Application Note
No. 358/2019

Polycyclic aromatic hydrocarbons in sediment

UniversalExtractor E-800:
Soxhlet warm extraction of a sediment sample using the UniversalExtractor E-800 for the determination of polycyclic aromatic hydrocarbons (PAHs)

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are chemical compounds that consist of fused aromatic rings and do not contain heteroatoms or carry substituents.

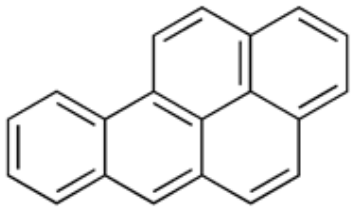

Figure 1: Formula of Benzo(a)pyrene.

PAHs occur in oil, coal and tar produced by carbonization of coal, but not in bitumen. They can also be found in grilled meat, cigarette smoke and automobile exhaust. PAH are persistent, ubiquitous and some of them have carcinogenic, mutagenic and teratogenic properties. There are more than 100 different PAH, but usually the 16 PAH defined by the United States Environmental Protection Agency (EPA) are analyzed. These are acenaphthene, acenaphthylene, anthracene, benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(ghi)perylene, benzo(k)fluoranthene, chrysene, dibenz(ah)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene and pyrene. Benzo(a)pyrene is often used as a lead substance.

This Application Note describes the extraction and determination of these EPA-PAHs in a dried sediment SETOC sample according to EPA 3541 [1]. The sample was extracted with the UniversalExtractor E-800 in the Soxhlet warm mode. The quantification was done by Labor Veritas Zurich, an ISO 17025 accredited laboratory.

2. Equipment

- UniversalExtractor E-800 Pro (with chamber heater)
- Syncore® Analyst with flushback module, R-12 with 1 mL appendix
- Vacuum Pump V-700 with Interface I-300 Pro and Recirculating Chiller F-308
- GC-MS/MS Thermo Scientific TSQ-Quantum XLS
- Analytical balance (accuracy ± 0.1 mg)

3. Chemicals and Materials

Chemicals:

- n-Hexane, for analysis, Reag. ACS, Sigma Aldrich (32293)
- Acetone, MS SUPRASOLV, Sigma Aldrich (1006582500)

Standard:

- Naphthalene-d_8; acenaphthene-d_{10}; ayrene-d_{10}; phenanthrene-d_{10}; chrysene-d_{12}; benzo(b)fluoranthene-d_{12}; indeno(1,2,3-cd)pyrene-d_{12}; anthracene-d_{10}; benzo(a)pyrene-d_{12}; benzo(ghi)perylene-d_{12}in acetonitrile.

For a safe handling please pay attention to all corresponding MSDS.

Materials:

- Sodium sulphate, anhydrous, Sigma Aldrich (798592)
- Extraction thimble 33 x 150, BUCHI (11067446)

Sample:

- Sediment samples, SETOC 777 (61), dry sample, Wageningen Evaluation Programs for analytical Laboratories, University of Wageningen [2].

4. Procedure

The extraction and analysis of PAH in sediment includes the following steps:

- Preparation of sample
- Extraction with UniversalExtractor E-800
- Concentration of the raw extracts using the Syncore®
- Quantification by GC-MS

4.1. Preparation of the sample

1. Place a paper thimble 33 x 150 into the holder.
2. Weigh in 10 g sodium sulphate into the paper thimble.
3. Weigh in 10 g of sediment sample using the analytical balance and mix with a spatula carefully.
4. Add 1.5 mL of the internal standard solution.

4.2. Extraction with UniversalExtractor E-800

1. Insert the paper thimble containing the sample into the extraction chamber
2. Adjust the optical sensor to the sample height
3. Add the solvent to the solvent beaker
4. Program the extraction method according to the parameters shown in Table 1.
5. Close the extraction shield
6. Start the extraction

Table 1: Extraction method for UniversalExtractor E-800.

Parameter	Value
Extraction method	Soxhlet warm
Solvent	n-Hexane / Acetone (1:1)
Solvent volume	150 mL
Extraction time	180 min
Extraction heating level	11
Chamber heating level	3
Rinse time	5 min
Rinse heating level	11
Drying time	5 min
Drying heating level	10

4.3. Concentration of the raw extracts using the Syncore®

1. Evaporate the raw extract (around 30 mL) to 1 mL using the Syncore® R-12 with vessels with 1 mL appendix using the parameters shown in Table 2.

