed for their amount of bound PAH. In monitoring stations, e. g. four currently present in Slovenia, air is filtered through special filters for 24 hours and these filters are subsequently extracted and analysed.

In this method six different PAH are measured, which are benzo(a)anthracene, chrysene, the sum of benzo(b, j, k)fluoranthene, benzo(a)pyrene, indeno(123-cd)pyrene, and dibenzo(ah)anthracene; with a main focus on benzo(a)pyrene.

#### Principle of the Method

The collected and cut filters, typically with a size of  $1\ \text{cm} \times 1\ \text{cm}$ , are extracted with 10 mL of acetone/n-hexane with added internal deuterated PAH standard in a microwave extractor ( $100\ ^\circ\text{C}$ , 20 min.). The extraction solvent is then transferred to 60 mL vials, which are put into the FREESTYLE system and processed with SPE/EVApuration methodology shown below.



## Procedure

The extracted raw extract in a 60 mL sealed vial is placed on the FREESTYLE system equipped with SPE and EVAporation module.

The sample is processed on the system using the method shown in the report on page 4.

The description of the process in brief:

The 6 mL SPE cartridge with 1 g silica is conditioned with two solvents (dichloromethane first, then n-hexane) and the sample is loaded quantitatively afterwards. The flow through containing the analytes is collected in a second 60 mL vial. A subsequent rinsing step with 5 mL of dichloromethane/n-hexane (3:2) is passed over the cartridge and collected in the collect vial as well. Finally the cartridge is dried with nitrogen in order to remove all solvents still present that could evaporate into the environment.

Now the EVAporation process starts by using heat/vacuum/shaking; after reaching a level of 3 mL the remaining solvent is blown-down to dryness by means of nitrogen, and finally precisely filled up to 1 mL acetone. The final extract is then transferred to a GC vial for measurement automatically.

The measurement of the analytes is performed with GC-MS.

The SPE and EVAporation processing steps are listed in the table below.

A detailed parameterisation is shown in the method report on page 5.






SPE steps	Fully automated
Conditioning	10 mL DCM, 5 mL/min.
Conditioning	10 mL n-hexane, 5 mL/min.
Loading	11 mL sample, 2 mL/min.
Elution	5 mL DCM/n-hexane 3:2, 2 mL/min.
Drying	20 mL air, 100 mL/min

Evaporation parameters	Fully automated
Temperature	Water heater 40 °C Bottom cone 42 °C
Vacuum	Volume defined to 3 mL, 210 mbar
Rinsing volume	3 mL n-hexane
Blow down with nitrogen	To dryness
Backfill to final volume	1 mL

## Devices and Materials

- |   |                            |
|---|----------------------------|
| 1. FREESTYLE BASIC  | P/N 12663                  |
| 2. FREESTYLE EVAporation  | P/N 13841                  |
| 3. FREESTYLE SPE  | P/N 12668                  |
| 4. Upgrade 3 to 6 solvents  | P/N 12952                  |
| 5. Blow-down function   | P/N 12905                  |
| 6. Special tray 60 mL vials,<br>for 12 samples                        | P/N 12399                  |
| 7. Special rack SPE cartridges,<br>for 18 SPE cartridges              | P/N 13946                  |
| 8. Column adapter 6 mL  | P/N 12809 (10 pcs/pck)     |
| 9. Reusable stainless steel needles                                   | P/N 13382 (12 pcs/pck)     |
| 10. Rack for GC vials, 60 positions                                   | P/N 11920                  |
| 11. 60 mL- vials  | P/N F060 (100 pcs/pck)     |
| 12. Screw cap for 60 mL vials   | P/N V0024-SL (100 pcs/pck) |
| 13. Seals cap 60 mL vials   | P/N V0025-D (100 pcs/pck)  |
| 14. GC vials  | P/N V0001 (100 pcs/pck)    |
| 15. Crimp cap for GC-vials with seal                                  | P/N V0001-B (100 pcs/pck)  |
| 16. Cooler  | P/N 12060, 230 VAC, 50 Hz  |
| 17. Liquid level sensor   | P/N 12709                  |
| 18. Dichloromethane for trace analysis                                |                            |
| 19. n-Hexane for trace analysis                                       |                            |
| 20. Acetone for trace analysis  |                            |
| 21. 6 mL standard polypropylene SPE cartridges filled with 1 g silica |                            |
| 22. Native and deuterated PAH standard                                |                            |
| 23. Standard laboratory glassware and –apparatus                      |                            |
| 24. Personal computer/Laptop according to specification               |                            |

