Biotage®

APPLICATION NOTE

PAH Analysis in Drinking Water using Disk SPE Automated with the SPE-DEX 5000

Alicia Cannon, Horizon Technology, Salem, NH USA

Key Words

PAH, Polycyclic aromatic hydrocarbons, USEPA 550.1

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous pollutants introduced into the environment from anthropogenic activities such as combustion of fossil fuels, tobacco smoking and even during food preparation. These compounds strongly adsorb to sediment or particulate matter, causing them to slowly biodegrade while remaining present in drinking water sources; mostly as leachates from water storage and distribution systems. Exposure to PAHs over time can lead to increased health risks including developmental and reproductive issues. This class of compounds has also been identified as a carcinogen. As a result, PAH's in drinking water must be monitored.

US EPA method 550.1 is a method used by regulatory agencies to determine PAH's in drinking water by liquid-solid extraction (LSE) and high performance liquid chromatography (HPLC).[1] The method outlines the steps needed to perform extractions of PAHs from drinking water sources and finished drinking water; as well as the quality control (QC) program requirements to ensure the method is operated under control.

Automation of the extraction process allows more hands-off time for the operator and ensures better precision between operators. US EPA drinking water methods have embraced the use of SPE, yielding smaller extracts that require less evaporation time and require less solvent recovery. Use of Horizon Technology's automated sample preparation product line allows users to achieve the precise and consistent data needed to comply with EPA method 550.1 QC specifications as stated in method, section 10.3.2., for Initial Demonstration of Capability (IDC); while at the same time, streamlining laboratory practices to increase lab productivity.

Experimental

The instrumentation used in the method included the SPE-DEX® 5000 disk extraction system (Horizon Technology). This is a three-position extraction system that automates disk conditioning, sample loading and elution of the disk. Atlantic® C18 disks (Horizon Technology) were used for sorption of the analytes. The eluent was dried of residual water using DryDisk® membrane drying with the DryVap® In-line drying and evaporations system.

Analysis of the prepared extracts was accomplished with the Prominence i-Series HPLC (Shimadzu Scientific Instruments)

Method Summary

1. Obtain 1-liter samples of DI water.
2. Acidify each sample with hydrochloric acid until pH <2.
3. Add surrogate compounds to the samples at a concentration of 5 µg/L.
4. Extract the samples using the SPE-DEX 5000 with 47-mm Atlantic C18 SPE Disks using the method shown in Table 1.
5. Dry and concentrate the extracts using the DryVap with a DryDisk to 0.5-mL final volume. See Table 2 for DryVap conditions.
6. Analyze the samples using conditions used in HPLC Table 3.

Table 1. SPE-DEX 5000 Extraction Method for 47-mm Atlantic C18 Disks

Step	Solvent	Solvent Vol. (mL)	Purge Time (s)	Pump Rate (s)	Sat. Time (s)	Soak Time (s)	Drain Time (s)	
1. Condition SPE Disk	MeCl	15	60	2	1	60	60	
2. Condition SPE Disk	MeOH	11	60	2	1	60	2	
3. Condition SPE Disk	Reagent Water	9	30	2	1	5	5	
4. Condition SPE Disk	Reagent Water	9	60	2	1	30	0	
Step		Sample Flow Rate (#)	Done Loading Sample Delay (s)					
5. Load Sample		2	45					
Step		Dry Time (s)	Pump Rate (#)	N2 Blanket				
6. Air Dry Disk Timer		60	6	Off				
Step	Solvent	Solvent Vol. (mL)	Purge Time (s)	Pump Rate (#)	N2 Blanket	Sat. Time (s)	Soak Time (s)	Elute Time (s)
7. Elute Sample Container	Acetoni-trile	7	60	2	Off	1	60	45
8. Elute Sample Container	MeCl	7	15	2	Off	1	60	45
9. Elute Sample Container	MeCl	7	15	2	Off	1	60	45
10. Elute Sample Container	MeCl	7	15	2	Off	1	60	45
11. Elute Sample Container	MeCl	7	15	6	Off	2	60	60

Table 2. DryVap Conditions

Parameter	Setting
Dry Volume	20
Heat Power	5
Auto Rinse Mode	Off
Heat Timer	Off
Vacuum Pump	-8 psi
Nitrogen	20 psi

Table 3. HPLC Conditions

Parameter	Setting
HPLC System	Shimadzu i-Prominence Series
Column	Pinnacle® II PAH, 4 um (250 mm x 4.6 mm) (Restek)
Detection	uV 220, 254 nm
Mobile Phase	60% ACN: 40% H2O
Elution	Gradient
Flow Rate	1.5 mL/min
Column Temperature	40 °C
Run Time	40 minutes

Results and Discussion

Figure 1 shows a chromatogram of the analytes of interest in a standard mix. Resolution is good under the conditions specified.

