DETERMINATION OF PAH IN GROUND, SURFACE AND DRINKING WATER USING SYMBIOSIS™ ENVIRON

September 2005
0053.061-01

APPLICATION INFO

Introduction

Polycyclic Aromatic Hydrocarbons (PAH), a group of chemically related compounds, are known for their potential carcinogenic properties. In the environment these compounds are formed during pyrolysis and incomplete combustion processes. They are found throughout the environment in air, water and soil. The (by law enforced) maximum acceptable concentration level of PAH in water is approximately 10 ppt for each individual component.

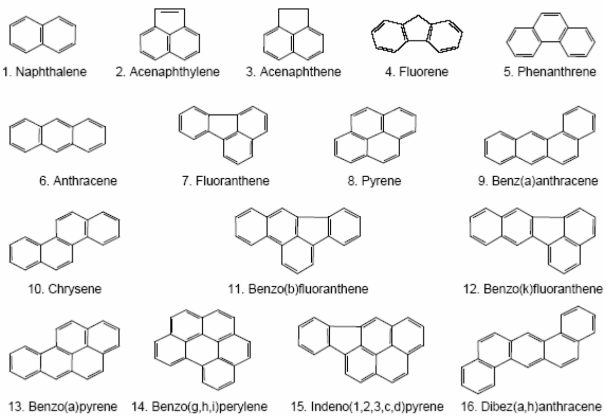

Figure 1: Polycyclic Aromatic Hydrocarbons.

Symbiosis™ Environ (see figure 3) is Spark Holland's unique solution for integrated online SPE-HPLC in environmental analyses. Water samples up to 1 L are pre-concentrated on a Solid Phase Extraction cartridge and eluted online (and fully automated) to an HPLC.

Figure 2: Symbiosis™ Environ & Triathlon

This Application note demonstrates the capability of the Symbiosis™ Environ in conjunction with the Triathlon autosampler and a fluorescence detector to analyse PAH in water at ppt levels using only 10 mL of water sample. The Symbiosis™ method is compared to a traditional offline method (NEN-EN-ISO 17993, "Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction").

Experimental

Sample pretreatment

To minimize adsorption of PAH to the glass wall of the sample container, each amber borosilicate sample container is pretreated by three rinses: isopropanol, 20% nitric acid; isopropanol. After rinsing each container is filled with a fixed volume of isopropanol. The water samples are added to the isopropanol and mixed to obtain a final concentration of 25 % isopropanol. All samples are stored in the dark at 4ºC.

Autosampler Conditions

10 mL sample is introduced by connecting the HPD of the Symbiosis Environ to the injector valve of the Triathlon (figure 2) excluding the sample loop, using a user programmable injection routine of the Triathlon.

SPE Conditions

SPE cartridge	Focus, L=10 mm I.D.=2 mm (Varian part number:12221301)	
Solvation 1	6 mL acetonitrile	6 mL/min.
Solvation 2	6 mL methanol	6 mL/min.
Equilibration	3 mL water	4 mL/min.
Sample load	10 mL	2 mL/min.
Washing	2 mL 10% methanol	2 mL/min.
Elution	5 min. with acetonitrile (mixed with water to form the LC gradient)*	

Table 1: SPE conditions

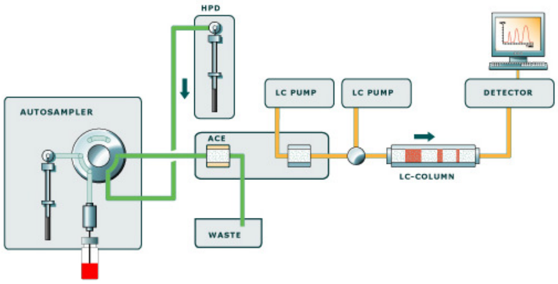

Figure 2: Schematic representation of flow path

HPLC Conditions

Figure 3 shows the total system configuration; The hydrophobic SPE cartridge is eluted with one of the Symbiosis high pressure LC pumps by eluting the SPE cartridge with 100% acetonitrile, ensuring a quick desorption. The eluent is mixed with water from a second high pressure LC pump using a high pressure and dynamic mixing chamber. In the proper mixing ratio the solvent is applied to an analytical column for separation and detection of PAH.