## Parameterization of the Method on the FREESTYLE System

			
LCTech FreeStyle - Report on Methods: SPE_H53 -> EVA      Date: 21.11.2014    Time: 09:18:55			
Name: PAH_PM10.fsh			
SPE - Method: PAH_PM10.spe	Online =====>		EVA - Method: PAH_PM10.evp
SPE:			
		SPE Column:	LCTech_6ml.col
Extension cannula:	yes		
Processing speed selection:	Standard (organic solvents)		
Rinsing intensity:	Standard rinsing cycle		
Use pressure limitation function during loading and washing:	no		
Step: Conditioning		Basic type: Conditioning	Step: - ID: 616
 Volume: 10 ml	Suction Speed: 25 ml/min Repetitions: 0 Waiting Time after Dosage: 0 sec.	Dispensing Speed: 5 ml/min Waiting Time after Step: 0 sec.	Port: 8 (DCM) Dispense: into Waste
Step: Conditioning		Basic type: Conditioning	Step: - ID: 617
 Volume: 10 ml	Suction Speed: 25 ml/min Repetitions: 0 Waiting Time after Dosage: 0 sec.	Dispensing Speed: 5 ml/min Waiting Time after Step: 0 sec.	Port: 7 (n-Hexane) Dispense: into Waste
Step: Load		Basic type: Load - Quantitative transfer in parallel mode	Step: - ID: 618
 Volume: 11 ml Vial Type: Type_H53@60	Suction Speed: 10 ml/min Waiting Time after Dosage: 0 sec.	Dispensing Speed: 2 ml/min Waiting Time after Step: 150 sec.	Dispense: into vials    Number of vials: 1 Vial Type: Type_H53@60
rinsing cycle included	Rinsing volume: 3 ml Suction Speed: 10 ml/min Port: 7 (n-Hexane)	Rinse repetitions: 0 x Dispensing Speed: 2 ml/min	Tube rinse volume: 2 ml
Step: Washing		Basic type: Washing	Step: - ID: 619
 Volume: 5 ml	Suction Speed: 10 ml/min Repetitions: 0 Waiting Time after Dosage: 0 sec.	Dispensing Speed: 2 ml/min Waiting Time after Step: 0 sec.	Port: 9 (DCM:n-Hexane 3:2) Drying time: 20 min Dispense: stay on actual position
Step: Drying		Basic type: Drying - Drying by defined air volume	Step: - ID: 620
 Air volume: 20 ml	Suction Speed: 100 ml/min	Dispensing Speed: 100 ml/min	Dispense: stay on actual position



FREESTYLE SPE with Rack H53

# APPLICATION NOTE | AN0008

EVA:	Temperature water heating 40 °C	Temperature bottom cone 42 °C
Sample input: suck from vial / vials into chamber over sample probe and tubing, option with rinsing cycle		
Number of vials: 1 x Type_H53@60	Vacuum at suction: 550 mbar	Maximum time vacuum suction: 15 min.
rinsing cycle included		
Rinsing volume: 4.5 ml	Rinsing steps: 5 x	Solvent from Port: 7 (n-Hexane)
Phase 1: Concentrate to level: 3 ml		
Vacuum absolute: 210 mbar		
Rinsing volume after phase 1: 3 ml	Rinsing steps: 1 x	Solvent from Port: 7 (n-Hexane)
Skip phase 2		
Time control for vacuum process: no		
to dryness: no		
Nitrogen blow-down: yes	Nitrogen blow-down - in max. 2.2 min. to dryness	
Remove Aliquot: no		
Solvent exchange: no		
Rinsing, filling up, mixing and transfer into vials:		
Rinsing volume at the end: 1 ml	Rinsing steps: 1 x	Solvent from Port: 1 (ACE)
Fill up to volume:	1 ml	Way of mixing: with gas / air, Volume = 5 ml
Concentrate: into vials / Direct Injection HPLC		
Nr.: 1	1 [each]	Type: Type1@1 ml
		Volume per vial 1 ml
Fill Quantitativ: no		
1. Cleaning cycle		
Rinsing volume: 3 ml	Rinsing steps: 4 x	Solvent from Port: 9 (DCM:n-Hexane 3:2)
2. Cleaning cycle		
Rinsing volume: 3 ml	Rinsing steps: 4 x	Solvent from Port: 1 (ACE)
include vacuum drying		
Vacuum: 40 mbar abs.	Drying time: 2 min.	



EVAporation chamber (without protective cover)



On-line connection from SPE directly into the EVAporation chamber

## GC Settings

GC-MS system	Agilent 6890N/5975B
Capillary	DB-5 UI 30 m x 0.25 mm x 0.25 µm
Carrier gas	Helium at 1.5 mL/min
Injection	1 µL; split/splitless mode
Temperature program	65 °C for 1 min Heat up to 200 °C with 16 °C/min Heat up to 320 °C with 8 °C/min Hold for 3 min

## Results

The process time of a sample including solvent exchange and transfer into a GC vial takes 1 h 19 min.

Measured data for a real sample collected November 5<sup>th</sup> 2014 (n = 7); all values are in ng/mL unless otherwise noted.

Number	1	2	3	4	5	6	7	Σn	x <sub>m</sub>	s	RSD [%]
Sample value*	60,8	62,2	63,6	61,0	63,2	61,8	63,9	7	62,3	1,2	2,0
Sample value + std. 30 ng	89,2	93,4	90,9	92,7	91,2	94,6	95,0	7	92,4	2,1	2,3
Practical value of std.	26,9	31,0	28,5	30,4	28,9	32,3	32,7	7	30,1	2,1	7,0
Theoretical value of std.	30	30	30	30	30	30	30	7			
Recovery MD/CRM [%]	89,6	103,4	95,1	101,2	96,2	107,7	109,0	7	<b>100,3</b>		

\* Value for benzo(a)pyrene

As it can be seen a certified standard with a concentration of 30 ng used for standard addition will be found with a concentration of 30,1 ng, and a recovery of 100,3 % in a seven-fold measurement, respectively.

## Acknowledgement

For conducting the experiments and provision of the experimental data we want to thank the **Slovenian Environment Agency / analytical laboratory (ARSO)**.

## Regulations

- 1 DIN EN ISO 15549:2008: Air quality – Standard method for the measurement of the concentration of benzo(a)pyrene in ambient air.
- 2 Commission Decision 2004/107/EC – relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air.
- 3 Official Journal of the Republic of Slovenia, 39/06; relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in outdoor air.

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