Table 2: Parameters for the Syncore® R-12.

Step	Pressure start	Pressure end	Time
1	950	350	1 min
2	350	350	1 min
3	350	300	1 min
4	300	300	2 min
5	300	270	1 min
6	270	270	15 min
7	270	200	3 min
Total time			**24 min**
Temperature platform			50 °C
Temperature cover			55 °C
Rotation			250 Rpm

4.4. Quantification by GC-MS

The PAHs were quantified using the parameters in Table 3.

Table 3: GC-MS parameters for the quantification of PAHs.

GC-MS/MS	Thermo Scientific TSQ-Quantum XLS
Column	15 m x 0.25 mm (i.d.), 0.25 µm film thickness, Mega-5 MS column.
Oven program	60°C (hold for 1 min); 60 °C – 150 °C at 30 °C/min; 150°C - 320 °C at 15 °C/min; hold for 4 min.

5. Result

The extraction by the UniversalExtractor E-800 confirms the consensus values of the reference SETOC sample. The sample was extracted in triplicate (n= 3) together with a blank sample. The results are shown Table 4 and Figure 2. Low variations between the three extractions were found.

Table 4: SETOC 777 Sediment (61) extraction by UniversalExtractor E-800, n= 3

	Mean value	RSD	SETOC value	RSD
	µg/kg	%	µg/kg	%
Naphthalene	421	2	-	-
Acenaphtylene	77	10	-	-
Acenaphthene	134	16	164	19
Fluorene	138	8	168	21
Phenanthrene	1253	5	1190	13
Anthracene	363	4	278	22
Fluoranthene	1927	8	1960	13
Pyrene	1447	8	1450	14
Benz(a)anthracene	1017	4	908	15
Chrysene	1207	2	1050	16
Benzo(b)fluoranthene	1377	5	1230	17
Benzo(k)fluoranthene	580	5	562	15
Benzo(a)pyrene	953	1	865	15
Indeno(1,2,3-cd)pyrene	890	2	742	17
Dibenzo(ah)anthracene	193	7	173	25
Benzo(ghi)perylene	587	1	708	12
Sum PAH	12883	4	11800	13

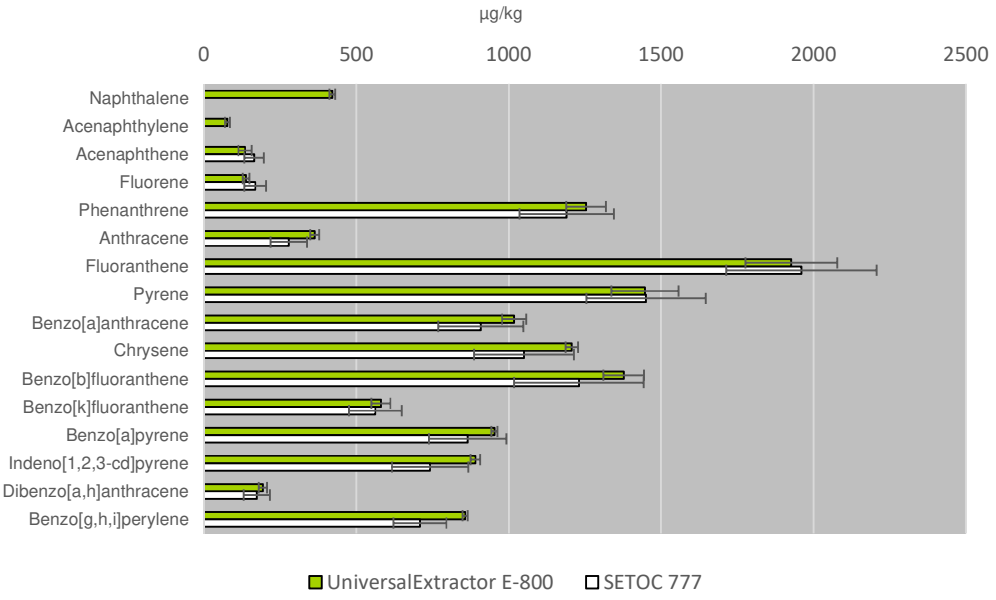

Figure 2: Results of the PAH determination of a sediment sample using the UniversalExtractor E-800 and SETOC consensus values.