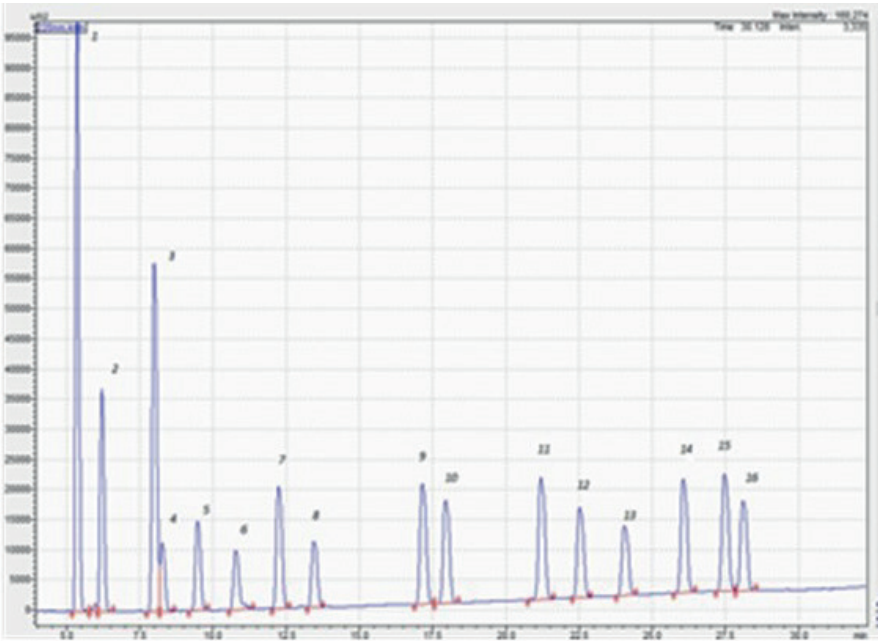

Figure 1. Chromatogram of the 16 compounds of interest, identified in the key table.

ID #	Compound
1	Naphthalene
2	Acenapthylene
3	Acenapthene
4	Fluorene
5	Phenanthrene
6	Anthracene
7	Fluoranthene
8	Pyrene
9	Benz(a)anthracene
10	Benzo(k)fluoranthene
11	Benzo(b)fluoranthene
12	Chrysene
13	Benzo(a)pyrene
14	Dibenz(a,h)anthracene
15	Benzo(ghi)perylene
16	Indeno(1,2,3-cd)pyrene

Nine samples were extracted on the SPE-DEX 5000, spiked at a concentration of 5.0 µg/L. Three samples were run simultaneously, with each run taking 35-40 minutes to complete. Extracts were then dried and concentrated, taking approximately 1 hour to 1 hour 15 minutes to achieve a 0.5-mL final end volume. Final extracts were prepared and ready for HPLC analysis in under 2 hours.

The results for nine replicate samples are shown in Table 4. QC requirements set forth in EPA Method 550.1 Section 10.3, Initial Demonstration of Capability (IDC) state that the recovery value for at least three out of four consecutively analyzed samples must fall in the range of R ±30% (or within R ±3 Sr if broader) using the values of R (mean recovery) and Sr (standard deviation of the %) for reagent water in Table 2 of the method. Table 2 of EPA Method 550.1 shows compound recoveries ranging from 70.5 % - 93.6 %. While analyzing 9 samples using the SPE-DEX 5000, Atlantic C18 Disk and the DryVap, the mean compound recovery (R) was found to range from 80.2 % - 95.7 % recovery throughout each run. The relative standard deviation (Sr) of the mean recovery throughout these runs was calculated to be 5.1-6.3, meeting the method IDC criteria of ±30%.

