

Improved Recoveries of Polycyclic Aromatic Hydrocarbons (PAHs) as Defined in EPA 550.1 and Simultaneous Removal of Humic Acids from Water Using Strata® PAH

Zeshan Aqeel, Seyed Sadjadi, and Erica Pike
Phenomenex, Inc., 411 Madrid Ave., Torrance, CA 90501 USA

Polycyclic aromatic hydrocarbon compounds (PAHs) are effectively extracted from water samples while humic acids, which often interfere with chromatographic separation, are removed from the sample using a SPE sorbent, Strata® PAH. It was also found that Strata PAH provides consistent, high recoveries of all 16 analytes listed under EPA Method 550.1.

Introduction

Polycyclic aromatic hydrocarbons (PAHs)¹ are byproducts of burning fuel and have been classified as carcinogenic, mutagenic, and teratogenic. These pollutants have been found to be present in foods as well as drinking water, which have caused the EPA to regulate the allowed levels of PAHs under EPA method 550.1. Under the EPA method, PAHs are extracted from water samples using a simple C18 solid phase extraction (SPE) sorbent. However, this sorbent simultaneously extracts humic acids which can cause interferences in subsequent analysis. Humic acids are produced as organic matter decays and are therefore major constituents of soil and water, meaning they are present in almost all samples tested for PAHs.²

In an effort to improve the analysis of PAHs, Phenomenex, Inc. has developed Strata PAH, a SPE sorbent that targets PAHs and simultaneously removes humic acids from the sample. PAHs can then be eluted while humic acids remain bound in the sorbent. Not only does Strata PAH produce cleaner extracts but it also produces higher recoveries of PAHs as compared to the EPA 550.1 method.

Experimental Conditions

100 µL of PAH standards in acetonitrile, obtained from ULTRA Scientific, Inc., were spiked into 100 mL of Water/Acetonitrile (75:25). The prepared PAH samples were then passed through the Strata PAH sorbent as directed in the method described in **Table 1**. After the extraction, samples were blown down to dryness under nitrogen gas at 35 °C. The samples were then reconstituted in 100 µL of dichloromethane and injected onto a Zebtron™ ZB-5ms GC column. A separate study was performed to ensure that the Strata PAH sorbent was capable of removing humic acids from water samples. Using humic acid standards, obtained from In-

ternational Humics Substances Society (IHSS) a 1 L solution containing 1 mg/L of standard in water was made. Using the same extraction procedure specified in **Table 1**, 100 mL of the solution was passed through a 1.5 g/6 mL Strata PAH tube while another 100 mL of the solution was passed through a 1 g/6 mL Strata C18-E tube as a control. Strata C18-E was selected as a control sorbent because C18 SPE sorbent is specified in EPA 550.1. The effluents from each sorbent were blown down to dryness under nitrogen gas at 35 °C and were reconstituted in 250 µL of 5 mM Ammonium formate buffer and 250 µL of methanol. 5 µL of each reconstituted sample was then analyzed using an Agilent® 1200SL HPLC coupled to an AB SCIEX™ 4000 QTRAP® (with Turbo V™ ion source) using a Kinetex® C8 2.6 µm core-shell column for analysis (**Figure 2**).

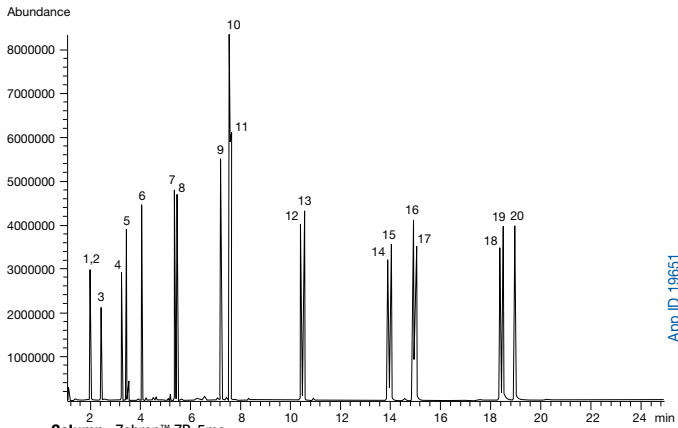
Table 1.
Strata PAH SPE Protocol

Strata PAH 1.5 g/ 6 mL SPE Tubes (Part Number 8B-S130-7CH)	
1	Condition: - 20 mL Dichloromethane - 20 mL Methanol - 20 mL D.I. Water
2	Load: - 100 µL PAH standards (100 µg/mL in Acetonitrile) spiked into 100 mL Water/Acetonitrile (75:25)
3	Wash: - 5 mL Methanol/D.I. Water (50:50)
4	Dry: - 15 seconds under 10" Hg vacuum
5	Elute: - 6 mL Dichloromethane