6. Method development

For method development the samples were extracted for 2 h, 3 h and 4 h. The results are shown in Table 5 and Figure 3.

Table 5: *Recoveries of PAHs after extraction times of 2h, 3h and 4h. Extraction performed on UniversalExtractor E-800, n = 3.*

	SETOC value	Recovery 2h	Recovery 3h	Recovery 4h
	µg/kg	%	%	%
Naphthalene	-			
Acenaphtylene	-			
Acenaphtene	164	68	82	70
Fluorene	168	79	82	79
Phenanthrene	1190	87	105	103
Anthracene	278	112	131	132
Fluoranthene	1960	99	98	91
Pyrene	1450	94	100	95
Benz(a)anthracene	908	92	112	104
Chrysene	1050	81	115	111
Benzo(b)fluoranthene	1230	110	112	117
Benzo(k)fluoranthene	562	90	103	102
Benzo(a)pyrene	865	86	110	106
Indeno(1,2,3-cd)pyrene	742	103	120	115
Dibenzo(ah)anthracene	173	104	112	103
Benzo(ghi)perylene	708	100	121	115

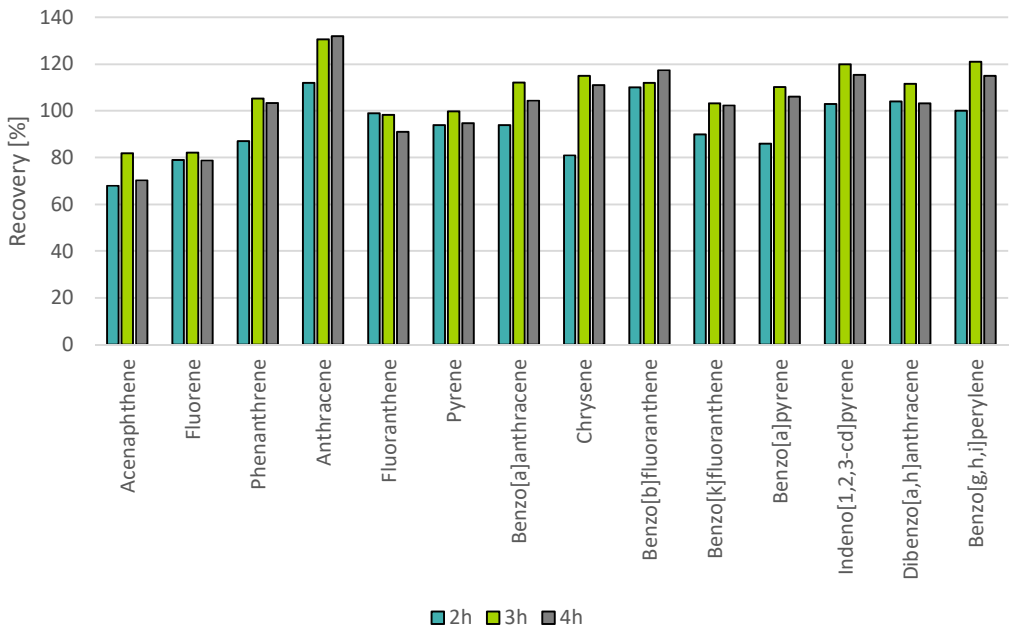

Figure 3: Recoveries of PAH determination with different extraction times 2 h, 3 h and 4 h. Extraction performed with UniversalExtractor E-800, n= 3.

An extraction time of 3h is sufficient for the extraction of PAHs from a sediment sample. A longer extraction time is not required. The recoveries received after 2h extraction time were too low.

7. Conclusion

The method presented in this Application Note demonstrates that the extraction by UniversalExtractor E-800 using the Soxhlet warm mode is a fast and reliable way to extract PAH from sediment samples.

8. Acknowledgements

We greatly acknowledge Labor Veritas Zürich, Mr. Pascal Leupin and Mr. Oleg Altergott for their support for the development of this Application Note.

9. References

[1] U.S. Environmental Protection Agency. Method 3541, Automated Soxhlet Extraction

[2] SETOC Round Robin, http://www.wepal.nl/website/products/SEToc.htm