Table 4. Replicate Spiked Samples

Compound	%Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	% Rec.	S_r (Std Dev)
Naphthalene	71.9	77.0	82.3	73.0	81.6	91.7	80.1	84.7	88.3	6.2
Acenapthylene	78.7	83.5	88.0	75.7	84.1	93.1	87.2	92.4	95.8	6.3
Acenapthene	76.7	81.8	83.8	75.9	84.7	94.3	83.7	86.2	92.2	5.8
Fluorene	78.3	83.0	85.8	76.7	85.4	94.1	87.2	87.8	96.2	6.1
Phenanthrene	82.3	88.7	90.4	80.0	89.1	98.3	88.8	89.7	97.9	5.7
Anthracene	80.8	86.5	88.2	87.6	95.9	91.8	73.3	87.2	96.1	6.8
Fluoranthene	81.9	88.1	88.2	81.2	87.7	97.2	87.7	89.3	98.7	5.5
Pyrene	82.8	89.2	89.4	81.3	88.6	97.3	87.6	89.3	97.2	5.1
Benz(a)anthracene	82.1	88.3	88.0	81.6	87.0	96.9	85.8	89.0	99.3	5.6
Benzo(k)fluoranthene	82.1	88.3	87.9	82.1	86.9	96.7	85.0	89.2	99.7	5.7
Benzo(b)fluoranthene	82.5	88.8	88.9	82.9	88.0	97.7	86.4	89.8	99.9	5.6
Chrysene	82.0	88.4	87.6	82.2	86.6	95.7	83.7	87.8	99.2	5.5
Benzo(a)pyrene	81.0	87.5	87.8	81.7	86.7	94.4	80.6	86.7	97.8	5.5
Dibenz(a,h)anthracene	78.5	84.2	83.6	78.4	84.0	86.7	80.7	89.8	97.9	5.8
Benzo(ghi)perylene	80.6	87.3	87.2	81.5	85.9	93.9	82.9	88.2	99.0	5.6
Indeno(1,2,3-cd)pyrene	81.1	87.9	87.5	82.2	86.7	95.4	83.4	87.7	99.5	5.7
R (Mean Recovery)	80.2	86.2	87.2	80.2	86.8	95.7	84.0	88.4	97.2	

Conclusion

Automated SPE for preparation of PAHs in drinking water gave excellent results, meeting the requirements set forth in US EPA method 550.1. In addition, the time for preparation was efficient and samples were prepared and ready for HPLC analysis in less than 2 hours. This is a powerful combination for laboratory efficiency.

References:

1. US EPA Method 550.1, US EPA https://www.o2si.com/docs/epa-method-550.1.pdf (1990).

EUROPE
Main Office: +46 18 565900
Toll Free: +800 18 565710
Fax: +46 18 591922
Order Tel: +46 18 565710
Order Fax: +46 18 565705
order@biotage.com
Support Tel: +46 18 56 59 11
Support Fax: + 46 18 56 57 11
eu-1-pointsupport@biotage.com

NORTH & LATIN AMERICA
Main Office: +1 704 654 4900
Toll Free: +1 800 446 4752
Fax: +1 704 654 4917
Order Tel: +1 704 654 4900
Order Fax: +1 434 296 8217
ordermailbox@biotage.com
Support Tel: +1 800 446 4752
Outside US: +1 704 654 4900
us-1-pointsupport@biotage.com

HORIZON TECHNOLOGY
Tel: +1 603 893 3663
Toll Free: +1 800 997 2997
Fax: +1 603 893 4994
sales@biotage.com

JAPAN
Tel: +81 3 5627 3123
Fax: +81 3 5627 3121
jp_order@biotage.com
jp-1-pointsupport@biotage.com

CHINA
Tel: +86 21 68162810
Fax: +86 21 68162829
cn_order@biotage.com
cn-1-pointsupport@biotage.com

KOREA
Tel: + 82 31 706 8500
Fax:+ 82 31 706 8510
korea_info@biotage.com
kr-1-pointsupport@biotage.com

INDIA
Tel: +91 22 4005 3712
india@biotage.com

Distributors in other regions are listed on www.biotage.com

Part Number: AN119-HOR

Horizon technology a part of Biotage®