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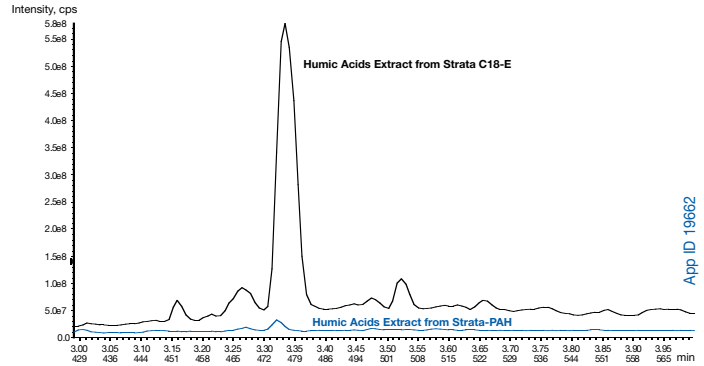
Figure 1.
GC Analysis of Polycyclic Aromatic Hydrocarbons (PAHs)
19651



App ID 19651

Column: Zebtron™ ZB-5ms
Dimensions: 30 meter x 0.25 mm x 0.25 µm
Part No.: 7HG-G010-11
Injection: Split 15:1 @ 310 °C, 1 µL
Carrier Gas: Helium @ 1.4 mL/min (constant flow)
Oven Program: 140 °C to 240 °C @ 15 °C/min to 275 °C @ 4 °C/min to 320 °C @ 10 °C/min for 5 min
Detector: MS @ 270 °C
Sample: 1. D8-Naphthalene
 2. Naphthalene
 3. 2-Methylnaphthalene
 4. Acenaphthalene
 5. Acenaphthene
 6. Fluorene
 7. Anthracene
 8. Phenanthrene
 9. Fluoranthene
 10. D10-Pyrene
 11. Pyrene
 12. Benz[a]anthracene
 13. Chrysene
 14. Benzo[b]fluoranthene
 15. Benzo[k]fluoranthene
 16. D12-Benzo[a]pyrene
 17. Benzo[a]pyrene
 18. Indeno[1,2,3-cd]pyrene
 19. Dibenzo[a,h]anthracene
 20. Benzo[g,h,i]perylene

Figure 2.
Effective Removal of Humic Acids



App ID 19662

Column: Kinetex 2.6 µm C8
Dimensions: 50 x 2.1 mm
Part No.: 00B-4497-AN
Mobile Phase: A: 5 mM Ammonium acetate
 B: Methanol
Gradient:

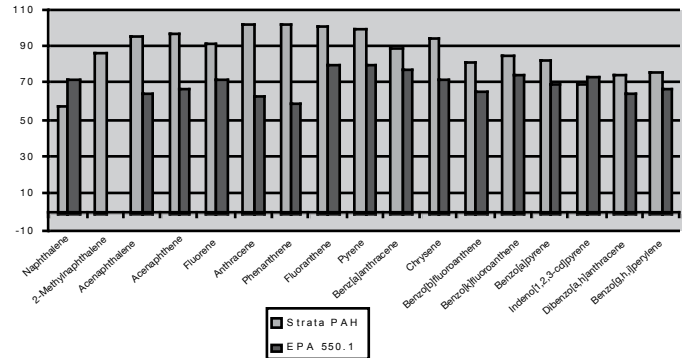
Time (min)	B (%)
0	15
2	95
6	95
6.01	15

Flow Rate: 0.4 mL/min
Temperature: Ambient
Detection: MS @ 580.4 amu / 536.5 amu (ambient)
Backpressure: 210 bar
Sample: Humic Acids from Suwannee River

Results and Discussion

The GC/MS analysis showed that recoveries of the 16 analyzed PAHs were consistently higher than those reported using the EPA 550.1 recommended method (**Figure 3 and Table 2**), except for naphthalene which proved to be difficult due to its volatility. In an effort to reduce the volatility issue, a deuterated form of naphthalene as well as 2-Methylnaphthalene were analyzed as well. In addition to higher recoveries, the LC/MS data shows that Strata PAH was also effective for removing humic acids from the extracted samples, thus providing a cleaner sample and lower background (as illustrated by the LC/MS baseline in **Figure 2**) as compared to the current extraction method recommended in EPA 550.1

Figure 3.
PAH Percent Recoveries from Tap Water³



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Table 2.
PAH Percent Recoveries from Tap Water

	Strata PAH %	EPA 550.1 %
Naphthalene	58.05	72.8
2-Methylnaphthalene	86.98	--
Acenaphthalene	95.86	64.1
Acenaphthene	97.47	67.1
Fluorene	91.50	72.5
Anthracene	102.1	63.3
Phenanthrene	103.1	59.5
Fluoranthene	101.1	80.7
Pyrene	99.45	80.7
Benz[a]anthracene	89.97	78.1
Chrysene	94.70	73.1
Benzo[b]fluoranthene	82.25	65.9
Benzo[k]fluoranthene	86.08	74.9
Benzo[a]pyrene	82.42	70.0
Indeno[1,2,3-cd]pyrene	70.33	74.0
Dibenzo[a,h]anthracene	74.63	64.7
Benzo[g,h,i]perylene	76.70	67.3

Conclusion

Strata PAH effectively extracted PAHs from water samples while providing benefits such as higher recoveries and improved base-line resolution as compared to the recommended method is outlined in EPA method 550.1.