Analytical Column	100 mm*4.6 mm*3 µm, Varian Chrompack (part number: CP29424)			
Mobile phase	A: water B: acetonitrile			
	Time (mm:ss)	Flow (mL/min)	A (%)	B (%)
	00:01	1.3	80	20
	02:30	1.3	80	20
	05:00	1.3	50	50
	15:00	1.3	0	100
	28:00	1.3	0	100
	30:00	1.3	80	20
	32:00	1.3	80	20

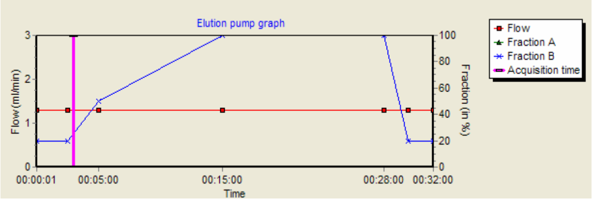

Table 2: LC Conditions

Temperature	25 °C		
UV-Detection	254 nm		
Fluorescence Detection	Compound	Excitation (nm)	Emission (nm)
	Naphtalene	275	325
	1-Methylnaphtalene	275	325
	Acenaphthene	275	325
	Fluorene	275	325
	Phenathrene	255	375
	Anthracene	255	375
	Fluoranthene	270	420
	Pyrene	270	420
	Triphenylene (IS)	270	420
	Benz(a)anthracene	275	383
	Chrysene	275	383
	Benzo(b)fluoranthene	295	410
	Benzo(k)fluoranthene	295	410
	Benzo(a)pyrene	295	410
	Dibenz(a,h)anthracene	301	420
	Benzo(ghi)perylene	301	420
	Indeno(1,2,3-c,d)pyrene	304	501

Results

The following samples are prepared using triphenylene as Internal Standard (IS).

- PAH standard solutions: See table 3
- Ground water samples:
  - low concentration level of PAH
  - high concentration level of PAH

PAH standards (µg/L)	**blank**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Naphtaleen	0.000	0.030	0.060	0.120	0.240	0.600	1.200	2.400	4.800	9.600	30.000
Acenafteen	0.000	0.010	0.020	0.040	0.080	0.200	0.400	0.800	1.600	3.200	
Fluoreen	0.000	0.010	0.020	0.040	0.080	0.200	0.400	0.800	1.600	3.200	
Fenanthreen	0.000	0.013	0.025	0.050	0.100	0.250	0.500	1.000	2.000	4.000	
Anthraceen	0.000	0.005	0.010	0.020	0.040	0.100	0.200	0.400	0.800	1.600	
Fluorantheen	0.000	0.043	0.085	0.170	0.340	0.850	1.700	3.400	6.800	13.600	
Pyreen	0.000	0.030	0.060	0.120	0.240	0.600	1.200	2.400	4.800	9.600	
Benzo(a)anth	0.000	0.008	0.015	0.030	0.060	0.150	0.300	0.600	1.200	2.400	
Chryseen	0.000	0.010	0.020	0.040	0.080	0.200	0.400	0.800	1.600	3.200	
Benzo(b)fluor	0.000	0.030	0.060	0.120	0.240	0.600	1.200	2.400	4.800	9.600	
Benzo(k)fluor	0.000	0.003	0.006	0.012	0.024	0.060	0.120	0.240	0.480	0.960	
Benzo(a)pyr	0.000	0.006	0.012	0.024	0.048	0.120	0.240	0.480	0.960	1.920	
di benzo(a,h)	0.000	0.015	0.030	0.060	0.120	0.300	0.600	1.200	2.400	4.800	
Benzo(ghi)	0.000	0.030	0.060	0.120	0.240	0.600	1.200	2.400	4.800		
Indeno(123)	0.000	0.120	0.240	0.480	0.960	2.400	4.800	9.600	19.200		

Table 3: PAH concentrations in standard solutions

The PAH standard solutions were processed using the newly developed XLC method and plotted against the NEN-EN-ISO 17993 method (see figures 4a-d). These results are summarized in table 4.

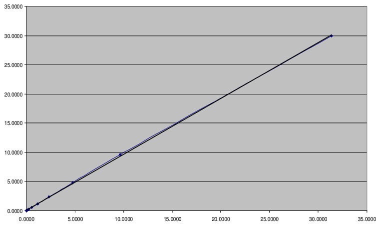

Figure 4a: Naphthalene correlation curve XLC-method vs. NEN-method using UV detection.

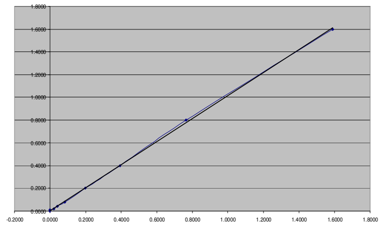

Figure 4b: Fluoreen correlation curve XLC-method vs. NEN-method using UV detection.

