DETERMINATION OF PAH

In Particulate Matter PM$_{10}$ with SPE/EVAporation
**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 μm, 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 cm x 1 cm, are extracted with 10 mL of acetone/n-hexane with added internal deuterated PAH standard in a microwave extractor (100 °C, 20 min.). The extraction solvent is then transferred to 60 mL vials, which are put into the FREESTYLE system and processed with SPE/EVAporation 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.

<table>
<thead>
<tr>
<th>SPE steps</th>
<th>Fully automated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conditioning</td>
<td>10 mL DCM, 5 mL/min.</td>
</tr>
<tr>
<td>Conditioning</td>
<td>10 mL n-hexane, 5 mL/min.</td>
</tr>
<tr>
<td>Loading</td>
<td>11 mL sample, 2 mL/min.</td>
</tr>
<tr>
<td>Elution</td>
<td>5 mL DCM/n-hexane 3:2, 2 mL/min.</td>
</tr>
<tr>
<td>Drying</td>
<td>20 mL air, 100 mL/min</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Evaporation parameters</th>
<th>Fully automated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>Water heater 40 °C</td>
</tr>
<tr>
<td></td>
<td>Bottom cone 42 °C</td>
</tr>
<tr>
<td>Vacuum</td>
<td>Volume defined to 3 mL, 210 mbar</td>
</tr>
<tr>
<td>Rinsing volume</td>
<td>3 mL n-hexane</td>
</tr>
<tr>
<td>Blow down with nitrogen</td>
<td>To dryness</td>
</tr>
<tr>
<td>Backfill to final volume</td>
<td>1 mL</td>
</tr>
</tbody>
</table>
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, for 12 samples P/N 12399
7. Special rack SPE cartridges, 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

**Parameterization Details**

**Name:** PAH_PM10.fsh

**SPE Column:** LCTech_6ml.col

### Conditioning

**Volume:** 10 ml  
**Suction Speed:** 25 ml/min  
**Dispensing Speed:** 5 ml/min  
**Port:** 8 (DCM)

### Load

**Volume:** 11 ml  
**Dispensing Speed:** 2 ml/min  
**Dispense into:** vials

### Washing

**Volume:** 5 ml  
**Dispensing Speed:** 2 ml/min  
**Dispense:** stay on actual position

### Drying

**Air Volume:** 20 ml  
**Dispensing Speed:** 100 ml/min  
**Dispense:** stay on actual position

**FREESTYLE SPE with Rack H53**
**EVAporation chamber (without protective cover)**

- **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
  - Rinsing cycle included
  - Rinsing volume: 4.5 ml

<table>
<thead>
<tr>
<th>Phase</th>
<th>Concentrate to level</th>
<th>Vacuum absolute</th>
<th>Rinsing after phase</th>
<th>Rinsing steps</th>
<th>Solvent from Port</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3 ml</td>
<td>210 mbar</td>
<td>3 ml</td>
<td>1 x</td>
<td>7 (n-Hexane)</td>
</tr>
<tr>
<td>2</td>
<td>Skip phase 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Time control for vacuum process: no</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **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
  - Fill up to volume: 1 ml
  - Concentrate into vials / Direct Injection HPLC
    - Nr.: 1 [each]
    - Type: Type 1@1 ml
    - Volume per vial: 1 ml

- **Fill Quantitatively:** no

<table>
<thead>
<tr>
<th>1. Cleaning cycle</th>
<th>Rinsing volume: 3 ml</th>
<th>Rinsing steps: 4 x</th>
<th>Solvent from Port: 9 (DCM:n-Hexane 3:2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2. Cleaning cycle</td>
<td>Rinsing volume: 3 ml</td>
<td>Rinsing steps: 4 x</td>
<td>Solvent from Port: 1 (ACE)</td>
</tr>
<tr>
<td></td>
<td>Include vacuum drying</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Vacuum: 40 mbar abs.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Drying time: 2 min.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**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 5th 2014 (n = 7); all values are in ng/mL unless otherwise noted.

<table>
<thead>
<tr>
<th>Number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>∑n</th>
<th>x_m</th>
<th>s</th>
<th>RSD [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample value*</td>
<td>60,8</td>
<td>62,2</td>
<td>63,6</td>
<td>61,0</td>
<td>63,2</td>
<td>61,8</td>
<td>63,9</td>
<td>7</td>
<td>62,3</td>
<td>1,2</td>
<td>2,0</td>
</tr>
<tr>
<td>Sample value + std. 30 ng</td>
<td>89,2</td>
<td>93,4</td>
<td>90,9</td>
<td>92,7</td>
<td>91,2</td>
<td>94,6</td>
<td>95,0</td>
<td>7</td>
<td>92,4</td>
<td>2,1</td>
<td>2,3</td>
</tr>
<tr>
<td>Practical value of std.</td>
<td>26,9</td>
<td>31,0</td>
<td>28,5</td>
<td>30,4</td>
<td>28,9</td>
<td>32,3</td>
<td>32,7</td>
<td>7</td>
<td>30,1</td>
<td>2,1</td>
<td>7,0</td>
</tr>
<tr>
<td>Theoretical value of std.</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>7</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recovery MD/CRM [%]</td>
<td>89,6</td>
<td>103,4</td>
<td>95,1</td>
<td>101,2</td>
<td>96,2</td>
<td>107,7</td>
<td>109,0</td>
<td>7</td>
<td>100,3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* 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.