References

1. www.wikipedia.org/wiki/Polycyclic_aromatic_hydrocarbon
2. www.wikipedia.org/wiki/Humic_acid
3. Jimmie W. Hodgeson, et al. EPA Method 550.1, July 1990

Ordering Information

Strata® PAH Solid Phase Extraction Tubes

Sorbent Mass	Part Number	Unit
750 mg	8B-S130-WCH	6 mL (30/box)
1.5 g	8B-S130-7CH	6 mL (30/box)

Zebron™ ZB-5ms GC Columns

ID(mm)	df(µm)	Temp. Limits °C	Part No.
10-Meter			
0.10	0.10	-60 to 325/350	7CB-G010-02
0.18	0.18	-60 to 325/350	7CD-G010-08
15-Meter			
0.25	0.25	-60 to 325/350	7EG-G010-11
20-Meter			
0.18	0.18	-60 to 325/350	7FD-G010-08
0.18	0.32	-60 to 325/350	7FD-G010-51
0.18	0.36	-60 to 325/350	7FD-G010-53
25-Meter			
0.20	0.33	-60 to 325/350	7GE-G010-14
30-Meter			
0.25	0.25	-60 to 325/350	7HG-G010-11
0.25	0.50	-60 to 325/350	7HG-G010-17
0.25	1.00	-60 to 325/350	7HG-G010-22
0.32	0.25	-60 to 325/350	7HM-G010-11
0.32	0.50	-60 to 325/350	7HM-G010-17
0.32	1.00	-60 to 325/350	7HM-G010-22
60-Meter			
0.25	0.25	-60 to 325/350	7KG-G010-11
0.32	0.25	-60 to 325/350	7KM-G010-11

Kinetex® Core-Shell HPLC/UHPLC Columns

1.7 µm Minibore Columns (mm)

Phases	50 x 2.1	100 x 2.1
C8	00B-4499-AN	00D-4499-AN

2.6 µm Minibore Columns (mm)

Phases	50 x 2.1	100 x 2.1
C8	00B-4497-AN	00D-4497-AN

2.6 µm Solvent MidBore™ Columns (mm)

Phases	50 x 3.0	100 x 3.0
C8	00B-4497-Y0	00D-4497-Y0

2.6 µm Analytical Columns (mm)

Phases	50 x 4.6	75 x 4.6	100 x 4.6	150 x 4.6
C8	00B-4497-E0	00C-4497-E0	00D-4497-E0	00F-4497-E0

Other phases and dimensions available, please inquire.

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Australia

t: 02-9428-6444
f: 02-9428-6445
auinfo@phenomenex.com

Austria

t: 01-319-1301
f: 01-319-1300
anfrage@phenomenex.com

Belgium

t: +31 (0)30-2418700
f: +31 (0)30-2383749
beinfo@phenomenex.com

Canada

t: (800) 543-3681
f: (310) 328-7768
info@phenomenex.com

Denmark

t: 4824 8048
f: 4810 6265
nordicinfo@phenomenex.com

Finland

t: (09)4789 0063
f: +45 4810 6265
nordicinfo@phenomenex.com

France

t: 01 30 09 21 10
f: 01 30 09 21 11
franceinfo@phenomenex.com

Germany

t: 06021-58830-0
f: 06021-58830-11
anfrage@phenomenex.com

Ireland

t: 01 247 5405
f: +44 1625-501796
eireinfo@phenomenex.com

Italy

t: 051 6327511
f: 051 6327555
italiainfo@phenomenex.com

Luxembourg

t: +31 (0)30-2418700
f: +31 (0)30-2383749
nlinfo@phenomenex.com

Mexico

t: (55) 5018 3791
f: (310) 328-7768
tecnicomx@phenomenex.com

The Netherlands

t: 030-2418700
f: 030-2383749
nlinfo@phenomenex.com

New Zealand

t: 09-4780951
f: 09-4780952
nzinfo@phenomenex.com

Norway

t: 810 02 005
f: +45 4810 6265
nordicinfo@phenomenex.com

Puerto Rico

t: (800) 541-HPLC
f: (310) 328-7768
info@phenomenex.com

United Kingdom

t: 01625-501367
f: 01625-501796
ukinfo@phenomenex.com

All other countries: Corporate Office USA

t: (310) 212-0555
f: (310) 328-7768
info@phenomenex.com

www.phenomenex.com

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