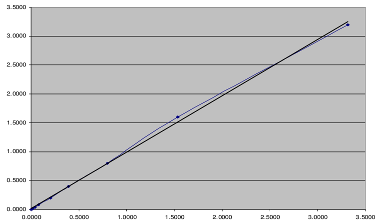

Figure 4c: Acenaphthalene correlation curve XLC-method vs. NEN-method using fluorescence detection.

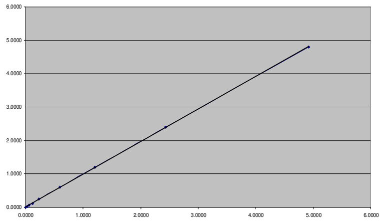

Figure 4d: Benzo(ghi) perylene correlation curve XLC-method vs. NEN-method using fluorescence detection.

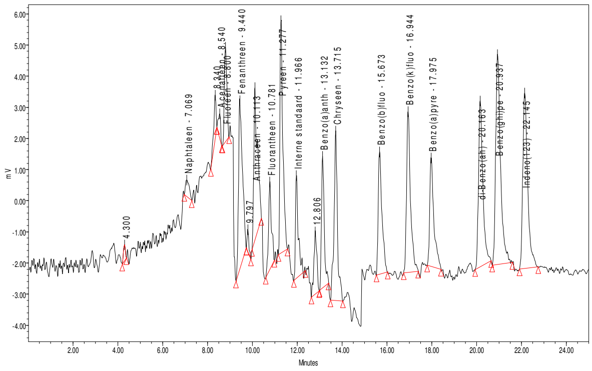

Figure 5a: Chromatogram representing typical ground water sample with a low concentration level of PAH using UV detection.

Figure 5a and 5b show representative chromatograms of ground water samples containing a low and high concentration level, respectively, of PAH using UV detection. The resolution of the individual compounds is presented in table 4.

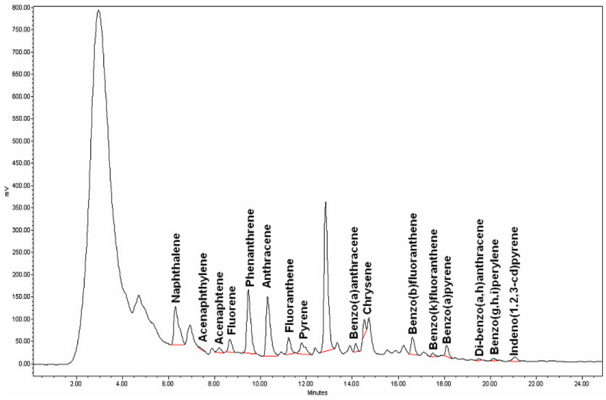

Figure 5b: Chromatogram representing typical ground water sample with a high concentration level of PAH using UV detection.

Figure 6a and 6b show representative chromatograms of ground water samples containing a low and high concentration level, respectively, of PAH using fluorescence detection.

Tabel 4: Results

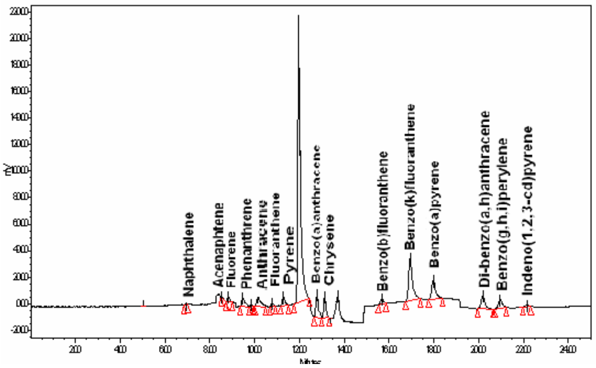

Figure 6a: Chromatogram representing typical ground water sample with a low concentration level of PAH using fluorescence detection.

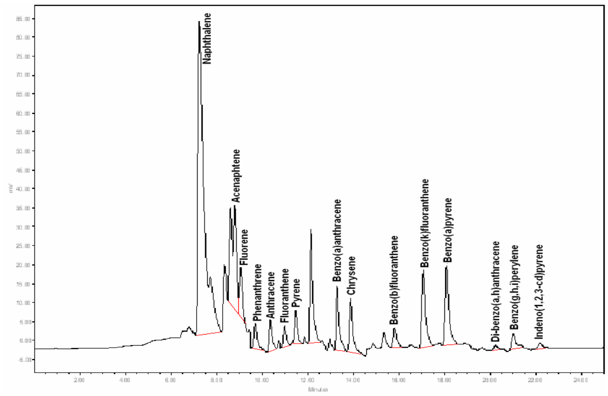

Figure 6b: Chromatogram representing typical ground water sample with a high concentration level of PAH using fluorescence detection.

Components	Correlation (R)		Detection limit (ng/L)		CV Low level (n = 8)		CV High level (n = 8)		Recovery Low level (%)		Recovery High level (%)		Resolution
	Flu	UV	Flu	UV	Flu	UV	Flu	UV	Flu	UV	Flu	UV	UV
Naphtalene	0.9993	0.9998	5	9	4.2	7.8	2.3	4.2	98	96	96	93	3.6
Acenaphthalene	-	0.9997	--	7	--	6.7	--	3.3	--	92	--	109	5.0
Acenaphtene	0.9988	0.9999	3	4	4.8	10.6	2.5	4.9	99	106	95	95	1.5
Fluorene	0.9999	0.9997	2	6	4.2	4.3	1.2	2.9	97	95	93	98	3.3
Fenanthrene	0.9995	0.9992	3	5	5.2	7.8	1.1	4.0	99	96	92	93	3.7
Anthracene	0.9999	0.9999	2	10	4.4	13.8	1.6	7.8	99	103	100	87	3.8
Fluoranthene	0.9989	0.9999	4	6	2.7	3.4	0.7	2.9	98	96	95	98	3.3
Pyrene	1.0000	0.9997	4	7	2.5	2.8	2.0	4.1	101	98	97	106	2.9
Benz(a)anthracene	0.9999	0.9994	2	5	2.3	6.6	2.0	6.3	101	97	96	104	3.4
Chrysene	1.0000	1.0000	2	5	4.3	3.1	0.7	3.0	99	98	97	105	2.5
Benzo(b)fluoranthene	1.0000	1.0000	2	7	1.2	2.3	1.0	3.0	97	96	97	83	10.8
Benzo(k)fluoranthene	0.9999	0.9994	0.5	7	2.0	13.1	1.0	13.6	97	98	97	95	4.8
Benzo(a)pyrene	1.0000	0.9999	5	5	6.2	11.8	12.1	11.4	91	104	107	104	4.4
Dibenz(a,h)anthracene	1.0000	0.9999	1	9	4.3	13.1	6.1	3.3	94	96	100	83	6.7
Benzo(ghi)perylene	1.0000	0.9994	3	7	10.7	10.0	4.7	3.0	110	105	103	101	4.3
Indeno(1,2,3-c,d)pyrene	0.9993	0.9881	5	6	3.8	3.4	2.8	2.9	95	95	97	105	2.7

Table 4: Results

The detection limits are lower (as low as 0.5 ppt) using fluorescence detection for all PAH components except acenaphthalene that can only be detected by UV detection (all individual detection limits are presented in table 4).
The XLC Method was validated by determining the Coefficient of Variation (CV) of eight injections containing a low concentration range of PAH and eight injections containing a high concentration range of PAH. The CV of the individual PAH are presented in table 4.

Conclusions

Polycyclic Aromatic Hydrocarbons (PAH) are in general difficult to analyze, especially when these compounds are present in groundwater or surface water.
From this study it is concluded that using the Symbiosis™ system, careful pretreatment of the glass sample containers, with isopropanol as a modifier and UV- or fluorescence detection, PAH can be analyzed fully automated with excellent recoveries (92 to 107 %) and acceptable reproducibility (CV = 0.7 to 13.8 %) in groundwater matrix.
The pre-concentration of 10 (up to 100) mL of sample volume, consisting of 25 % isopropanol and 75 % water, enables the determination of analyte concentrations as low as 2 ng/L with fluorescence detection.
The developed method shows excellent correlation (r=0.9881-1.000) with the NEN-EN-ISO-17993 and proofed to be an excellent alternative for the normally used liquid-liquid extraction method.

References

NEN-EN-ISO 17993: Water quality - Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction.
This International Standard specifies a method using liquid-liquid extraction and high performance liquid chromatography (HPLC) with fluorescence detection for the determination of 15 selected PAH (see Table 1) in drinking water and ground water in concentrations above 0,005 µg/L (for each single compound) and surface waters in concentrations above 0,01 µg/L. This method is, with minor modifications, also suitable for the analysis of waste water. The method may be applicable to other PAH, but needs to be validated for each additional compound.

eurofins | analytico
Jan Volkers
Eurofins Analytico Milieu B.V.
PO Box 459
3770 AL Barneveld
The Netherlands